

Stability Modification of Biodegradable Polyesters under Abiotic Conditions

Ing. Petra Dróhslar, Ph.D.

Doctoral Thesis Summary



Tomas Bata University in Zlín

Centre of Polymer Systems

Doctoral Thesis Summary

Stability Modification of Biodegradable Polyesters under Abiotic Conditions

**Modifikace stability biologicky rozložitelných polyesterů
za abiotických podmínek**

Author: **Ing. Petra Dróhsler, Ph.D. (Válková)**

Degree programme: P3924 Material Sciences and Engineering

Degree course: 3911V040 Biomaterials and Biocomposites

Supervisor: prof. Ing. Vladimír Sedlařík, Ph.D.

Reviewers: Prof. Ing. Adriána Kovalčík, PhD.

Prof. Dr. Milan Krácalík

Zlín, August 2024

© Petra Dróhslér

Published by **Tomas Bata University in Zlín** in the Edition **Doctoral Thesis Summary**.

The publication was issued in the year 2024.

Key words: *biodegradable polymer, polylactide, modification of polymers, additives, degradation, stability*

Klíčová slova: *biorozložitelný polymer, polylaktid, modifikace polymerů, aditiva, degradace, stabilita*

Full text of the doctoral thesis is available in the Library of TBU in Zlín.

ISBN 978-80-7678-290-7

TABLE OF CONTENT

ABSTRACT	5
INTRODUCTION	6
1. THEORETICAL BACKGROUND	7
1.1 Polylactic acid	7
1.2 Degradation of PLA	13
1.3 Natural-based pro-degradation stability modifiers	16
AIMS OF WORK	19
2. EXPERIMENTAL PART	20
2.1 Effect of an antioxidant based on red beetroot extract on the abiotic stability of polylactide and polycaprolactone	21
2.2 Comparative degradation study of a biodegradable composite based on polylactide with halloysite nanotubes and a polyacrylic acid copolymer	22
3. SELECTED EXPERIMENT RESULTS	24
3.1 Effect of an antioxidant based on red beetroot extract on the abiotic stability of polylactide and polycaprolactone	24
3.2 Comparative degradation study of a biodegradable composite based on polylactide with halloysite nanotubes and a polyacrylic acid copolymer	29
CONCLUSIONS	36
CONTRIBUTIONS TO SCIENCE AND PRACTICE	38
REFERENCES	39
LIST OF FIGURES	49
LIST OF TABLES	50
LIST OF ABBREVIATIONS	51
CURRICULUM VITAE	53
LIST OF PUBLICATIONS	56

ACKNOWLEDGEMENTS

I would like to thank all the people who supported, helped and encouraged me during my doctoral studies.

First and foremost, I would like to thank my supervisor prof. Ing. Vladimír Sedlařík, Ph.D. for his guidance and for giving better directions to my work along with opportunities to implement ideas. During my studies, he gave me the opportunity to work on interesting projects and also to participate in various conferences, trainings and other events, which gave me valuable experience that I can apply in my future work.

My thanks also go to my mentor for my internship in Poland, Dr Aneta Tor-Świątek. I am grateful for the friendly working environment she nurtured, along with her professionalism, kindness, advice and willingness to help me in everything.

An aspect of research and study that should not be overlooked is the social dimension. My gratitude extends to friends and colleagues at the Polymer Centre and other faculties of Tomas Bata University in Zlín, for their cooperation, assistance and goodwill.

Finally, I am deeply grateful to my family and closest friends for all their support, patience and boundless affection.

ABSTRACT

This work is focused on stability modification of the degradation extent and rate of biodegradable polyesters such as polylactide (PLA), its copolymers and polycaprolactone (PCL) with the motivation to expand their applicability range. The theoretical part summarizes the current state of the art of PLA-based materials, including their associated properties, application and degradation mechanisms. The experimental section brings authentic research results of the dissertation aimed at stability modification of PLA and PCL by non-toxic and environmentally friendly additive extracted from waste biomass. Second study is focused on chemical modifications of PLA structure by means of copolymerization reactions with the acrylic acid. Such alteration accelerated the process of polymer degradation, additionally supported and correlated by incorporating an inorganic filler. The results were as anticipated, revealing that a beneficial effect had been exerted on the degradation mechanisms of polylactide, as confirmed by various analytical techniques.

Key words: *biodegradable polymer, polylactide, modification of polymers, additives, degradation, stability*

ABSTRAKT

Tato práce se zaměřuje na modifikaci stability, která ovlivňuje především rychlost degradace vybraných biodegradabilních polyesterů, jako je polylaktid (PLA), jeho kopolymery a polykaprolakton (PCL) za účelem rozšíření aplikačního rozsahu. Teoretická část shrnuje u materiálu na bázi PLA současný stav jeho vlastností, dosud dostupné modifikace, aplikační potenciál a také degradační mechanismus za různých podmínek. Experimentální část nabízí nové možnosti modifikace degradační stability polymeru PLA s výsledky výzkumu zaměřené na netoxické a ekologicky šetrné aditiva. V první části byl srovnáván vliv aditiva z odpadní biomasy v polymerech PLA a PCL. Druhá studie je zaměřena na chemické modifikace struktury PLA pomocí kopolymeračních reakcí s kyselinou akrylovou. Pro zvýšení tohoto efektu a korelaci dalších vybraných vlastností byla současně provedena úprava pomocí anorganického nanoplniva. Výsledky prokázaly požadovaný vliv na degradační mechanismus sledovaného polymeru dle typů aditiva, které bylo potvrzeno jednotlivými analýzami.

Klíčová slova: *biorozložitelný polymer, polylaktid, modifikace polymerů, aditiva, degradace, stabilita*

INTRODUCTION

Polymers have become indispensable to modern life for their broad spectrum of applicability. Despite boasting wide-ranging properties, being easy to process and proving relatively inexpensive, a major drawback is that most of them come from non-renewable sources, especially fossil fuels. As a consequence, energy and materials unsustainable for the environment are utilized during the production, processing and recycling of them [1].

The notion of turning to biodegradable plastics instead is interesting, particularly with respect to avoiding the undesirable accumulation of waste matter. Biodegradable alternatives can be formulated from either natural or synthetic resins [2].

Poly(lactide) (PLA) has proven especially suitable in this regard. A recyclable polyester, it is produced from renewable feedstock or waste products rich in polysaccharides, i.e. starch primarily sourced from the agricultural sector. High-molecular-weight PLA is prominent in the manufacture of disposable goods for consumers, whereas polymers of low or medium molecular weight are typically applied in modern medicine, such as in controlled drug release systems or implants [3].

Although PLA shows promise as an alternative to conventional plastic materials, limitations exist in relation to its properties. For instance, it is weak when it comes to bending, gas impermeability and impact strength. Another limitation relates to the rate of degradation, which transpires too quickly for some applications, examples products intended for the automotive industry and in certain packaging materials. Conversely, the rapid onset of degradation processes is an advantage for disposable packaging and pharmaceutical items. Applying and incorporating fillers and additives is a possibility, however, they have to be compatible with PLA and meet overall biodegradability and safety requirements [1], [3].

The degradation mechanism of PLA tends to be dependent on the nature of the end group and the external environment. It is also advantageous to target the end groups of PLA and chemically modify them. A notable effect is achieved with PLA of low and medium molar mass, wherein the end groups constitute a significant part of the macromolecules; an aspect which pertains to the supramolecular chemistry of PLA, as reported in the literature [3], [4].

This thesis summarizes the current knowledge of PLA, as well as innovative and proven options for its modification and applicability. Attention is paid to the degradation mechanism of this biodegradable polymer and the primary factors that influence it. Novel means of modifying PLA are subsequently presented, potentially broadening the scope of its application. The experimental part focuses on the effects exerted by naturally and synthetically derived additives on the properties and stability of PLA (e.g. its degradation kinetics) under abiotic and/or biotic conditions.

1. THEORETICAL BACKGROUND

1.1 Polylactic acid

PLA represents one of the most common and commercially applied forms of bioplastic. Production of it is rising globally, and expected to ramp up to almost 5.3 million tons by 2026, in connection with the development of biodegradable polymers [5].

PLA is a biodegradable polyester with a monomer of lactic acid (2-hydroxypropanoic acid), occurs in two optically active configurations of D(−) and L(+) enantiomers, obtained by fermenting carbohydrates from renewable crops like sugar beet, corn and other forms of biomass. The whole process can be carried out by bacteria or by a chemical process, which potentially leads to the formation of a racemic mixture of both enantiomers [6], [7].

An amorphous or semi-crystalline polymer, PLA typically has a melting point (T_m) of 160 – 190 °C and glass transition temperature (T_g) of 55 – 65 °C. In terms of mechanical properties, it is known as a brittle material for its high tensile modulus (3 GPa) and yield strength (50 – 70 MPa), with low elongation at break (5 – 7 %) [8], [9]. PLA is a thermoplastic polymer that is characterized by biocompatibility and biodegradability. Processing it is relatively simple, requiring just standard equipment and technology to produce fibres, films or thin sheets and 3D filament by blowing, extrusion or electrospinning techniques [10], [11], [12].

- **PLA synthesis routes**

Three primary methods exist for PLA synthesis (Figure 1): **direct condensation polymerization**; **ring-opening polymerization (ROP)** of lactide; and **azeotropic dehydrative polycondensation**. A less common alternative to the first of these is azeotropic distillation, wherein water formed during polycondensation is removed by an azeotropic solvent and subsequent esterification gives rise to high-molecular-weight PLA. Mitsui Toatsu Chemicals patented this process in 1994 [9], [13].

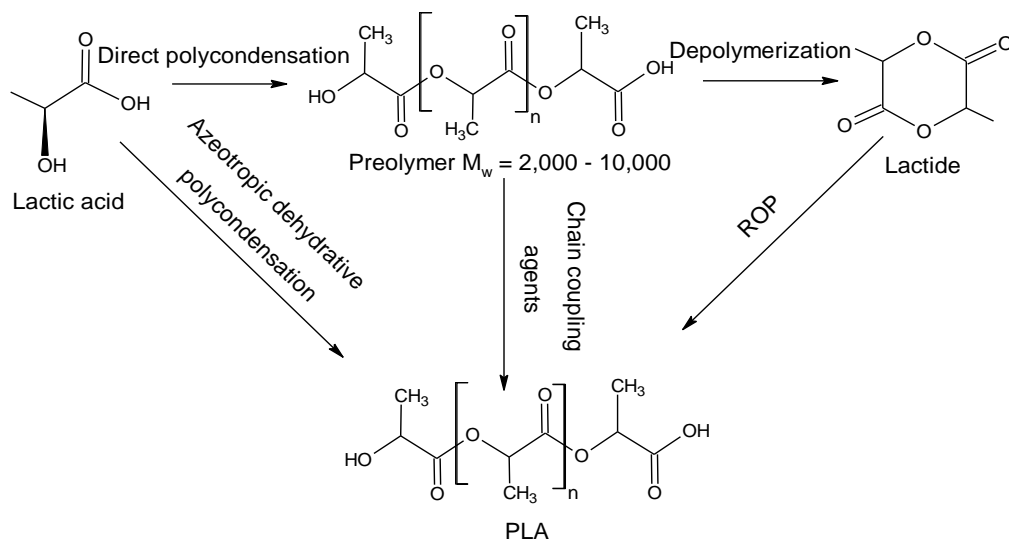


Figure 1. Methods for PLA synthesis [14].

Application of PLA

The primary method for fabricating PLA at present is ROP, as it engenders high-molecular-weight PLA suitable for various processing techniques, e.g. extrusion, injection moulding and electrospinning. Figure 2 summarizes the preparation of PLA and its applications [15].

Referred to as a carbon-neutral life-cycle material, PLA can be produced not only from starch, but also food-related waste. It is possible to fully recycle PLA at the end of its useful life. Notable in this regard is chemical recycling, an alternative means of obtaining the monomer needed for fabricating virgin biopolymers. This procedure takes place at the end of the life cycle of PLA and contributes to its circular economic value [16], [17].

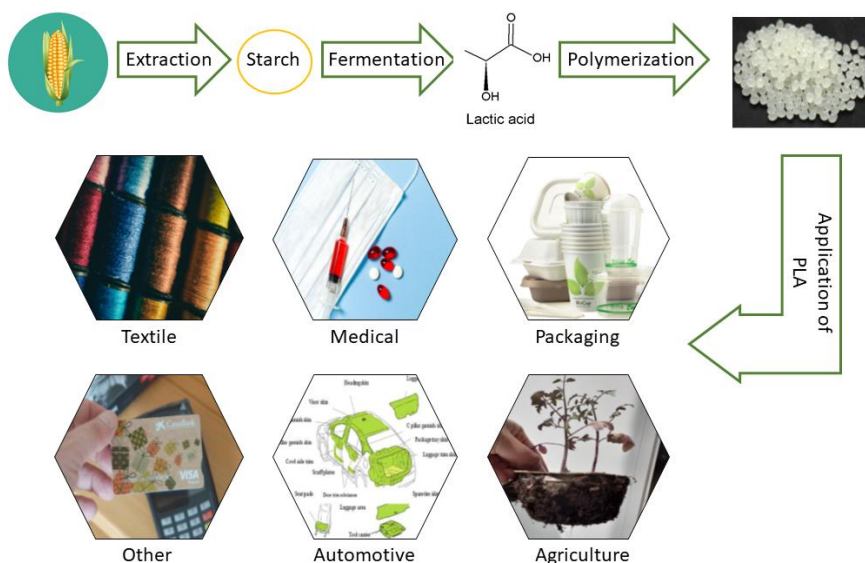


Figure 2. Schematic diagram of the general preparation of PLA and its most common applications.

From an environmental perspective, the PLA biopolymer has a lot to offer. The consumption of fossil fuels is lower than for other materials during production, to the extent of approximately 25 – 55 %. The carbon dioxide (CO₂) released at the end point of its life cycle (e.g. by incineration or composting) equals the amount of CO₂ absorbed by the plants grown that constitute its raw materials. The greenhouse gas emissions for PLA (1 600 kg CO₂/metric tonne) are sometimes far lower than for PET or nylon (4 140 and 7 150 kg CO₂/metric tonne, respectively). Moreover, less water is needed for its manufacture [18], [19].

- **Packaging**

Plastics are primarily employed for this application, and over 335 million tonnes per year are produced for this purpose worldwide. The food industry stands out in this regard, as up to 40% of packaging takes the form of disposable tableware items, including cutlery, foil and bags [20].

PLA clearly shows potential as an alternative to petroleum-based plastics, and it has been widely studied for use in food packaging. However, it also has certain disadvantages that limit its acceptance in this regard, although they relate to low flexibility, poor dimensional stability and ineffective barrier properties [21].

- **Medical applications**

The possibility of sterilization by irradiation, for example, facilitates biomedical applications for PLA. The breadth of options in this context is wide, from deployment in regenerative tissue engineering to orthopaedic, cardiac and dental items. PLA-based medical products (pins, rods, studs, screws and inserts produced on 3D printers) feature in customized tissue engineering scaffolds and rapidly fabricated medical equipment, such as personal protective equipment. Other common examples include implants in the form of membranes and those for arthroscopic purposes or spinal surgery [22], [23].

A notable use of PLA is as a pharmaceutical drug-delivery system. PLA has proven suitable as a carrier for the controlled administration of medication, examples comprising anticancer, antidiarrhoeal, antipsychotic, antibiotic, anti-inflammatory and antidiabetic drugs and opioid antagonists. Disadvantages exist, however, as PLA exhibits reduced cell adhesion and a low rate of degradation, attributed to its hydrophobicity and biological inertness. As a result, inflammation can arise *in vivo*, causing bacterial adhesion, the formation of biofilm and even complications associated with necrosis [24].

- **Agriculture**

Another key sector for PLA application is agriculture. PLA could replace high-density polyethylene structures for plant protection, which serve as a non-chemical means of creating a physical barrier between pests and crops. The material has also found favour in drug-delivery systems that treat plants through gradual release of their contents into soil, as well as in containers, flower pots and

planters. Moreover, PLA is non-toxic and biodegradable. Plant pots made of PLA have been designed with modifications in their walls that allow parts to be easily broken off, thus facilitating the growth of roots and the action of biocomposites for accelerated decomposition of the container [25], [26].

- **Automotive**

The automotive industry has been gradually veering away from parts made of metal and metal alloys and often replacing them with light plastic ones instead. Manufacturers state this decision has been taken in order to reduce the weight of vehicles so their fuel consumption is lower, thereby cutting the emission of greenhouse gases. They also place emphasis on safety and protecting the environment, hence consideration is paid to the use of biodegradable polymers, especially PLA. Not only are the internal parts of vehicles now made of plastic, but also external elements, such as bumpers, body panels, laminated safety glass, mouldings and a host of others, accounting for approximately 18% of the weight of a vehicle on average [27], [28].

Toyota was the first to adopt PLA, in 2003, followed by Ford and Mazda, which applied the material in doors and other interior parts in 2006 [28].

- **Textiles**

The global trend in the textile industry is also to promote an image of being green marketing by returning to a natural, ecological approach. Combinations of fibres from different polymers possess heightened properties but complicate recycling activities [29].

PLA fibres are produced in a non-toxic manner, in contrast, and retain a level of biological resistance. However, the maintenance of clothing containing PLA fibers is still a problem. In this regard, there is a risk that ironing clothes at high temperature, but also washing conditions, recommended at temperatures of 35 – 55 °C and pH 8 or 10 and subsequent drying should not include the use of a tumble dryer [29], [30].

- **Further applications**

PLA shows potential as a conductive fibre for 3D printing purposes. Neat PLA serves as an effective insulator in applications involving low voltage and temperature [31].

Construction is another area where efforts are being made to create sustainable buildings that impact the environment to a lesser degree. PLA composites have been employed as thermal insulators, within the reinforcements of partition walls and as flame-retardant, non-woven fabrics, the latter being a composite supplemented with ammonium polyphosphate and lignin [32], [33].

- **Modifications to the PLA matrix**

PLA is characterized by properties that resemble those of conventional petroleum-based plastics, so has the potential to supersede the latter. On the other hand, the SWOT analysis (strengths, weaknesses, opportunities and threats) reveals (Fig. 3) that PLA also has undesirable properties. Possible solutions exist to rectify these issues, however, including modifying PLA through techniques like **copolymerization (i)** and **blending** with fillers/additives **(ii)** [34], [35].

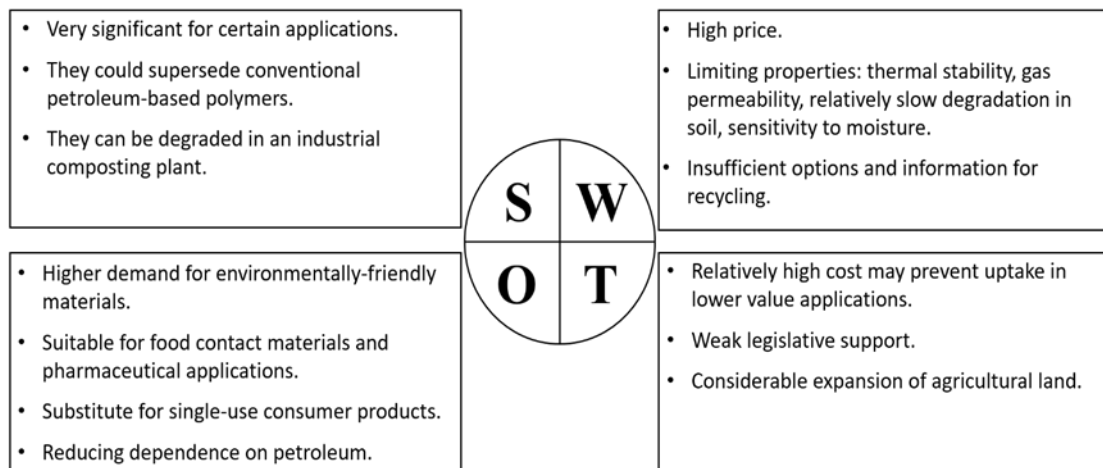


Figure 3. SWOT analysis of applying biodegradable polymers in packaging materials [36], [37], [38].

1) Copolymerization

Chemical modification of PLA primarily consists of introducing various functional side groups (e.g. carboxyl, amine and hydroxyl) into it. Under direct PLA polymerization conditions, it is possible to add in monomers that attach to the –OH or –COOH end groups [39].

The reaction is terminated by hydrolysis to form a hydroxyl end group with functional alkoxy-substituted initiators. Macromers with active end groups are also produced that assist in the fabrication of high-molecular-weight polymers during post-polymerization reactions. Significantly supporting the strength, toughness and hydrophilic, controlled degradable properties of PLA, this process concurrently gives rise to a multitude of new macromolecular architectures (linear, branched, stellar and dendritic) which emerge. The most common of these are the copolymers of poly(lactic-co-polyethylene glycol(PLA-co-PEG) and poly-lactide-co-poly- ϵ -caprolactone (PLA-co-PCL), as well as a type of poly(lactic-co-glycolic acid) (PLGA) [34].

Another chemical method of modification involves grafting a polymer chain onto a solid surface. Two techniques for this currently exist, referred to as “grafting from” and “grafting to”. Referred to as graft copolymers, types with polylactide are formed in combination with chitosan, cellulose, starch, PEG,

vinyl-based polymers, lignin, dextran, methyl methacrylate, maleic anhydride and graphene oxide [34], [40].

2) PLA blending

Categorized as physical modification, blending primarily consists of altering the mechanical, optical and thermal properties of PLA. Supplementation with plasticizers, nanomaterials and solid fillers is possible during the procedure, and changes in orientation can also be made. It gives rise to mixed systems with different structures and properties suitable for numerous applications.

Bio-based materials suffer from the disadvantages of poor degradability and recyclability, though. A recent trend in research has been to prepare completely biodegradable polymers containing PLLA, PDLA, hyaluronic acid, polycaprolactone (PCL) or PHA, with the intention of tackling these drawbacks. Other examples include elastomers, thermoplastic starch, PEG and tributyl citrate [9], [34], [41].

The most commonly applied fillers are plant-derived bio-fibres in **biocomposites with natural, organic reinforcements** comprise flax, hemp, jute, sisal, kenaf and coir, generally classified as bast, leaf or seed fibres. Synthetic examples include carbon fibres and tubes or graphene, which are capable of maintaining desirable thermal, conductive and mechanical properties, albeit at a high price. **Inorganic biocomposites** are based on minerals such as bentonite, talc, calcium carbonate, barium sulphate, montmorillonite, silicates and mica. Supplementation is possible with metal oxide nanoparticles, e.g. iron(III) oxide (Fe_2O_3), aluminium(III) oxide (Al_2O_3), zinc oxide (ZnO) and titanium(III) oxide (Ti_2O_3) [42], [43], [44].

Lastly, supplementing PLA with **additives** results in alteration of the properties of the material. A wide assortment exists for this purpose, the most common of which are as antioxidants (butylated hydroxyanisole and butylated hydroxytoluene), compatibilizers (ethylene-ethylacrylate and ethylene-butyl acrylate and multifunctional epoxy styrene-acrylic), heat stabilizers - metallic salts (barium-zinc and calcium-zinc) and organometallic (organotin) and non-metallic organic stabilizers (tetrabromobisphenol-A), plasticizers (esters of phthalic acid (dioctyl phthalate) and vegetable oils), dyes and pigments (triphenylmethane, azo, anthraquinone, perylene and indigoid dyes or natural colourants from plants), blowing agents (N_2 or CO_2 and sodium bicarbonate), biocides, flame retardants, hardeners or aroma/smell modifiers [45], [46], [47], [48], [49].

1.2 Degradation of PLA

The degradation mechanism of PLA occurs naturally by the simple hydrolysis of ester bonds. Upon complete degradation, PLA decomposes into water, carbon dioxide and biomass. The rate of degradation is affected by biological, physical and chemical factors, including pH, humidity, oxygen, the isomer ratio, the temperature of hydrolysis and shape and size of the material. Other aspects in this context include crystallinity, porosity, purity, morphology, the presence of terminal carboxyl or hydroxyl groups, crosslinking and resistance to electromagnetic radiation, bacteria and the inorganic filler substances deployed [50].

- **Abiotic hydrolysis of PLA**

Abiotic hydrolysis consists of degradation by physical factors, especially in an aqueous medium where hydrolytic cleavage to poly (α -hydroxyl) esters occurs. At temperatures of at least 30°C, slow hydrolysis of the ester bonds in PLA transpires, leading to the release of smaller oligomers and monomers (Fig. 4). The rate of degradation depends on the crystalline phase of the polymer. Degradation of semi-crystalline PLA in an aqueous medium takes place in two steps. The first phase begins with the diffusion of water into the amorphous areas, which are less organized and allow water to penetrate more easily. The second phase begins once most of the amorphous regions have been degraded, and continues to the centre of the crystalline domains. If the diffusion of water is faster than the hydrolytic reactions, however, hydrolysis occurs randomly throughout the polymer. This aspect leads to overall and uniform loss in molecular weight. The resulting oligomers and monomers diffuse outwardly and cause gradual erosive effects until a balance between diffusion and chemical kinetics is reached [51], [52].

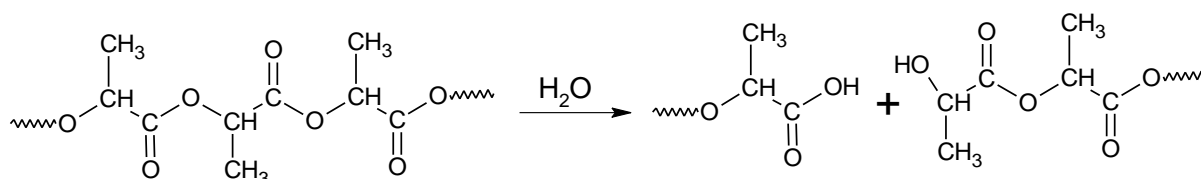


Figure 4. Hydrolytic degradation of PLA in the presence of water [53].

The effect of pH is crucial in the case of PLA degradation. Exposure to an acidic environment brings about accelerated degradation via autocatalysis. The rapid cleavage of the chain at low pH catalyses the formation of monomers, which are carboxylic acids (lactic acid), leading to accelerated degradation and decrease in pH. Mention has to be made of the molecular weight of the polymer in this context [54].

- **Biodegradation of PLA**

As previously mentioned, PLA is a biodegradable polymer. It is necessary for legislation to clarify the differences between the terms “biodegradable” and “biodegradable plastic” as stipulated in ASTM D883-12. Decomposed plastic is defined as undergoing a significant change in its chemical structure under specific environmental conditions, leading to the loss of some properties. This standard also defines biodegradable plastic as a plastic material with a degradation mechanism induced by the actions of naturally occurring microorganisms such as bacteria, fungi and algae [55], [56].

Recovering these polymers through recycling would be beneficial from an environmental perspective, yet this does not always prove advantageous in terms of energy consumption. Therefore, it is currently preferable to compost PLA at the end of its life cycle. The phase of initial hydrolysis is crucial to biodegradation under the given conditions, which follows **microbial** (*Amycolatopsis*, *Bacillus stearothermophilus* and *Tritirachium album* or *viride*) and **enzymatic activity** (lipases, serine proteases, cutinases, carboxylesterase and esterases) in tandem [57], [58], [59].

- **Biodegradation mechanisms of other biodegradable polymers**

There are also other important representatives of biodegradable polymers such as polycaprolactone (PCL), polybutyl succinate (PBS) and poly-3-hydroxybutyrate (P3HB). Biodegradability of these is initiated by random chain cleavage and erosion, which is responsible for both abiotic and biotic hydrolysis. The most successful of them is P3HB, which after copolymerization with 3-hydroxyvalerate can undergo hydrolysis more easily even in an environment in which other polymers rarely degrade. Although, each of the forementioned polymers requires different condition for optimal decomposition, it is not possible to create the same standards for a suitable comparison. It can be different temperatures, pH of the environment and decomposition time or the presence of suitable microorganisms [60].

- **Impact of products on the environment**

In addition to awareness of the PLA biopolymer itself, i.e. its production, processing, potential applications and degradation mechanism, study has to be made of the environmental impacts of the associated degradation products. In connection with this, conducting a life cycle assessment (LCA) is an option, thereby calculating the impact on the environment by means of analyses directly related to pre-production (the extraction and production of raw materials), manufacture, distribution, usage, recycling and disposal. As a consequence, it is possible to define the scope of an issue within the framework of an inventory analysis, quantifying the energy consumed and hazardous substances emitted by a product during its life cycle [61].

The ISO 14040:2006 and ISO 14044:2006 standards stipulate the principles and methodology required for carrying out LCA studies [62].

The LCA analysis compared two water bottles made of PET and PLA. The results concluded that PET bottles had a lower environmental impact than PLA bottles because of the associated agricultural burdens and issues, i.e. growing suitable crops, global warming potential, water, eutrophication, acidification, particulates and unavoidable land use. However, PLA demonstrates clear advantages over PET in the long term in terms of consuming non-renewable resource consumption, landfilling and global warming issues, but neither option is currently ideal [63].

1.3 Natural-based pro-degradation stability modifiers

PLA degradation follows a natural course, albeit somewhat inappropriate for any corresponding processing or storage. The properties of PLA are modified to suit specific industrial applications, especially in relation to products with a long life cycle, as demanded by the automotive, construction and electronics sectors. Various methods are employed in efforts to delay, mitigate or prevent the onset of degradation processes. However, the requirement exists for this material to biodegrade rapidly once it has reached the end of its useful life such as for single-use packaging. For this purpose, additives or fillers are added that accelerate the onset of degradation.

- **Stability of PLA**

When employing PLA in applications necessitating durability, it is important to know in advance how environmental conditions will affect the degradation behaviour of the material and to determine its intended life cycle. Other factors are crucial with regard to what is expected of the material in connection with processing it, and its mechanical (toughness, elasticity), thermal or barrier properties. Carrying out modifications to PLA with the aim of improving its processing properties, unfortunately, can mean those pertaining to its subsequent degradation are impacted negatively [64].

Increasing the stability of PLA primarily requires eliminating a hydrolytic reaction by some means. Certain methods exist for stabilizing PLA: (i) by **crosslinking amorphous regions**; (ii) applying a **chain extender**; (iii) **increasing the degree of crystallinity** (iii); and (iv) adding an **antioxidant** [65], [66].

1) Crosslinking PLA

Various methods can be conducted to obtain a PLA networking structure, one of which being irradiation. PLA is predominantly degraded by **direct ionizing radiation**, therefore, polyfunctional monomers (PFM) are applicable for inducing crosslinking in this degradable type of polymer. PFMs are characterized by high reactivity and their ability to react with the polymer. They give rise to a crosslinked structure, hence have been widely utilized as crosslinking agents in polyolefins and vinyl monomers. The crosslinking of linear PLA macromolecules without double bonds in the main chain is achieved by applying high-energy radiation to create free valence forces through the impact of hydrogen atoms from the main chain. For example, γ -irradiation and electron beam irradiation constitute typical means for PLA crosslinking, preferably in the presence of PFM, and often with a tiny amount of triallyl isocyanurate as a crosslinking agent [65], [67].

Another possibility is the application of **chemical crosslinking** to implement crosslinking structures in PLA, with peroxide crosslinking representing one of the largest applicable curing groups [68].

The third option is referred to as **photo-initiated crosslinking**, which has proven particularly well suited to biomedical applications, as it allows rapid crosslinking under mild, solvent-free, reaction conditions and high temperatures. The process involves functionalizing the ends of the PLA chains with double bonds, prior to exposing them to UV or visible radiation. Photoactive additives such as substituted phenylacetophenone (“Irgacure”, a so-called photoinitiator) or camphorquinone are then added to initiate free radical polymerization [69].

2) Chain extension

The aspects of chain length and its number of entanglements relate to the stability of the polymer under thermal stress. Modification by such means not only brings about enhancement in these properties, but also a parallel rise in melt viscosity and operating temperature. This phenomenon can be obtained with a chain extender that connects the polymer chains and raises thermal stability, while also functioning as a compatibilizer to some extent. In general, the chain extender may possess bi- or higher functional groups, e.g. diisocyanate, dianhydride and diamine, and epoxies such as tris (nonylphenyl) phosphite, polycarbodiimide and “Joncryl” (a multifunctional, styrene-acrylic oligomer) [65], [70], [71].

Widely applied to polymers and PLA in particular, several types of Joncryl with special functions exist, examples being ADR (a chain extender), ADF (a flow modifier), ADP (a plasticizer) and ADD (a dispersant) [47].

3) Increase in the degree of crystallinity of PLA

By combining enantiomeric content, modifications are made that affect crystallization kinetics and thus other properties (mechanical, thermal and so on). Crucial factors comprise the amount of D-form, the processing temperature and period of time given over to cooling. Optimal development of the crystalline structure happens when fabrication occurs at 100°C for a period of 35 seconds, thereby enhancing the thermal stability of PLA. Crystalline forms of PLA, α , β and γ are created; during the crystallization stage, the α -form and γ -form grow, triggered by epitaxial crystallization [65], [72].

A more commonly used method involves the direct application of a nucleating agent within the PLA processing procedure. Several types of nucleating agents exist, generally classified as inorganic (talc and clay), organic (derivatives of sorbitol, starch and lignin) and inorganic-organic hybrid materials (polyhedral oligomeric silsesquioxanes and their derivatives) [73], [74].

4) Antioxidants

Adding an antioxidant prolongs the life cycle of a material, and if combined with an antimicrobial activity, the pertinence of it for food packaging and biomedical applications is obvious. The most common class of antioxidants are polyphenols (8,000 phenolic structures have been identified in plants). The principle behind the antioxidant effect of polyphenols is the ability to donate a

phenolic hydrogen to the generated free radical. The resulting phenoxy radicals are resonantly stabilized and react with other free radicals. The foremost compound associated with polyphenols is α -tocopherol, while lignin has attracted the greatest attention of the phenolic varieties. Synthetic antioxidants include butylated hydroxyanisole, butylated hydroxytoluene and tert-butylhydroquinone [75], [76], [77], [78].

- **Pro-degradation of PLA**

Although PLA is one of the most widely applied biodegradable polymers, it often encounters problems with its slow or insufficient degradation. The aim of research is to facilitate the quickest possible onset of the degradation mechanism commencing with hydrolysis, thereby accelerating the degradation of PLA. In this context, a great many studies have investigated methods for hastening such biodegradation further with the aid of environmentally-friendly fillers, the resultant material being referred to as a “green composite” [79].

An option is employ an **inorganic filler**, examples including carbon nanotubes, zinc oxide, magnesium oxide, calcium oxide or a small amount of a nanoclay, for instance, montmorillonite. Certain kinds of **plant-based matter** are also applicable, such as fibres (hemp, flax), wood flour or modified cellulose nanocrystals. **Copolymers or compounds** can be incorporated to support and accelerate PLA degradation. Performed by introducing additional monomers with different chemical structures into PLA chains, copolymerization lends copolymer molecules lower regularity, increased fluidity and greater hydrophilicity. A known copolymer of lactic and glycolic acids is PLGA, now a frequently deployed polymer in medical applications (sutures, microparticles and implants).

A further option is to utilize **microorganisms** that promote the degradation of PLA polymer. Beyond the consideration of adding a filler to a PLA composite, attention should be paid to providing **optimal conditions** for degradation, which include temperature, humidity and pH [79], [80], [81], [82], [83].

AIMS OF WORK

This dissertation describes the effects exerted by additives of natural and synthetic origin on the degradation mechanisms of biodegradable polymers. The experimental part is split into two sections on the following topics:

1. Examining the stabilizing influence of an antioxidant derived from agricultural produce.
 - Extracting and stabilizing antioxidants from agricultural produce, i.e. crops of low quality.
 - Developing a methodology to characterize the antioxidants extracted.
 - Proposing a suitable method for incorporating a stabilized antioxidant in the given biodegradable polymer – PLA
 - Discerning a suitable means for characterizing biosystems, with an emphasis on aspects that affect the stabilization of the polymers, i.e. their mechanical, thermal, chemical and morphological properties.
 - Evaluation of results.

2. Investigating the synergistic effects of nanofillers and hydrophilic polymers on the mechanical properties and degradation kinetics of PLA-based systems.
 - Synthesizing and characterizing the chemical additive PLA-g-PAA.
 - Preparing PLA composites supplemented with an HNT nanofiller and PLA-g-PAA.
 - Determining the physical properties of the materials by SEM, TGA and FTIR.
 - Researching the effects of natural abiotic and biotic ageing on the materials.
 - Evaluation of results.

2. EXPERIMENTAL PART

The prior chapter of this work summarizes the physical and chemical properties of a widely used biodegradable polymer - PLA. It provides a comprehensive overview of how this material could be variously industrial applications. Description is given of its degradation mechanism and external factors that influence it, divided into abiotic and biotic sections. It also discourses on the latest options for modification of the material that alter its stability.

This experimental part reports on practical research related to supplementing PLA with additives, with the aim of potentially modifying and improving its degradation properties of PLA for a range of applications. In this regard, emphasis is placed on testing natural, readily-available additives suited to incorporation in the polymer matrix, along with maintaining the overall biodegradability of the materials.

The first part focused on the preparation of a composite supplemented with an inorganic filler and natural antioxidant. The filler functioned as both a carrier and stabilizer for the antioxidant component. Since the current trend is to opt for alternative, environmentally-friendly resources, research concentrated on natural antioxidants applicable for biodegradable polymers that could substitute for conventional synthetic products. Antioxidants found in beetroot were selected for this purpose, a choice informed by data in the literature. To this end, samples of PLA composites were fabricated by the casting method. Chemical and physical changes to them were monitored during an artificial ageing test, followed by analysis of their thermal, mechanical and morphological and colour properties.

The second and last part describes modifying PLA to bring about accelerated hydrolysis and degradation. This was achieved with a copolymer produced in the laboratory comprising PLA and polyacrylic acid, PLA-g-PAA. An inorganic filler (halloysite) was also added into it to support and accelerate the degradation. The properties of this composite material were characterized in general, though work focused more on comprehensively studying the degradation processes that occurred during abiotic and biotic hydrolysis, as well as under laboratory composting conditions. This research offers an optimal amount of selected additives to accelerate biodegradation. However, it also offers the potential for disposable packaging materials, for which no further recycling processes can be carried out and it would be advisable to process the material in technical composting plants.

2.1 Effect of an antioxidant based on red beetroot extract on the abiotic stability of polylactide and polycaprolactone

Beetroot extract (BRE) was prepared in ethanol and then was applied to bentonite (BE) as a suitable additive for these applications. The additive thus prepared was added to the dissolved polymer. This procedure for formulating the polymer composites is illustrated in Figure 5, while the composition and names of the tested formulations are given in Table 1.

Accelerated ageing of the samples was performed in a climatic chamber set to the temperature of 45°C and 70% relative humidity under UV irradiation for 720 hours. The experiment was devised in accordance with EN ISO 4892-3 [84].

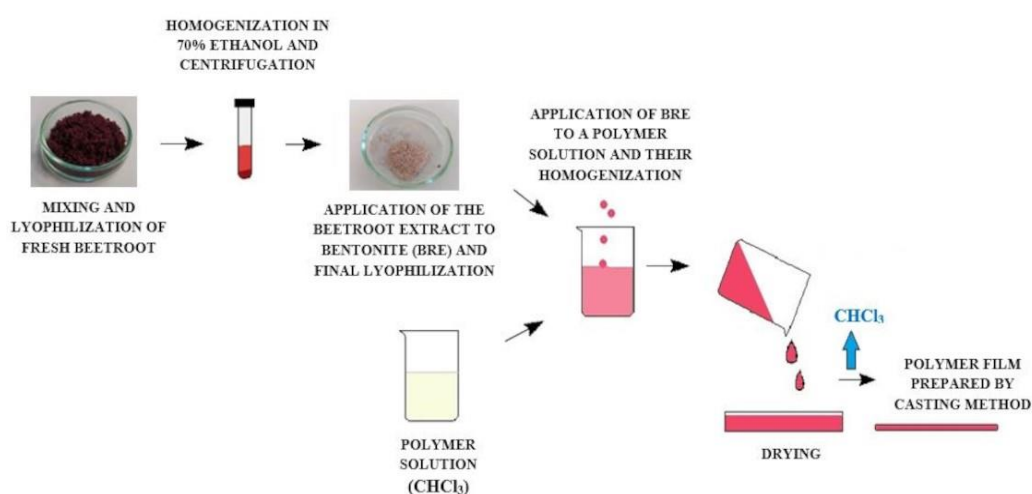


Figure 5. Method for fabrication of the samples.

Table 1. Composition of the prepared samples.

Name	Composition
PLA	Neat PLA
PLA-BE	PLA+ 5% w/w bentonite
PLA-BRE	PLA + 5% w/w bentonite with beetroot extract
PCL	Neat PCL
PCL-BE	PCL+ 5% w/w bentonite
PCL-BRE	PCL + 5% w/w bentonite with beetroot extract

The presence of the antioxidant component in the beetroot extract was detected using two spectrophotometric methods. The **Folin-Ciocalteu reagent method** (FCM) was adopted to determine the polyphenol content in the BRE. The results were expressed as mg equivalents of gallic acid per 100 g of beetroot. The antioxidant activity of BRE was determined by a basic method involving the scavenging of free radicals with **DPPH**. The results were expressed as mg

equivalents of ascorbic acid per 100 g of beetroot. And also by the **HPLC-ESI-MS/MS** spectrometric method.

Thermal analyses were performed to discern the oxidizing capacity of the BRE polymer films, the techniques comprising **DSC** ($-20 - 300\text{ }^{\circ}\text{C}$, $50\text{ ml}\cdot\text{min}^{-1}$, N_2) and **TGA** ($25 - 800\text{ }^{\circ}\text{C}$, $10\text{ K}\cdot\text{min}^{-1}$, N_2). Further DSC measurements were obtained by analysing the **thermal stability** of the samples ($20 - 400\text{ }^{\circ}\text{C}$, $20\text{ ml}\cdot\text{min}^{-1}$, O_2).

Mechanical tests characterized the stability of the samples as regards material strength when ageing. To this end, their **tensile strengths** were gauged on a universal tester, under modified conditions based on EN ISO 527-3 [85].

Tensile testing was conducted at a constant rate of uniaxial deformation of $50\text{ mm}\cdot\text{min}^{-1}$. The factor of ageing (A_f) was calculated concurrently [86].

The cryo-fracture surfaces and the surfaces of the samples were gauged in a high vacuum environment by **scanning electron microscopy** (SEM).

The characterization of the samples, which is detailed in the dissertation, also included FTIR and colorimetry analysis. The results are summarized here in the conclusion. All results are summarized here in the conclusion.

2.2 Comparative degradation study of a biodegradable composite based on polylactide with halloysite nanotubes and a polyacrylic acid copolymer

The preparation process of PLA-g-PAA first involved dehydration (160°C , 200 mBar, 4 h, 180 rpm). After this time, the appropriate amount (0.5 wt% MSA and PAA (5%)) was added dropwise with constant stirring. After one hour, the pressure was reduced to 20 kPa (165°C ; using an oil pump) and the water was distilled off. One hour later, the pressure was reduced to 1 kPa and the reaction continued for another 20 hours. After cooling, the product was dissolved in acetone. The obtained polymer solution was precipitated into a mixture of methanol and distilled water in a ratio of 1:10 (v/v) and filtered. Finally, the product was dried in an oven. Table 2 summarizes the properties of the derived prepolymer in the form of a white powder.

Table 2. Characterization of the prepared additive PLA-g-PAA.

Sample label	PAA (wt.%)	M_w ($\text{g}\cdot\text{mol}^{-1}$)	\bar{D} (-)	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)
PLA-g-PAA	5	28,000	2.8	52.6	136.2

The PLA was dried at 60°C for 24 hours prior to being processed. Neat PLA and PLA composites were obtained by melt blending (190°C , 100 rpm); the mixture emanating from the extruder was cut into small pieces and subsequently

pressed into foils at 190°C for 5 minutes and cooled. The designations given to the prepared samples and their compositions are detailed in Table 3.

Table 3. Designations and compositions of the samples.

No. of sample	PLA (wt.%)	HNT (wt.%)	PLA-g-PAA (wt.%)	Designation
1	100	-	-	PLA
2	95	5	-	PLA/5H
3	80	20	-	PLA/20H
4	95	-	5	PLA/5PLA-g-PAA
5	80	-	20	PLA/20PLA-g-PAA
6	75	20	5	PLA/20H/5PLA-g-PAA
7	75	5	20	PLA/5H/20PLA-g-PAA

The samples were monitored for mechanical properties (**tensile tests**), which were affected by the addition of individual additives. The speed of the crosshead was set to 10 mm·min⁻¹ according to the EN ISO 527-3 standard [85]. And last but not least, the morphology of the samples after the introduction of additives was monitored using **SEM**.

The following characterization related to samples that were subjected to abiotic, biotic degradation. The rate of PLA **abiotic hydrolysis** was observed for 60 days at a steady temperature of 58°C in sodium phosphate buffer (Na-PB, 0.1 mol·l⁻¹, pH 7) s inhibující látkou (NaN₃, 0,2 wt.%). Supernatants were analyzed for carbon present by **TOC-L** and also by **GPC** analysis (mobile phase THF with BHT, flow rate set at 1.0 mL·min⁻¹, PS standards in the range of 580 – 6,000,000 g·mol⁻¹). The biodegradation under **composting test** was performed according to ISO 14855-1:2012 [87]. The amount of carbon dioxide (CO₂) released is measured, along with the degree of decomposition of the given material at the end of the assessment period. The flasks were incubated at 58°C for 48 days. The samples were analyzed by **gas chromatography** (GC). **Degradation kinetics** were mathematically calculated for both hydrolysis and biodegradation. The calculation is based on first-order kinetics and determines the initial stages of the decomposition and subsequently its course using a model. Analytical solutions related to the selected models were described by Stloukal et al. [88].

The characterization of the samples, which is detailed in the dissertation, also included FTIR analysis, TGA, surface wettability (contact angle) and composting test (according to ISO 14855-1:2012 [87]) including DSC and a phytotoxicity test. All results are summarized here in the conclusion.

3. SELECTED EXPERIMENT RESULTS

3.1 Effect of an antioxidant based on red beetroot extract on the abiotic stability of polylactide and polycaprolactone

Awareness of impacts to the natural environment and the unsustainable consumption of oil have generated interest in environmentally-friendly materials. In this context, the research presented herein focused on improving the polymers PLA and PCL by supplementing them with a natural, inexpensive and readily available AO obtained from beetroot (*Beta vulgaris*). Such AOs usually need to be stabilized, so study was made as to incorporating the AO in a common inert carrier (bentonite).

Results determining the content of polyphenolic substances using the FCM method in the beet extract actually contained 93 mg. Subsequent measurements revealed that the antioxidant activity of the BRE by the DPPH method corresponded to 114 mg per the equivalent amount of 100 g of ascorbic acid.

Figure 6 shows a representative, total ion chromatogram (TIC) for the BRE determined by mass spectrometry in positive ion mode. The point at 2.98 minutes, a $[M+H]^+$ molecular peak of m/z 549.1336, presented a fragment of m/z 387.0809 and was consistent with previous findings on the fragmentation of neobetanin (Figure 7, part A). The molecular ion at 2.49 minutes had a value for m/z of 551.1509, which yielded fragments after dissociation of m/z 389.0976 (Figure 7, part B) typical for betanin or isobetanin (2.61 minutes). In coelution with betanin and isobetanin, the following were identified: 2'-O-glucosyl-betanin ($t_R = 2.52$ minutes; $[M+H]^+ = 713.2034$); and 2'-O-glucosyl-isobetanin ($t_R = 2.63$ minutes; $[M+H]^+ = 340.1132$).

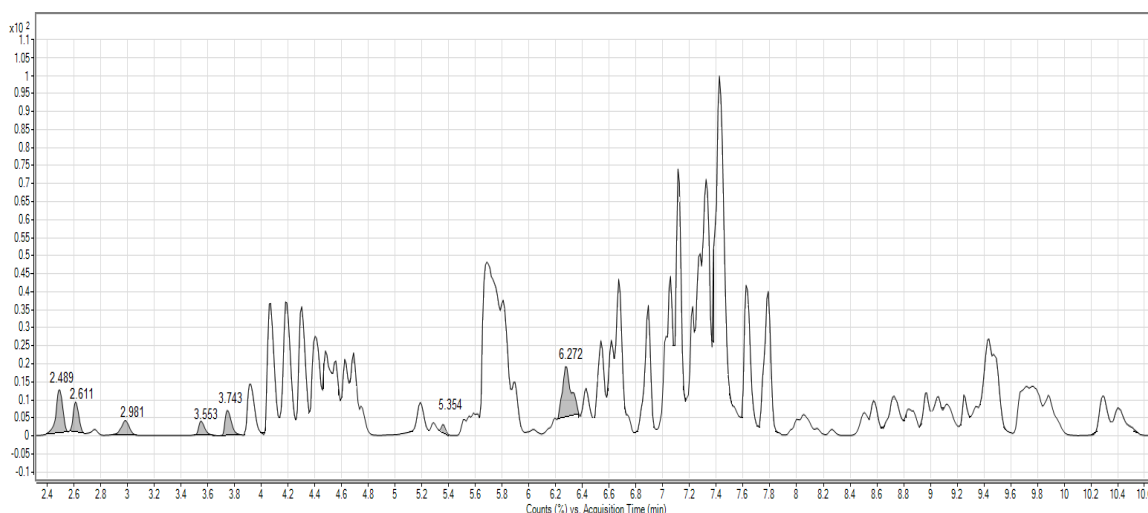


Figure 6. Representative TIC of the diluted BRE; the retention times were attributed by mass spectrometry analysis.

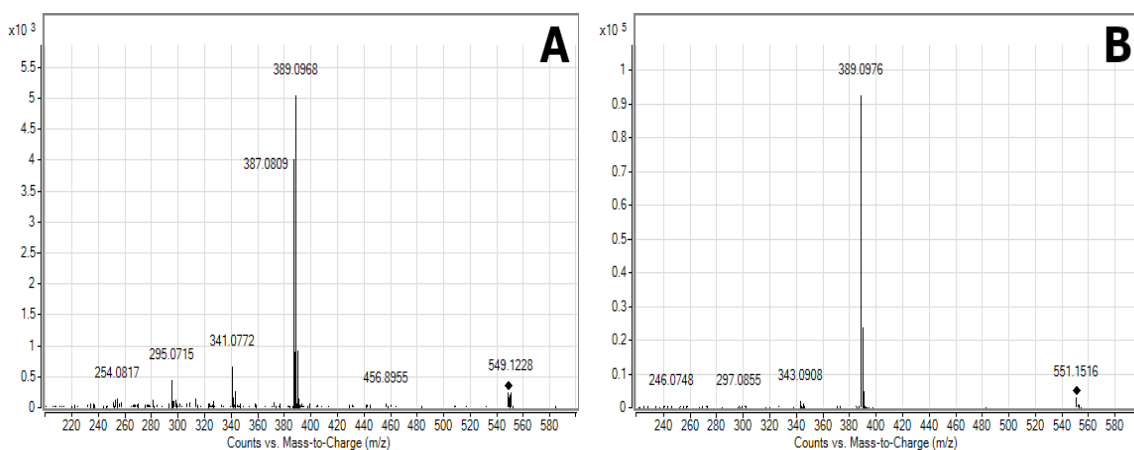


Figure 7. Positive electrospray tandem mass spectra for (A) neobetainin and (B) betainin or isobetainin.

The introduction of bentonite into PLA may have resulted in an increase in T_g in the N_2 atmosphere and also increased the T_{onset} temperature in the oxygen atmosphere. However, due to accelerated aging, the sample containing the AO component was observed to maintain the same temperature T_g ($57^\circ C$).

Table 4. DSC data for the neat PLA and PLA composites before and after the UV ageing test.

Sample	T_g [$^\circ C$]	T_m [$^\circ C$]	ΔH_m [J/g]	T_{onset} [$^\circ C$]	T_{peak} [$^\circ C$]	ΔH [J/g]
PLA	53	146	36.4	254	355	1805
PLA-BE	57	143	38.5	267	349	1564
PLA-BRE	57	145	38.0	265	347	1746
PLA-UV	49	151	41.9	212	-	-
PLA-BE-UV	53	133	37.1	216	-	-
PLA-BRE-UV	57	135	38.6	218	-	-

According to DSC measured at N_2 , no significant changes were observed in the resulting thermal properties for PCL. Although the thermal stability of PCL with AO decreased with O_2 , on the other hand, the internal enthalpy of this thermal degradation also decreased. In the case of PCL-BRE, AO acted as an antidegradant - a disruptor of the chain autoxidation reaction. Even in the case of the samples after the aging test, this phenomenon was noticeable. In addition, BRE had an effect on T_m , which was shown by the absence of chain fragments that would cause double-melting, as in the remaining samples.

Table 5. DSC data for the neat PCL and PCL composites before and after the UV ageing test.

Sample	T _{m1} [°C]	T _{m2} [°C]	ΔH _m [J/g]	T _{onset} [°C]	T _{peak} [°C]	ΔH [J/g]
PCL	65	-	88.3	245	312	3168
PCL-BE	65	-	86.4	240	314	2254
PCL-BRE	66	-	90.1	236	281	1157
PCL-UV	39	66	91.5	215	286	254
PCL-BE-UV	38	64	99.2	216	288	307
PCL-BRE-UV	-	64	92.5	208	265	143

When measuring TGA, the influence of bentonite on thermal degradation is obvious, which it improves in many cases. However, even BRE samples slow down the onset of degradation, which is visible especially in PLA samples.

Table 6. Summary of TGA curves for the PLA, PCL and composites.

Samples	T _{onset} (°C)	T ₁₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)	Mass Loss (%)
PLA	359	123	337	355	100
PLA-BE	358	140	336	357	95
PLA-BRE	357	136	335	356	95
PLA-UV	354	149	315	348	100
PLA-BE-UV	343	156	316	342	95
PLA-BRE-UV	347	175	322	346	95

Samples	T _{onset} (°C)	T ₁₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)	Mass Loss (%)
PCL	368	333	363	350	100
PCL-BE	378	307	346	449	95
PCL-BRE	378	315	348	443	95
PCL-UV	350	278	326	350	99
PCL-BE-UV	381	302	359	397	95
PCL-BRE-UV	379	281	354	398	95

Increase in Young's modulus (see Figure 8) was evident, especially in the PLA samples that had undergone ageing. These exhibited interesting behaviour regarding rise in the modulus instigated by crosslinking of the PLA chains and crystallization. The point of maximum stress of the materials was also researched (Figure 9). A slight increase in this parameter was observed for the composites with bentonite, as the latter acted as a nucleating agent.

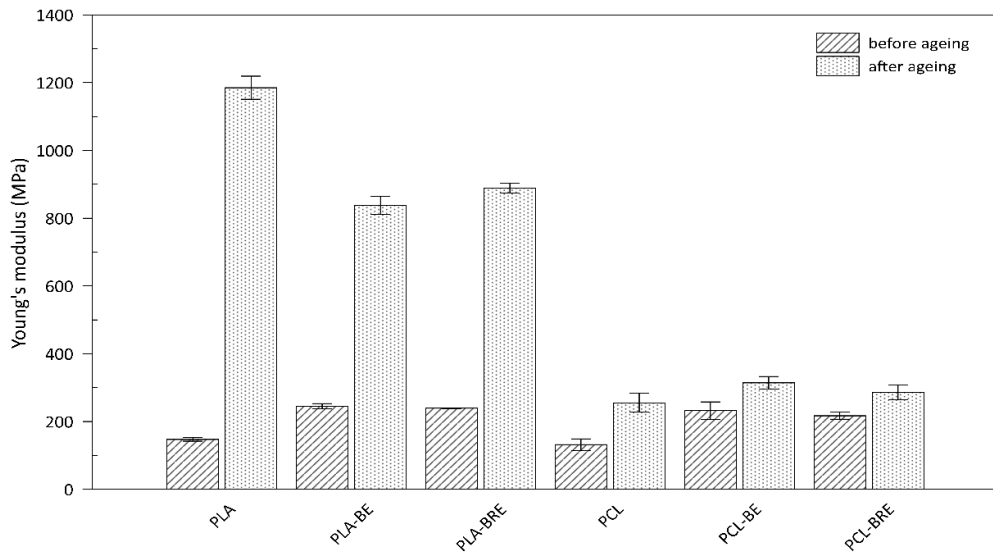


Figure 8. Mechanical properties of the PLA and PCL samples as per Young's modulus.

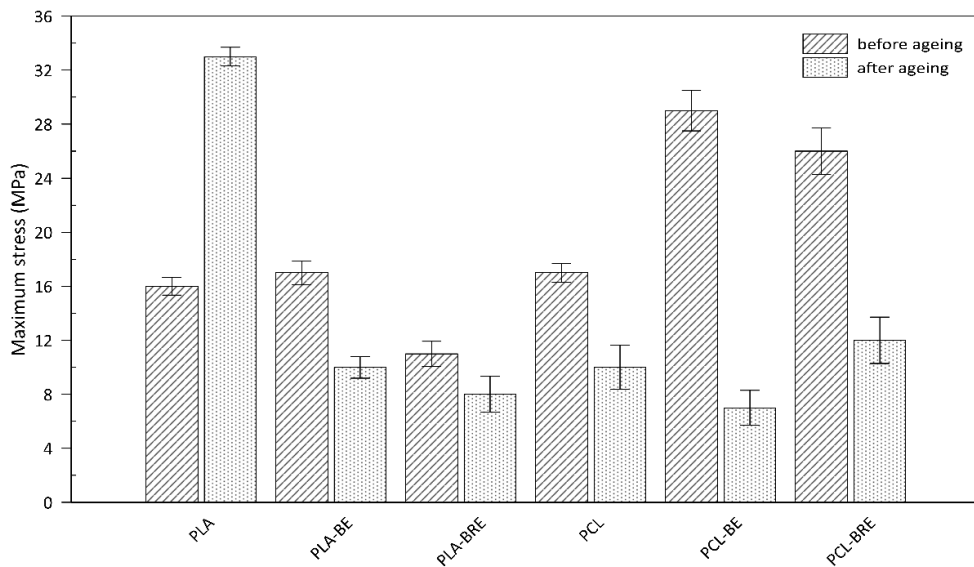


Figure 9. Mechanical properties of the PLA and PCL samples as per maximum stress.

According to the results in Table 4 relating to the ageing factor (A_f), few samples appeared to be stable under extreme conditions in the climatic chamber. However, the PCL sample supplemented with AO evinced a suitable A_f .

Table 7. Comparison of the mechanical properties of the PLA and PCL composites prior and following ageing

Samples	Before solar ageing		After solar Ageing		A_f (-)
	σ (MPa)	ε (%)	σ (MPa)	ε (%)	
PLA	15 ± 1	354 ± 18	16 ± 2	24 ± 6	0.07 ± 0.01
PLA-BE	16 ± 2	301 ± 25	6 ± 2	5 ± 1	0.01 ± 0.00
PLA-BRE	10 ± 1	363 ± 14	1 ± 1	9 ± 1	0.00 ± 0.00
PCL	17 ± 1	1006 ± 9	8 ± 3	14 ± 6	0.01 ± 0.01

PCL-BE	22 ± 2	1008 ± 6	6 ± 3	8 ± 3	0.00 ± 0.01
PCL-BRE	22 ± 2	1062 ± 8	11 ± 3	375 ± 42	0.15 ± 0.00

Optical SEM was used to obtain images of the refractive surfaces of the PLA and PCL samples (Figure 10 and 11; A–F), taken before and after exposure in the UV chamber, as well as the surfaces of the sample after the UV chamber (G–I). Although the effect of irradiation was perceptible solely on the irradiated surfaces of the materials, it was more noticeable in the PCL samples. Degradation had significantly impacted the surface of the neat PCL, which showed cavities after exposure. The PLA and PCL samples containing BRE also presented signs of degradation, though merely mild in extent and with only a thin surface layer affected.

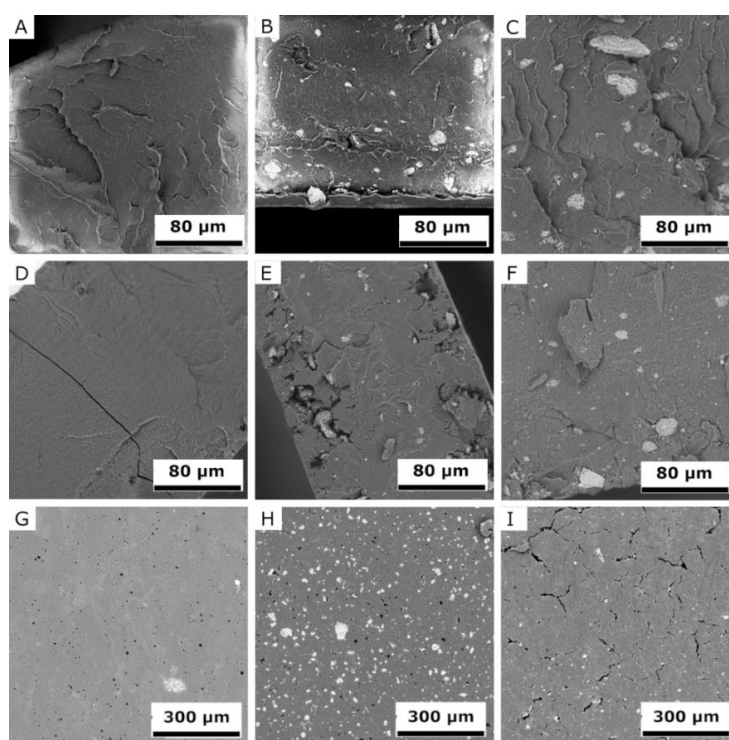


Figure 10. SEM images detailing change in the PLA samples prior to and following exposure in a UV chamber, comprising the fracture surfaces of samples (A) PLA; (B) PLA-BE; (C) PLA-BRE; (D) PLA-UV; (E) PLA-BE-UV; and (F) PLA-BRE-UV; and the surfaces of the samples (G) PLA-UV; (H) PLA-BE-UV; and (I) PLA-BRE-UV.

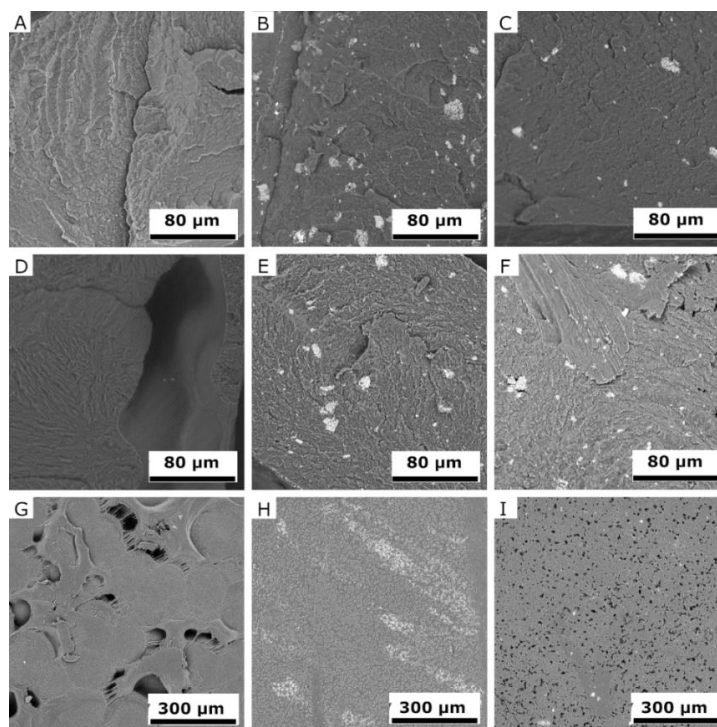


Figure 11. SEM images detailing change in the PCL samples prior to and following exposure in a UV chamber, comprising the fracture surfaces of samples (A) PCL; (B) PCL-BE; (C) PCL-BRE; (D) PCL-UV; (E) PCL-BE-UV; and (F) PCL-BRE-UV; and the surfaces of samples (G) PCL-UV; (H) PCL-BE-UV; and (I) PCL-BRE-UV.

3.2 Comparative degradation study of a biodegradable composite based on polylactide with halloysite nanotubes and a polyacrylic acid copolymer

The aim of this study was to develop a new, optimized composite supplemented with HNTs in combination with a multi-combed copolymer (PLA-g-PAA), the purpose being to accelerate the degradation processes of PLA by an applicable technological procedure. The first step involved characterizing the resulting composites in relation to certain properties - mechanical, thermal and wettability, i.e. those important for manufacturers. The unique and compact structure instigated by the additives was believed to lend high compatibility to the PLA polymer matrix, enhance mechanical and thermal properties, and help accelerate hydrolysis. Crucial to this research was the act of monitoring the rate of degradation and its course in various environments (abiotic and biotic), wherein changes in molecular weight were observed alongside the release of carbon or carbon dioxide. Kinetic models for the given types of degradation processes were also derived from the experimental data. With consideration of potential real-world applications, a disintegration experiment was carried out under composting conditions in laboratory conditions. Emulating the function of a municipal

composting plant, the intention was to explore the degradation behaviour of materials disposed of at the end of their life cycles.

The Young's modulus of the PLA/5H and PLA/20H nanocomposites increased in parallel with a rise in HNT content. In the case of PLA/5H, the value went up by 15%, and sample PLA/20H exceeded neat PLA in this regard by 25%. These values indicated that the films with HNT possessed greater stiffness. An opposite trend was seen for composite with 20 % PLA-g-PAA, whereby it was lower (up to 5 %) than for neat PLA. The combination of PLA with a lower concentration of HNT and a higher concentration of PLA-g-PAA in the composite films was advantageous because, in some cases, it could match the values for the neat PLA material, giving it more stability.

Table 8. Mechanical properties of the neat PLA and PLA composites.

Sample	E (MPa)	ϵ (%)	σ (MPa)
PLA	4 000 \pm 70 ^a	1.7 \pm 0.1 ^a	49 \pm 3 ^{a,c}
PLA/5H	4 600 \pm 130 ^{b,e}	1.4 \pm 0.3 ^{a,b,d,e}	48 \pm 3 ^{a,c}
PLA/20H	5 000 \pm 120 ^c	1.1 \pm 0.3 ^b	34 \pm 3 ^{b,d}
PLA/5PLA-g-PAA	3 900 \pm 120 ^{a,d}	2.0 \pm 0.3 ^c	51 \pm 2 ^c
PLA/20PLA-g-PAA	3 800 \pm 100 ^d	1.8 \pm 0.2 ^{a,c}	47 \pm 3 ^{a,c,d}
PLA/20H/5PLA-g-PAA	4 700 \pm 70 ^e	1.1 \pm 0.2 ^{b,d}	31 \pm 2 ^d
PLA/5H/20PLA-g-PAA	4 000 \pm 130 ^a	1.4 \pm 0.1 ^e	45 \pm 3 ^a

** The mean values followed by the same superscript letters in the same column do not exhibit differences at the 5% significance level according to Tukey's test.*

The presence of additives was observed in the fractured cross-sections. The HNT nanoparticles were observed as white particles in Figure 12 b', c', e', f', as highlighted by the blue arrows. The presence of carboxyl groups in the PLA also form bonds with hydrogen atoms in the hydroxyl groups of the HNT, giving rise to films which possess both thermal stability and increased mechanical strength. The PLA-g-PAA comb copolymer is characterized by numerous PLA side chains with a high concentration of terminal carboxyl groups, furthering compatibility with the PLA matrix.

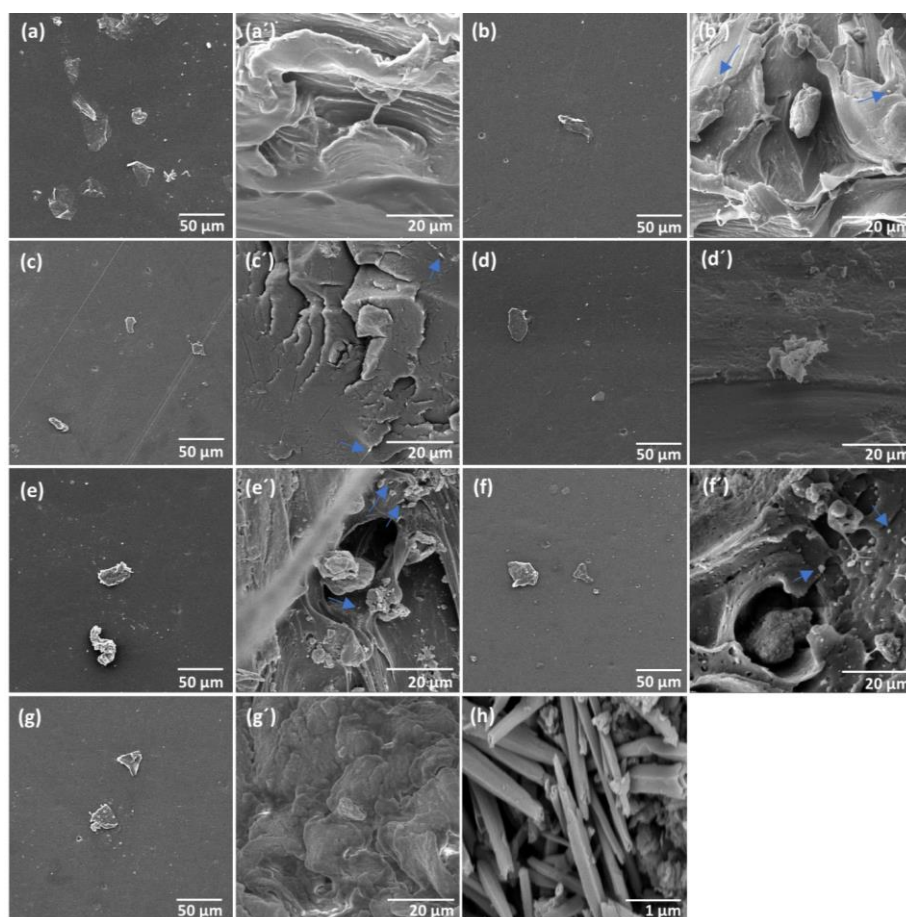


Figure 12. Electron micrographs of the surfaces and fractured surfaces of the thin films: (a, a') PLA; (b, b') PLA/5H; (c, c') PLA/5H/20PLA-g-PAA; (d, d') PLA/5PLA-g-PAA; (e, e') PLA/20H; (f, f') PLA/20H/20PLA-g-PAA; (g, g') PLA/20PLA-g-PAA; and (h) HNT; (blue arrows indicate HNT particles).

The hydrolysis experiment revealed that the mineralization of PLA accelerated as a consequence of an increase in the concentration of the PLA-g-PAA additive. This happens the fastest at the highest concentration of this kind additive (~5 days), which is half the time faster than for neat PLA (~11 days). Such acceleration was quantified by the length of lag phase C calculated from a kinetic model. The opposite effect was found for the PLA/HNT composites, primarily those containing 20% HNT. It is known that applying a higher quantity of such nanoparticles could block the release of carboxyl groups from PLA to a certain extent. However, the combination of the additives in PLA accelerated hydrolysis, and a composite containing 5% HNT and 20% PLA-g-PAA stood out in this regard. Under the given conditions, the rate constant increased from 0.041 day^{-1} for neat PLA to approximately 0.067 day^{-1} for PLA with the mentioned percentage of both fillers.

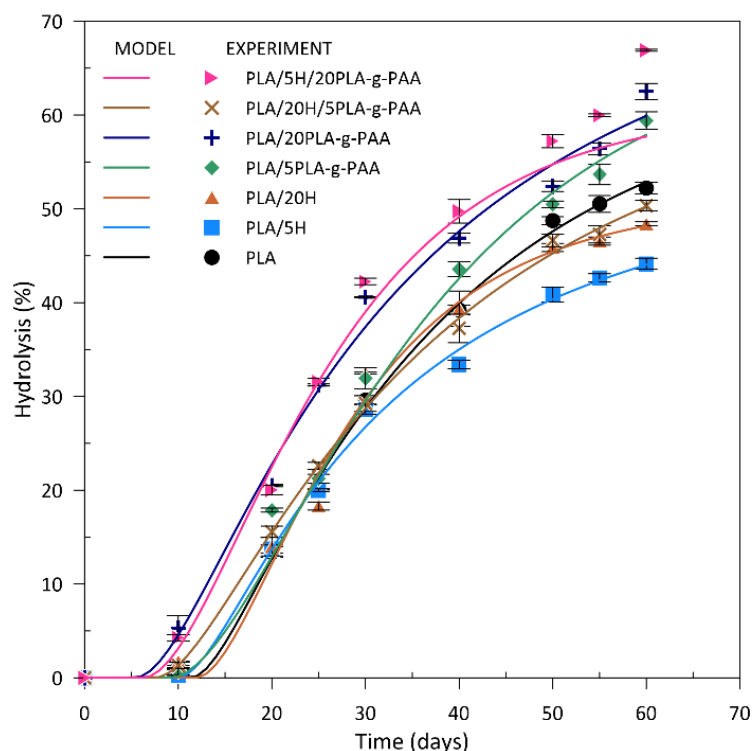


Figure 13. Carbon content of the neat PLA and PLA composites during abiotic hydrolysis, in 0.1 M Na-PB (pH~7) at 58°C.

Table 9. Parameters of the kinetic model and coefficients of determination (R^2) for the abiotic hydrolysis of the PLA and PLA composites.

Sample	$C_{aq,0}^a$ (%)	$C_{h,0}^b$ (%)	k_{hr}^c (day ⁻¹)	C^d (days)	R^2
PLA	0	30.81	0.041	11.3	0.999
PLA/5H	0	30.41	0.023	9.9	0.998
PLA/20H	0	49.14	0.030	11.9	0.992
PLA/5PLA-g-PAA	0	38.14	0.054	9.0	0.994
PLA/20PLA-g-PAA	0	41.27	0.058	5.4	0.993
PLA/20H/5PLA-g-PAA	0	36.44	0.036	7.5	0.999
PLA/5H/20PLA-g-PAA	0	60.70	0.067	6.2	0.988

^a Percentage of initial, intermediate.

^b Percentage of initial, readily hydrolysable.

^c Rate constant for first-order hydrolysis.

^d Duration of the lag phase during the initial biodegradation phase.

Experimental data obtained from mathematical evaluation with first-order kinetics described the random cleavage of the ester bonds. The rate constants

determined for chain cleavage confirmed that the phenomenon was accelerated in the PLA sample supplemented with PLA-g-PAA. The random cleavage of ester bonds in neat PLA was expressed as a rate constant of 0.1479 days^{-1} , while for PLA specimens with PLA-g-PAA it ranged from ca 0.2056 to 0.2734 days^{-1} . HNT nanoparticles had the opposite effect on hydrolysis, as the rate constant shifted from 0.1430 to 0.1302 day^{-1} .

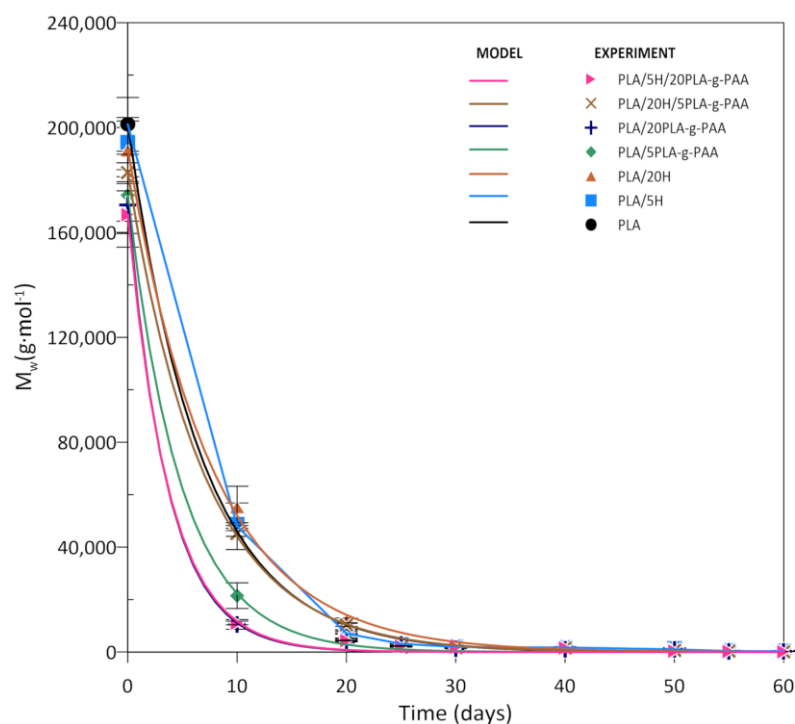


Figure 14. Reduction in molecular weight during abiotic hydrolysis of the neat PLA and various composites with additives, according to the kinetic model.

Table 10. Parameters of the first-order kinetic model and coefficients of determination (R^2) for random scission of the PLA and PLA composites.

Sample	$M_{w,0}^a$ ($\text{g}\cdot\text{mol}^{-1}$)	u^b (day^{-1})	R^2
PLA	201,467	0.1479	0.9994
PLA/5H	194,800	0.1430	0.9992
PLA/20H	191,672	0.1302	0.9988
PLA/5PLA-g-PAA	174,073	0.2056	0.9995
PLA/20PLA-g-PAA	170,412	0.2734	0.9991
PLA/20H/5PLA-g-PAA	183,008	0.1424	0.9995
PLA/5H/20PLA-g-PAA	166,819	0.2657	0.9990

^a Initial weight average M_w at time $t = 0$.

^b Rate constant of abiotic hydrolysis.

All the samples demonstrated a faster onset of the degradation mechanism than neat PLA, the quickest being reported for samples containing the PLA-g-PAA additive at 20 wt.%. As in the biotic degradation and abiotic hydrolysis experiments, samples containing the additive PLA-g-PAA tended to accelerate the hydrolysis of neat PLA, further supported by increasing its concentration. This additive also heightened degradation when combined with a low amount of the inorganic filler - HNT. Even both combined composites will accelerate the initial lag phase by 1/2 the time compared to neat PLA.

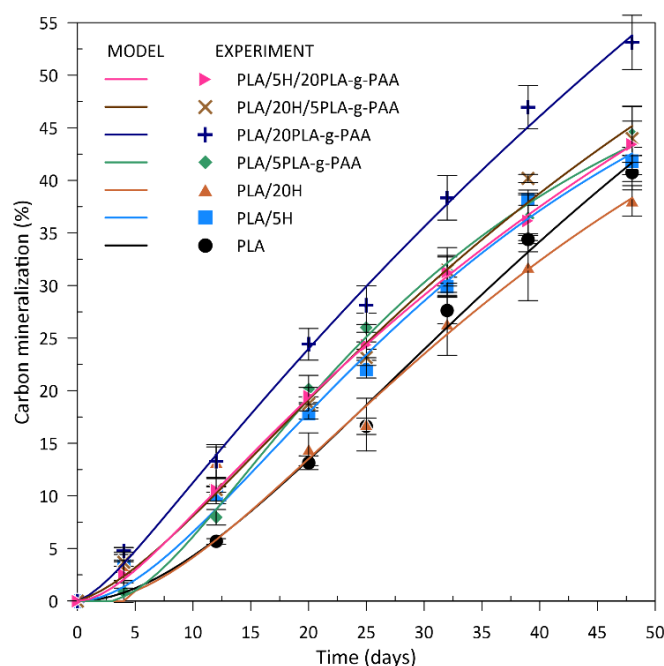


Figure 15. Biodegradation of the PLA, PLA with HNTs and PLA-g-PAA/HNT nanocomposite films, as converted to carbon during mineralization.

Table 11. Parameters of the kinetic model and coefficients of determination (R^2) for the biodegradation of the PLA and PLA composites.

Sample	$C_{aq,0}$ ^a (%)	$C_{h,0}$ ^b (%)	k_{aq} ^c (day ⁻¹)	k_{hr} ^d (day ⁻¹)	C^e (days)	R^2
PLA	0	32.61	0.0952	0.0238	2.0	0.9904
PLA/5H	0	37.55	0.1042	0.0295	1.5	0.9852
PLA/20H	0	31.62	0.0764	0.0307	4.0	0.9918
PLA/5PLA-g-PAA	0	24.35	0.1654	0.0348	1.8	0.9969
PLA/20PLA-g-PAA	0	25.54	0.2417	0.0364	0.3	0.9971
PLA/20H/5PLA-g-PAA	0	34.06	0.0747	0.0246	0.7	0.9982
PLA/5H/20PLA-g-PAA	0	39.86	0.2509	0.0397	0.9	0.9995

^a Percentage of initial, intermediate, solid carbon.

^b *Percentage of initial, readily hydrolysable, solid carbon.*

^c *Rate constant for mineralizing water-soluble carbon into carbon dioxide.*

^d *Rate constant for first-order hydrolysis.*

^e *Duration of the lag phase during the initial biodegradation phase prior to the onset of CO₂ production.*

CONCLUSIONS

The demand for ecological materials, especially biodegradable polymers, is growing significantly. PLA is a foremost biopolymer and considered one of the most promising sustainable alternatives to petroleum-based options. The rise in interest in PLA is mainly due to its interesting physical and mechanical properties, low carbon footprint, the possibility of recycling or biodegradability at the end of a life cycle of a product, and the various means of processing it that only necessitate standard equipment. In terms of large scale applications, PLA is commonly used in manufacture of sustainable packaging materials or medical and textile fibres. As yet this material has not been deemed suitable for more durable applications (e.g. in motor vehicles, electrical and electronic products, mechanical components, etc.), where performant materials are required.

In alignment with recent trends, it is advantageous to employ natural additives obtained from waste products from sectors such as agriculture. PLA constitutes an inexpensive commodity material suitable for food packaging. The natural antioxidants commercially available are difficult to apply to polymers, and their effectiveness in this material is limited. It would be desirable for certain products made of PLA to undergo rapid degradation, though. The polymer is known for its protracted degradation process that is influenced by several factors. Numerous municipal composting plants are currently unwilling to handle it, and not all PLA-based products are suitable for chemical recycling.

In relation to current knowledge, an overview of this topic was given in the theoretical part of this manuscript, and the research objectives of the work were defined. Based on this, the experimental part of the work was devoted to preparing novel biodegradable polymer systems in the form of mixed films and nanoparticles that were based on PLA and modified with additives that alter stabilization.

In the first experimental section, preparation was optimized of an extract containing an antioxidant component (AO) comprising betalains sourced from beetroot. For maximum efficiency, the extract was incorporated on a carrier of inorganic origin. Polymer films (PLA and PCL) were processed in a cast mould and the properties were monitored during an artificial ageing process in a UV chamber. Testing revealed the effect exerted by the AO additive, manifested in one respect as both a reduction and change in colour. Determining the thermal stability of the samples by DSC analysis revealed that the AO in the PLA sample neither affected T_g nor diminished the onset of degradation in an oxygen atmosphere. Thermal degradation of the AO-supplemented PLA sample, prior to and following UV exposure, commenced at higher temperatures than the pure matrix. The PCL sample containing the AO component additionally demonstrated stable behaviour, as confirmed by internal enthalpy.

The second part focused on accelerating the degradation of the PLA matrix by applying selected additives. Comparison was made as to the content and concentrations of the given additives PLA-g-PAA and HNTs on the degradation rate and efficiency in the abiotic and biotic environments, including in compost. The results confirmed that the effect of the PLA-g-PAA additive was to accelerate degradation in all environments. In the case of the HNT additives, this ability was influenced by the environment and the given amount, optimally up to 5 wt.%. A positive finding concerns the fact that during the decomposition of the composites, no impact was discerned against the properties of the compost that would impair its quality, as confirmed by a phytotoxicity test.

Both research papers usher in benefits pertaining to the stability of the investigated biopolymers and the ability to modify them with additives (even natural ones). It would be appropriate in future research to explore matters such as enhancing the incorporation of a natural AO, thereby permitting industrial heat treatment methods for polymer fabrication. In the case of the second paper, it would be interesting in the future to observe conditions at landfill sites, where the decomposition of plastics occurs most frequently.

CONTRIBUTIONS TO SCIENCE AND PRACTICE

The presented dissertation investigates a selection of natural and synthetic additives for their ability to modify biopolymers, specifically polylactide. The aim is to obtain a biodegradable material for which it is possible to regulate the degradation mechanism, hence its relevance to contemporary academic and industrial research.

Furthermore, this work deals with the preparation and optimization of the composition of the additives to ensure their effective action in the polymer matrix. The related findings show great potential, especially in terms of application in practice.

The main contribution to science pertains to the preparation and characterization of new biodegradable systems for slowing down the degradation mechanism of a PLA-based material modified with natural and synthetic additives. This transpired via the following experiments:

- incorporation of a natural antioxidant on an inorganic carrier and preparation of films with the potential to reduce the degradation processes of the given biodegradable polymer, as well as extend the life cycle of the final product with a view to potential in the packaging industry;
- preparation of a composite based on polylactide and polyacrylic acid, supplemented with a nanoclay in order to achieve the maximum degradation effect in technical composting plants with the potential as a material in disposable packaging.

The results presented in this work were processed within the infrastructure of the Polymer Centre. The results obtained also constitute part of a project wherein the findings of applied research in the form of a utility model or a functional sample were achieved and were (or will be) published in international journals with an impact factor.

REFERENCES

- [1] BANERJEE, Ritima and Suprakas Sinha RAY. An overview of the recent advances in polylactide-based sustainable nanocomposites. *Polymer Engineering & Science*. 2021, **61**(3), 617–649. ISSN 0032-3888. Available at: doi:10.1002/pen.25623
- [2] NAMPOOTHIRI, Kesvan Madhavan, Nimisha Rajendran NAIR and Rojan Pappy JOHN. An overview of the recent developments in polylactide (PLA) research. *Bioresource Technology*. 2010, **101**(22), 8493–8501. ISSN 0960-8524. Available at: doi:10.1016/J.BIORTECH.2010.05.092
- [3] KOST, Bartłomiej, Małgorzata BASKO, Melania BEDNAREK, Marta SOCKA, Bartosz KOPKA, Grzegorz ŁAPIENIS, Tadeusz BIELA, Przemysław KUBISA and Marek BRZEZIŃSKI. The influence of the functional end groups on the properties of polylactide-based materials. *Progress in Polymer Science*. 2022, **130**, 101556. ISSN 0079-6700. Available at: doi:10.1016/j.progpolymsci.2022.101556
- [4] GIEŁDOWSKA, Małgorzata, Michał PUCHALSKI, Grzegorz SZPARAGA and Izabella KRUCIŃSKA. *Investigation of the Influence of PLA Molecular and Supramolecular Structure on the Kinetics of Thermal-Supported Hydrolytic Degradation of Wet Spinning Fibres*. 2020. ISBN 1996-1944. Available at: doi:10.3390/ma13092111
- [5] RESEARCHANDMARKETS.COM. *Polylactic Acid Market Size, Share & Trends Analysis Report By End-use (Packaging, Textile, Agriculture, Automotive & Transport, Electronics), By Region (North America, APAC, Europe), And Segment Forecasts, 2021 - 2028*. 2021. Available at: <https://www.grandviewresearch.com/industry-analysis/polylactic-acid-pla-market>
- [6] ZHONG, Yajie, Patrick GODWIN, Yongcan JIN and Huining XIAO. Biodegradable polymers and green-based antimicrobial packaging materials: A mini-review. *Advanced Industrial and Engineering Polymer Research*. 2020, **3**(1), 27–35. ISSN 25425048. Available at: doi:10.1016/j.aiepr.2019.11.002
- [7] MONTANÉ, Xavier, Josep Maria MONTORNÈS, Adrianna NOGALSKA, Magdalena OLKIEWICZ, Marta GIAMBERINI, Ricard GARCIA-VALLS, Marina BADIA-FABREGAT, Irene JUBANY and Bartosz TYLKOWSKI. Chemical Technologies and Processes. In: Katarzyna STASZAK, Karolina WIESZCZYCKA and Bartosz TYLKOWSKI, eds. . B.m.: De Gruyter, 2020, p. 281–296. ISBN 9783110656367. Available at: doi:10.1515/9783110656367-010
- [8] JIANG, Long and Jinwen ZHANG. Biodegradable and Biobased Polymers. In: *Applied Plastics Engineering Handbook: Processing, Materials, and Applications: Second Edition*. B.m.: Elsevier Inc., 2017, p. 127–143. ISBN 9780323390408. Available at: doi:10.1016/B978-0-323-39040-

8.00007-9

- [9] ZUZA, Ester, Emilio MEAURIO and Jose-Ramon SARASUA. Biodegradable polylactide-based composites. In: *Composites from Renewable and Sustainable Materials*. 2016. ISBN 978-953-51-2793-2. Available at: doi:10.5772/65468
- [10] ZHANG, Yachuan, Junghoon HAN and Zhiqiang LIU. Starch-based edible films. In: *Environmentally Compatible Food Packaging*. B.m.: Elsevier Inc., 2008, p. 108–136. ISBN 9781845691943. Available at: doi:10.1533/9781845694784.1.108
- [11] ÖZ, Ayse Tulin, Özge SÜFER and Yasemin Çelebi SEZER. Poly (lactic acid) films in food packaging systems. *Food Science & Nutrition Technology*. 2017, **2**(4), 000131. ISSN 2574-2701. Available at: doi:10.23880/FSNT-16000131
- [12] HOSSEINI, Majid and Abdel Salam Hamdy MAKHLOUF. *Industrial Applications for Intelligent Polymers and Coatings*. 1st ed. B.m.: Springer International Publishing, 2016. ISBN 9783319268934. Available at: doi:10.1007/978-3-319-26893-4
- [13] AURAS, Rafael, Bruce HARTE and Susan SELKE. An overview of polylactides as packaging materials. *Macromolecular Bioscience*. 2004, **4**(9), 835–864. ISSN 1616-5187. Available at: doi:10.1002/mabi.200400043
- [14] GUPTA, Bhuvanesh, Nilesh REVAGADE and Jöns HILBORN. Poly(lactic acid) fiber: An overview. *Progress in Polymer Science*. 2007, **32**(4), 455–482. ISSN 00796700. Available at: doi:10.1016/j.progpolymsci.2007.01.005
- [15] GARCÍA IBARRA, V., R. SENDÓN and A. RODRÍGUEZ-BERNALDO DE QUIRÓS. Antimicrobial Food Packaging Based on Biodegradable Materials. *Antimicrobial Food Packaging*. 2016, 363–384. Available at: doi:10.1016/B978-0-12-800723-5.00029-2
- [16] BISHOP, George, David STYLES and Piet Nicolaas Luc LENS. Environmental performance of bioplastic packaging on fresh food produce: A consequential life cycle assessment. *Journal of Cleaner Production*. 2021, **317**, 128377. ISSN 09596526. Available at: doi:10.1016/j.jclepro.2021.128377
- [17] LAMBERTI, Fabio M, Luis A ROMÁN-RAMÍREZ and Joseph WOOD. Recycling of bioplastics: routes and benefits. *Journal of Polymers and the Environment*. 2020, **28**(10), 2551–2571. ISSN 1566-2543. Available at: doi:10.1007/s10924-020-01795-8
- [18] KARAMANLIOGLU, Mehlika, Richard PREZIOSI and Geoffrey D ROBSON. Abiotic and biotic environmental degradation of the bioplastic polymer poly(lactic acid): A review. *Polymer Degradation and Stability*. 2017, **137**, 122–130. ISSN 01413910. Available at: doi:10.1016/j.polymdegradstab.2017.01.009

- [19] NASROLLAHZADEH, Mahmoud. *Biopolymer-Based Metal Nanoparticle Chemistry for Sustainable Applications: Volume 2: Applications*. B.m.: Elsevier, 2021. ISBN 9780128221235. Available at: doi:10.1016/C2020-0-03104-X
- [20] ROY, Swarup and Jong-Whan RHIM. Preparation of bioactive functional poly(lactic acid)/curcumin composite film for food packaging application. *International Journal of Biological Macromolecules*. 2020, **162**(1), 1780–1789. ISSN 01418130. Available at: doi:10.1016/j.ijbiomac.2020.08.094
- [21] BALLA, Evangelia, Vasileios DANIILIDIS, Georgia KARLIOTI, Theocharis KALAMAS, Myrika STEFANIDOU, Nikolaos D. BIKIARIS, Antonios VLACHOPOULOS, Ioanna KOUMENTAKOU and Dimitrios N BIKIARIS. Poly(lactic Acid): A versatile biobased polymer for the future with multifunctional properties—From monomer synthesis, polymerization techniques and molecular weight increase to PLA applications. *Polymers*. 2021, **13**(11), 1822. ISSN 2073-4360. Available at: doi:10.3390/polym13111822
- [22] DESTEFANO, Vincent, Salaar KHAN and Alonzo TABADA. Applications of PLA in modern medicine. *Engineered Regeneration*. 2020, **1**, 76–87. ISSN 26661381. Available at: doi:10.1016/j.engreg.2020.08.002
- [23] ONG, Kevin L, Brian Min YUN and Joshua B WHITE. New biomaterials for orthopedic implants. *Orthopedic Research and Reviews*. 2015, **2015**(7), 107–130. ISSN 1179-1462. Available at: doi:10.2147/ORR.S63437
- [24] LIU, Shan, Shuhao QIN, Min HE, Dengfeng ZHOU, Qingdong QIN and Hao WANG. Current applications of poly(lactic acid) composites in tissue engineering and drug delivery. *Composites Part B: Engineering*. 2020, **199**, 108238. ISSN 13598368. Available at: doi:10.1016/j.compositesb.2020.108238
- [25] KNOCH, Simon, Francine PELLETIER, Mikaël LAROSE, Gérald CHOUINARD, Marie-Josée DUMONT and Jason R TAVARES. Surface modification of PLA nets intended for agricultural applications. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2020, **598**, 124787. ISSN 09277757. Available at: doi:10.1016/j.colsurfa.2020.124787
- [26] BAIKIN, Alexander S., Mikhail A. KAPLAN, Elena O. NASAKINA, Lyudmila A. SHATOVA, Alena M. TSAREVA, Anastasia A. KOLMAKOVA, Elena A. DANILOVA, Ya A. TISHUROVA, Nikolai F. BUNKIN, Sergey V. GUDKOV, Konstantin N. BELOSLUDTSEV, Alexei P. GLINUSHKIN, Alexey G. KOLMAKOV and Mikhail A. SEVOSTYANOV. Development of a biocompatible and biodegradable polymer capable of long-Term release of biologically active substances for medicine and agriculture. *Doklady Chemistry*. 2019, **489**(1), 261–263. ISSN 0012-5008. Available at: doi:10.1134/S0012500819110041
- [27] BOUZOUITA, Amani. *Elaboration of polylactide-based materials for automotive application : study of structure-process-properties interactions*.

- B.m., 2016. Université de Valenciennes et du Hainaut-Cambresis, Université de Mons, Mons, Belgium.
- [28] AKAMPUMUZA, Obed, Paul Musili WAMBUA, Azzam AHMED, Wei LI and Xiao-Hong QIN. Review of the applications of biocomposites in the automotive industry. *Polymer Composites*. 2017, **38**(11), 2553–2569. ISSN 02728397. Available at: doi:10.1002/pc.23847
- [29] LÓPEZ AZNAR, Nuria. Sustainable fibers for textile applications. *Industrial Biotechnology*. 2019, **15**(5), 290–292. ISSN 1550-9087. Available at: doi:10.1089/ind.2019.29187.nla
- [30] YANG, Yadie, Minglonghai ZHANG, Zixin JU, Po Ying TAM, Tao HUA, Muhammad Waseem YOUNAS, Hasan KAMRUL and Hong HU. Poly(lactic acid) fibers, yarns and fabrics: Manufacturing, properties and applications. *Textile Research Journal*. 2021, **91**(13–14), 1641–1669. ISSN 0040-5175. Available at: doi:10.1177/0040517520984101
- [31] BENIAK, Juraj, Ľubomír ŠOOŠ, Peter KRIŽAN, Miloš MATUŠ and Vít RUPRICH. *Resistance and Strength of Conductive PLA Processed by FDM Additive Manufacturing*. 2022. ISBN 2073-4360. Available at: doi:10.3390/polym14040678
- [32] DASSANAYAKA, Dumindu, Dilshan HEDIGALLA and Ujithe GUNASEKERA. Biodegradable Composite for Temporary Partitioning Materials. In: *2020 Moratuwa Engineering Research Conference (MERCon)*. B.m.: IEEE, 2020, p. 453–458. ISBN 978-1-7281-9975-7. Available at: doi:10.1109/MERCon50084.2020.9185232
- [33] RETI, Christelle, Mathilde CASETTA, Sophie DUQUESNE, René DELOBEL, Jérémie SOULESTIN and Serge BOURBIGOT. Intumescent biobased-poly lactide films to flame retard nonwovens. *Journal of Engineered Fibers and Fabrics*. 2009, **4**(2), 155892500900400. ISSN 1558-9250. Available at: doi:10.1177/155892500900400206
- [34] REN, Jie. *Biodegradable Poly(Lactic Acid): Synthesis, Modification, Processing and Applications*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2010. ISBN 978-3-642-17595-4. Available at: doi:10.1007/978-3-642-17596-1
- [35] PUTHUMANA, Manju, P SANTHANA GOPALA KRISHNAN and Sanjay Kumar NAYAK. Chemical modifications of PLA through copolymerization. *International Journal of Polymer Analysis and Characterization*. 2020, **25**(8), 634–648. ISSN 1023-666X. Available at: doi:10.1080/1023666X.2020.1830650
- [36] MARSH, Kenneth and Betty BUGUSU. Food packaging - roles, materials, and environmental issues. *Journal of Food Science*. 2007, **72**(3), R39–R55. ISSN 0022-1147. Available at: doi:10.1111/j.1750-3841.2007.00301.x
- [37] LEONG, Teen Wei and Rashad YAZDANIFARD. Edible food packaging as an eco-friendly technology using green marketing strategy. *Global Journal of Commerce & Management Perspective*. 2013, **2**(6), 8–11.

- [38] KERSHAW, Peter. *Exploring the potential for adopting alternative materials to reduce marine plastic litter*. 2018. ISBN 978-92-807-3703-5. Available at: doi:10.13140/RG.2.2.26075.87849
- [39] ZOU, Wei, Jintao HUANG, Jingtao SU, Wei ZENG, Yong LIANG, Rongyuan CHEN, Haichen ZHANG, Yonggang MIN and Zhanhu GUO. Review on modification of poly (lactic acid) in physical and mechanical properties. *ES Food & Agroforestry*. 2021, **6**, 3–11. ISSN 26877295. Available at: doi:10.30919/esfaf562
- [40] MAHARANA, Tungabidya, Sasmita PATTANAIK, Anita ROUTARAY, Nibedita NATH and Alekha Kumar SUTAR. Synthesis and characterization of poly(lactic acid) based graft copolymers. *Reactive and Functional Polymers*. 2015, **93**(4), 47–67. ISSN 13815148. Available at: doi:10.1016/j.reactfunctpolym.2015.05.006
- [41] SIN, Lee Tin and Bee Soo TUEEN. *Poly(lactic Acid): A Practical Guide for the Processing, Manufacturing, and Applications of PLA*. B.m.: Elsevier, 2019. *Plastics Design Library*. ISBN 9780128144725. Available at: doi:10.1016/C2017-0-01057-1
- [42] NCUBE, Lindani Koketso, Albert Uchenna UDE, Enoch Nifise OGUNMUYIWA, Rozli ZULKIFLI and Isaac Nongwe BEAS. Environmental impact of food packaging materials: A review of contemporary development from conventional plastics to polylactic acid based materials. *Materials*. 2020, **13**(21), 4994. ISSN 1996-1944. Available at: doi:10.3390/ma13214994
- [43] MOUSTAFA, Hesham, Ahmed Mahmoud YOUSSEF, Nabila A. DARWISH and Ahmed I. ABOU-KANDIL. Eco-friendly polymer composites for green packaging: Future vision and challenges. *Composites Part B: Engineering*. 2019, **172**, 16–25. ISSN 13598368. Available at: doi:10.1016/j.compositesb.2019.05.048
- [44] PIEKARSKA, Klaudia, Przemyslaw SOWINSKI, Ewa PIORKOWSKA, Md.M.-Ul. HAQUE and Mariano PRACELLA. Structure and properties of hybrid PLA nanocomposites with inorganic nanofillers and cellulose fibers. *Composites Part A: Applied Science and Manufacturing*. 2016, **82**, 34–41. ISSN 1359835X. Available at: doi:10.1016/j.compositesa.2015.11.019
- [45] NWAKAUDU, Adanze Angela, M.S. NWAKAUDU, C.I. OWUAMANAM and Nnamdi Chibuike IHEATURU. The use of natural antioxidant active polymer packaging for food preservation: A review. *Applied Signals Reports*. 2015, **2**(4), 38–50.
- [46] BIRON, Michel. Recycling Plastics: Advantages and Limitations of Use. In: Michel B T - *A Practical Guide to Plastics Sustainability* BIRON, ed. *A Practical Guide to Plastics Sustainability*. B.m.: Elsevier, 2020, p. 411–467. ISBN 978-0-12-821539-5. Available at: doi:10.1016/B978-0-12-821539-5.00009-4
- [47] STANDAU, Tobias, Mohammadreza NOFAR, Dominik DÖRR, Holger

- RUCKDÄSCHEL and Volker ALTSTÄDT. A Review on multifunctional epoxy-based Joncryl® ADR chain extended thermoplastics. *Polymer Reviews*. 2022, **62**(2), 296–350. ISSN 1558-3724. Available at: doi:10.1080/15583724.2021.1918710
- [48] HÖFER, Rainer. Processing and performance additives for plastics. In: Krzysztof MATYJASZEWSKI and Martin B T - Polymer Science: A Comprehensive Reference MÖLLER, eds. *Polymer Science: A Comprehensive Reference*. Amsterdam: Elsevier, 2012, p. 369–381. ISBN 978-0-08-087862-1. Available at: doi:10.1016/B978-0-444-53349-4.00272-7
- [49] FLEISCHMANN, Carolin, Melanie LIEVENBRÜCK and Helmut RITTER. Polymers and dyes: Developments and applications. *Polymers*. 2015, **7**(4), 717–746. ISSN 2073-4360. Available at: doi:10.3390/polym7040717
- [50] ZAABA, Nor Fasihah and Mariatti JAAFAR. A review on degradation mechanisms of polylactic acid: Hydrolytic, photodegradative, microbial, and enzymatic degradation. *Polymer Engineering & Science*. 2020, **60**(9), 2061–2075. ISSN 0032-3888. Available at: doi:10.1002/pen.25511
- [51] HAKKARAINEN, Minna. Aliphatic Polyesters: Abiotic and Biotic Degradation and Degradation Products. In: Ann-Christine ALBERTSSON, ed. *Degradable Aliphatic Polyesters*. B.m.: Springer Berlin Heidelberg, 2002, p. 113–138. ISBN 978-3-540-42249-5. Available at: doi:10.1007/3-540-45734-8_4
- [52] ELSAWY, Moataz Ahmed, Ki-Hyun KIM, Jae-Woo PARK and Akash DEEP. Hydrolytic degradation of polylactic acid (PLA) and its composites. *Renewable and Sustainable Energy Reviews*. 2017, **79**, 1346–1352. ISSN 13640321. Available at: doi:10.1016/j.rser.2017.05.143
- [53] ROSLI, Noor Afizah, Mehlika KARAMANLIOGLU, Hanieh KARGARZADEH and Ishak AHMAD. Comprehensive exploration of natural degradation of poly(lactic acid) blends in various degradation media: A review. *International Journal of Biological Macromolecules*. 2021, **187**, 732–741. ISSN 01418130. Available at: doi:10.1016/j.ijbiomac.2021.07.196
- [54] CHAMAS, Ali, Hyunjin MOON, Jiajia ZHENG, Yang QIU, Tarnuma TABASSUM, Jun Hee JANG, Mahdi ABU-OMAR, Susannah L SCOTT and Sangwon SUH. Degradation rates of plastics in the environment. *ACS Sustainable Chemistry & Engineering*. 2020, **8**(9), 3494–3511. Available at: doi:10.1021/acssuschemeng.9b06635
- [55] GORRASI, Giuliana and Roberto PANTANI. Hydrolysis and Biodegradation of Poly(lactic acid). In: Maria Laura DI LORENZO and René ANDROSCH, eds. *Synthesis, Structure and Properties of Poly(lactic acid)*. B.m.: Springer Cham, 2017, p. 119–151. ISBN 978-3-319-64229-1. Available at: doi:10.1007/12_2016_12

- [56] WEST CONSHOHOCKEN, PA: ASTM International. *ASTM Standard D883-12. Standard terminology relating to plastics*. 2012
- [57] TOKIWA, Yutaka and Buenaventurada P. CALABIA. Biodegradability and biodegradation of poly(lactide). *Applied Microbiology and Biotechnology*. 2006, **72**(2), 244–251. ISSN 0175-7598. Available at: doi:10.1007/s00253-006-0488-1
- [58] DEVANSHI, Sutaria, Kamlesh R. SHAH, Sudipti ARORA and Sonika SAXENA. Actinomycetes as an environmental scrubber. In: *Crude Oil - New Technologies and Recent Approaches*. B.m.: IntechOpen, 2022. Available at: doi:10.5772/intechopen.99187
- [59] BUTBUNCHU, Natthicha and Wasu PATHOM-AREE. Actinobacteria as promising candidate for polylactic acid type bioplastic degradation. *Frontiers in Microbiology*. 2019, **10**, 2834. ISSN 1664-302X. Available at: doi:10.3389/fmicb.2019.02834
- [60] MOUHOUBI, Rakine, Merel LASSCHUIJT, Salma RAMON CARRASCO, Hubert GOJZEWSKI and Frederik R WURM. End-of-life biodegradation? how to assess the composting of polyesters in the lab and the field. *Waste Management*. 2022, **154**, 36–48. ISSN 0956-053X. Available at: doi:https://doi.org/10.1016/j.wasman.2022.09.025
- [61] GIRONI, Fausto and Vincenzo PIEMONTE. Life cycle assessment of polylactic acid and polyethylene terephthalate bottles for drinking water. *Environmental Progress & Sustainable Energy*. 2011, **30**(3), 459–468. ISSN 19447442. Available at: doi:10.1002/ep.10490
- [62] MORETTI, Christian, Lorie HAMELIN, Line Geest JAKOBSEN, Martin H JUNGINGER, Maria Magnea STEINGRIMSDOTTIR, Linda HØIBYE and Li SHEN. Cradle-to-grave life cycle assessment of single-use cups made from PLA, PP and PET. *Resources, Conservation and Recycling*. 2021, **169**, 105508. ISSN 09213449. Available at: doi:10.1016/j.resconrec.2021.105508
- [63] TAMBURINI, Elena, Stefania COSTA, Daniela SUMMA, Letizia BATTISTELLA, Elisa Anna FANO and Giuseppe CASTALDELLI. Plastic (PET) vs bioplastic (PLA) or refillable aluminium bottles – What is the most sustainable choice for drinking water? A life-cycle (LCA) analysis. *Environmental Research*. 2021, **196**, 110974. ISSN 00139351. Available at: doi:10.1016/j.envres.2021.110974
- [64] PORFYRIS, Athanasios D., S VASILAKOS, Christos ZOTIADIS, Constantine D. PAPASPYRIDES, K MOSER, L VAN DER SCHUEREN, Guy BUYLE, Silvia PAVLIDOU and Stamatina VOUYIOUKA. Accelerated Ageing and Hydrolytic Stabilization of Poly(lactic acid) (PLA) under Humidity and Temperature Conditioning. *Polymer Testing*. 2018, **68**, 315–332. ISSN 01429418. Available at: doi:10.1016/j.polymertesting.2018.04.018
- [65] LASKE, Stephan, Wolfgang ZIEGLER, Markus KAINER, Johannes

- WUERFEL and Clemens HOLZER. Enhancing the temperature stability of PLA by compounding strategies. *Polymer Engineering & Science*. 2015, **55**(12), 2849–2858. ISSN 00323888. Available at: doi:10.1002/pen.24176
- [66] D'URSO, Luciana, Maria ACOCELLA, Gaetano GUERRA, Valentina IOZZINO, Felice DE SANTIS and Roberto PANTANI. PLA melt stabilization by high-surface-area graphite and carbon black. *Polymers*. 2018, **10**(2), 139. ISSN 2073-4360. Available at: doi:10.3390/polym10020139
- [67] NAGASAWA, Naotsugu, Ayako KANEDA, Shinichi KANAZAWA, Toshiaki YAGI, Hiroshi MITOMO, Fumio YOSHII and Masao TAMADA. Application of poly(lactic acid) modified by radiation crosslinking. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*. 2005, **236**(1–4), 611–616. ISSN 0168583X. Available at: doi:10.1016/j.nimb.2005.04.052
- [68] YANG, Sen-lin, Zhi-Hua WU, Wei YANG and Ming-Bo YANG. Thermal and mechanical properties of chemical crosslinked polylactide (PLA). *Polymer Testing*. 2008, **27**(8), 957–963. ISSN 01429418. Available at: doi:10.1016/j.polymertesting.2008.08.009
- [69] BEDNAREK, Melania, Katarina BORSKA and Przemysław KUBISA. Crosslinking of polylactide by high energy irradiation and photo-curing. *Molecules*. 2020, **25**(21), 4919. ISSN 1420-3049. Available at: doi:10.3390/molecules25214919
- [70] KHANKRUA, Rattikarn, Sommai PIVSA-ART, Hamada HIROYUKI and Supakij SUTTIRUENGWONG. Effect of chain extenders on thermal and mechanical properties of poly(lactic acid) at high processing temperatures: Potential application in PLA/Polyamide 6 blend. *Polymer Degradation and Stability*. 2014, **108**, 232–240. ISSN 0141-3910. Available at: doi:https://doi.org/10.1016/j.polymdegradstab.2014.04.019
- [71] NAJAFI, Naqi, Marie Claude HEUZEY, Pierre J. CARREAU and Paula Marie WOOD-ADAMS. Control of thermal degradation of polylactide (PLA)-clay nanocomposites using chain extenders. *Polymer Degradation and Stability*. 2012, **97**(4), 554–565. ISSN 01413910. Available at: doi:10.1016/j.polymdegradstab.2012.01.016
- [72] ALIOTTA, Laura, Patrizia CINELLI, Maria Beatrice COLTELLI, Maria Cristina RIGHETTI, Massimo GAZZANO and Andrea LAZZERI. Effect of nucleating agents on crystallinity and properties of poly (lactic acid) (PLA). *European Polymer Journal*. 2017, **93**, 822–832. ISSN 00143057. Available at: doi:10.1016/j.eurpolymj.2017.04.041
- [73] KOVALCIK, Adriana, Ricardo A. PÉREZ-CAMARGO, Christian FÜRST, Pavel KUCHARCZYK and Alejandro J. MÜLLER. Nucleating efficiency and thermal stability of industrial non-purified lignins and ultrafine talc in poly(lactic acid) (PLA). *Polymer Degradation and Stability*. 2017, **142**, 244–254. ISSN 01413910. Available

at: doi:10.1016/j.polymdegradstab.2017.07.009

- [74] HERC, Agata S., Joanna BOJDA, Maria NOWACKA, Piotr LEWIŃSKI, Waldemar MANIUKIEWICZ, Ewa PIORKOWSKA and Anna KOWALEWSKA. Crystallization, structure and properties of polylactide/ladder poly(silsesquioxane) blends. *Polymer*. 2020, **201**, 122563. ISSN 00323861. Available at: doi:10.1016/j.polymer.2020.122563
- [75] BRITO, Jordan, Hanna HLUSHKO, Ashleigh ABBOTT, Aliaksei ALIAKSEYEU, Raman HLUSHKO and Svetlana A. SUKHISHVILI. Integrating antioxidant functionality into polymer materials: Fundamentals, strategies, and applications. *ACS Applied Materials & Interfaces*. 2021, **13**(35), 41372–41395. ISSN 1944-8244. Available at: doi:10.1021/acsami.1c08061
- [76] NAGARAJAN, Subhalakshmi, Ramaswamy NAGARAJAN, Jayant KUMAR, Adele SALEMME, Anna Rita TOGNA, Luciano SASO and Ferdinando BRUNO. Antioxidant activity of synthetic polymers of phenolic compounds. *Polymers*. 2020, **12**(8), 1646. ISSN 2073-4360. Available at: doi:10.3390/polym12081646
- [77] KIRSCHWENG, Balázs, Dóra TÁTRAALJAI, Enikő FÖLDES and Béla A. PUKÁNSZKY. Natural antioxidants as stabilizers for polymers. *Polymer Degradation and Stability*. 2017, **145**, 25–40. ISSN 01413910. Available at: doi:10.1016/j.polymdegradstab.2017.07.012
- [78] BOARINO, Alice, Aigoul SCHREIER, Yves LETERRIER and Harm-Anton KLOK. Uniformly dispersed poly(lactic acid)-grafted lignin nanoparticles enhance antioxidant activity and UV-barrier properties of poly(lactic acid) packaging films. *ACS Applied Polymer Materials*. 2022, **4**(7), 4808–4817. ISSN 2637-6105. Available at: doi:10.1021/acsapm.2c00420
- [79] MAZZANTI, Valentina, Martina SALZANO DE LUNA, R PARIANTE, Francesco MOLLICA and Giovanni FILIPPONE. Natural fiber-induced degradation in PLA-hemp biocomposites in the molten state. *Composites Part A: Applied Science and Manufacturing*. 2020, **137**, 105990. ISSN 1359835X. Available at: doi:10.1016/j.compositesa.2020.105990
- [80] TEIXEIRA, Stefanie, Katarzyna Morawa EBLAGON, Filipa MIRANDA, Mamuel Fernando R. PEREIRA and José Luis FIGUEIREDO. Towards controlled degradation of poly(lactic) acid in technical applications. *C*. 2021, **7**(2), 42. ISSN 2311-5629. Available at: doi:10.3390/c7020042
- [81] ALIMUZZAMAN, Shah, Rong Hugh GONG and Mahmudul AKONDA. Biodegradability of nonwoven flax fiber reinforced polylactic acid biocomposites. *Polymer Composites*. 2014, **35**(11), 2094–2102. ISSN 02728397. Available at: doi:10.1002/pc.22871
- [82] SHINODA, Hosei, Yukiko ASOU, Takeshi KASHIMA, Takazo KATO, Yvonne TSENG and Tadashi YAGI. Amphiphilic biodegradable copolymer, poly(aspartic acid-co-lactide): acceleration of degradation rate

- and improvement of thermal stability for poly(lactic acid), poly(butylene succinate) and poly(ϵ -caprolactone). *Polymer Degradation and Stability*. 2003, **80**(2), 241–250. ISSN 01413910. Available at: doi:10.1016/S0141-3910(02)00404-4
- [83] SHOGREN, Randal L., William M. DOANE, Donald V. GARLOTTA, John W. LAWTON and Julious L. WILLETT. Biodegradation of starch/polylactic acid/poly(hydroxyester-ether) composite bars in soil. *Polymer Degradation and Stability*. 2003, **79**(3), 405–411. ISSN 01413910. Available at: doi:10.1016/S0141-3910(02)00356-7
- [84] EN ISO 4892-3:2016. *Plastics — Methods of exposure to laboratory light sources — Part 3: Fluorescent UV lamps (EN ISO 4892-3:2016)*. B.m.: European standard; CEN: Brussels, Belgium. 2016. ISBN 2831886376
- [85] EUROPEAN STANDARD. *EN ISO 527-3:2018 Plastics—Determination of Tensile Properties—Part 3: Test Conditions for Films and Sheets*. Belgium, 2019: CEN: Brussels. 2019
- [86] LATOS-BROZIO, Malgorzata and Anna MASEK. Environmentally friendly polymer compositions with natural amber acid. *International Journal of Molecular Sciences*. 2021, **22**(4), 1556. ISSN 1422-0067. Available at: doi:10.3390/ijms22041556
- [87] ISO 14855-1. *ISO 14855-1:2012 Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions — Method by analysis of evolved carbon dioxide — Part 1: General method*. B.m.: Geneva, Switzerland, 2012. 2012
- [88] KUCHARCZYK, Pavel, Alena PAVELKOVÁ, Petr STLOUKAL and Vladimír SEDLARÍK. Degradation behaviour of PLA-based polyesterurethanes under abiotic and biotic environments. *Polymer Degradation and Stability*. 2016, **129**, 222–230. ISSN 01413910. Available at: doi:10.1016/j.polymdegradstab.2016.04.019

LIST OF FIGURES

Figure 1. Methods for PLA synthesis [14].	8
Figure 2. Schematic diagram of the general preparation of PLA and its most common applications.	8
Figure 3. SWOT analysis of biodegradable polymers in packaging.	11
Figure 4. Hydrolytic degradation of PLA in the presence of water.	13
Figure 5. Method for fabrication of the samples.	21
Figure 6. Representative TIC of the diluted BRE; the retention times were attributed by mass spectrometry analysis.	24
Figure 7. Positive electrospray tandem mass spectra for (A) neobetanin and (B) betanin or isobetanin.	25
Figure 8. Mechanical properties of the PLA and PCL samples as per Young's modulus.	27
Figure 9. Mechanical properties of the PLA and PCL samples as per maximum stress.	27
Figure 10. SEM images detailing change in the PLA samples prior to and following exposure in a UV chamber, comprising the fracture surfaces of samples (A) PLA; (B) PLA-BE; (C) PLA-BRE; (D) PLA-UV; (E) PLA-BE-UV; and (F) PLA-BRE-UV; and the surfaces of the samples (G) PLA-UV; (H) PLA-BE-UV; and (I) PLA-BRE-UV.	28
Figure 11. SEM images detailing change in the PCL samples prior to and following exposure in a UV chamber, comprising the fracture surfaces of samples (A) PCL; (B) PCL-BE; (C) PCL-BRE; (D) PCL-UV; (E) PCL-BE-UV; and (F) PCL-BRE-UV; and the surfaces of samples (G) PCL-UV; (H) PCL-BE-UV; and (I) PCL-BRE-UV.	29
Figure 12. Electron micrographs of the surfaces and fractured surfaces of the thin films: (a, a') PLA; (b, b') PLA/5H; (c, c') PLA/5H/20PLA-g-PAA; (d, d') PLA/5PLA-g-PAA; (e, e') PLA/20H; (f, f') PLA/20H/20PLA-g-PAA; (g, g') PLA/20PLA-g-PAA; and (h) HNT; (blue arrows indicate HNT particles).....	31
Figure 13. Carbon content of the neat PLA and PLA composites during abiotic hydrolysis, in 0.1 M Na-PB (pH~7) at 58°C.	32
Figure 14. Reduction in molecular weight during abiotic hydrolysis of the neat PLA and various composites with additives, according to the kinetic model.	33
Figure 15. Biodegradation of the PLA, PLA with HNTs and PLA-g-PAA/HNT nanocomposite films, as converted to carbon during mineralization.	34

LIST OF TABLES

Table 1. Composition of the prepared samples.	21
Table 2. Characterization of the prepared additive PLA-g-PAA.	22
Table 3. Designations and compositions of the samples.	23
Table 4. DSC data for the neat PLA and PLA composites before and after the UV ageing test.	25
Table 5. DSC data for the neat PCL and PCL composites before and after the UV ageing test.	26
Table 6. Summary of TGA curves for the PLA, PCL and composites.	26
Table 7. Comparison of the mechanical properties of the PLA and PCL composites prior to and following ageing.	27
Table 8. Mechanical properties of the neat PLA and PLA composites.	30
Table 9. Parameters of the kinetic model and coefficients of determination (R^2) for the abiotic hydrolysis of the PLA and PLA composites.	32
Table 10. Parameters of the first-order kinetic model and coefficients of determination (R^2) for random scission of the PLA and PLA composites.	33
Table 11. Parameters of the kinetic model and coefficients of determination (R^2) for the biodegradation of the PLA and PLA composites.	34

LIST OF ABBREVIATIONS

ΔH	Reaction enthalpy
3D	Three dimensional
Al_2O_3	Aluminium oxide
AO	Antioxidant
BE	Bentonite
BRE	Bentonite with beetroot extract
DPPH	2,2-diphenyl-1-picrylhydrazyl
DSC	Differential scanning calorimetry
ESI-MS/MS	Electrospray ionization tandem mass spectrometry
FCM	Folin-Ciocalteu method
FCR	Folin – Ciocalteu reagent
Fe_2O_3	Iron(III) oxide
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatograph
GPC	Gel permeation chromatography
HNT	Halloysite
HPLC	High-performance liquid chromatography
LC	Liquid crystal
LCA	Life cycle assessment
MSA	Methanesulfonic acid
M_w	Molecular weight
Na-PB	Sodium phosphate buffer
PAA	Polyacrylic acid
PCL	Polycaprolactone
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PFM	Polyfunctional monomers
pH	Potential of hydrogen
PHA	Polyhydroxyalkanoates
PLA	Polylactic acid, Polylactide
PLGA	Poly(lactic-co-glycolic acid)
ROP	Ring-opening polymerization
SEM	Scanning electron microscopy
SFE	Free surface energy
$Sn(Oct_2)$	Tin(II) 2-ethylhexanoate

SWOT	Strengths, weaknesses, opportunities and threats
T _g	Glass transition temperature
TGA	Thermogravimetric analysis
TIC	Total iron chromatogram
TiO ₂	Titanium dioxide
Ti ₂ O ₃	Titanium(III) oxide
T _m	Melting temperature
T _{max}	Temperature at the maximum rate of weight loss of samples
TOC-L	Total Organic Carbon Analyze
T _{onset}	Initial degradation temperatures
T _{peak}	Highest temperature peak measured at O ₂
UV	Ultraviolet
ZnO	Zinc oxide

CURRICULUM VITAE

Personal information

Ing. Petra Dróhslér (Válková)

Podlesí III 4945, 760 05, Zlín, Czech Republic

pvalkova@utb.cz

Sex Female || *Date of birth* 25/05/1992 || *Nationality* Czech

Education

- 2017 – to date Doctor's degree
Tomas Bata University in Zlín, University institute, Zlín
Material Sciences and Engineering
- 2015 – 2017 Master's degree – Ing.
Tomas Bata University in Zlín, Fakulty of Technology, Zlín
Food Technology, Food Chemistry and Analysis
- 2011 – 2015 Bachelor's degree – Bc.
Tomas Bata University in Zlín, Fakulty of Technology, Zlín
Food Technology and Evaluation, Food Chemistry and Analysis

Languages

- Mother tongue Czech
- Other languages English – Level B2
Spanish – Level A1

Training abroad

- 1/11/2021–03/12/2021 Erasmus traineeship
Lublin University of Technology, Faculty of Mechanical
Engineering, Department of Polymer Processing, Lublin
(Poland)
Mechanical recycling of biodegradable polymer

Work experience

06/2021 – 09/2022	Principal investigator Project 01/3/2021/GAMA - Recycling of biodegradable waste by processing for cultivation applications
06/2020 – 12/2021	Member of research team Project 07/1/2020/GAMA2 – The technology of plastic recycles processing with mineral fillers for composites preparation (06/2020-12/2021)
06/2020 – 12/2021	Member of research team Project 09/1/2020/GAMA2 – Novel biodegradable composition based on degradable polymer and material with natural origin (06/2020-12/2021)
01/2020 – to date	Member of research team Project 8J20PL026 – Biodegradable polymer nanocomposite systems with improved thermal and mechanical properties (01/2020-12/2022)
2019 – to date	Member of research team Project QK1910392 – Environmentally friendly soil conservation materials for the crop production intensification based on renewable resource (VaV pro MZE II, 2019-2023)
06/2018 – 12/2019	Member of research team Project 07/3/2018/GAMA – Development of biodegradable material with improved processing properties
2018 – 2019	Member of research team Project TJ01000330 – Novel plastics stabilizers based on natural bioactive compounds (ZETA 1, 2018-2019)

2017 – 2020 Member of research team
Project TH02020836 – Development of novel plastic based environmentally friendly food packaging materials with added value (EPSILON 2017-2020)

Work on projects within Internal Grant Agency (IGA)

01/2021 – 12/2021 Member of research team
Tomas Bata University in Zlín, Centre of Polymer Systems
Project IGA/CPS/2021/002 – Preparation and characterization of nanocomposite systems

01/2020 – 12/2020 Principal investigator
Tomas Bata University in Zlín, Centre of Polymer Systems
Project IGA/CPS/2020/002 – Bioactive polymer systems for environmental applications

01/2019 – 12/2019 Member of research team
Tomas Bata University in Zlín, Centre of Polymer Systems
Project IGA/CPS/2019/006 –Polymeric composites for bioapplications

01/2018 – 12/2018 Principal investigator
Tomas Bata University in Zlín, Centre of Polymer Systems
Project IGA/CPS/2018/003 – Functionalized Polymer Composites

09/2017 – 12/2017 Member of research team
Tomas Bata University in Zlín, Centre of Polymer Systems
Project IGA/CPS/2017/005 – Bioactive systems for medical and industrial applications

LIST OF PUBLICATIONS

Papers published in international journals with impact factor:

1. CRUZ FABIAN, Dalila Rubicela, DURPEKOVA, Silvie, DUSANKOVA, Miroslava, CISAR, Jaroslav, DROHSLER, Petra, ELICH, Ondrej, BORKOVA, Marketa, CECHMANKOVA, Jarmila, and SEDLARIK, Vladimir. Renewable Poly(Lactic Acid)Lignocellulose Biocomposites for the Enhancement of the Water Retention Capacity of the Soil. *Polymers*, 2023, 15(10), 2243. <https://doi.org/10.3390/polym15102243>
1. CISAR, Jaroslav, DROHSLER, Petra, PUMMEROVA, Martina, SEDLARIK, Vladimir and SKODA, David. Composite Based on PLA with Improved Shape Stability under High-Temperature Conditions. *Polymer*, 2023, 276, 125943. <https://doi.org/10.1016/j.polymer.2023.125943>
2. DROHSLER, Petra, YASIR, Muhammad, CRUZ FABIAN, Dalila Rubicela, CISAR, Jaroslav, YADOLLAHI, Zahra & SEDLARIK, Vladimir. Comparative Degradation Study of a Biodegradable Composite Based on Polylactide with Halloysite Nanotubes and a Polyacrylic Acid Copolymer. *Materials Today Communications*, 2022, 33, 104400. <https://doi.org/10.1016/j.mtcomm.2022.104400>
4. BERGEROVA, Eva Domincova, KIMMER, Dusan, KOVAROVA, Miroslava, LOVECKA, Lenka, VINCENT, Ivo, DROHSLER, Petra, KOBOLOVA, Klaudia & SEDLARIK, Vladimir. Effect of Polyurethane Structure on Arsenic Adsorption Capacity in Nanofibrous Polymer/Ferrous Sulphate-Based Systems. *Environmental Science: Water Research & Technology*, 2022, 8(11), 2663-2681. <https://doi.org/10.1039/D2EW00566B>
5. MUNTEANU Andrei, RONZOVA, Alena, KUTALKOVA, Erika, DROHSLER, Petra, MOUCKA, Robert, KRACALIK, Milan, BILEK, Ondrej MAZLAN, A. Saiful & SEDLACIK, Michal. Reprocessed Magnetorheological Elastomers with Reduced Carbon Footprint and their Piezoresistive Properties. *Scientific Reports*, 2022, 12(1), 12041. <https://doi.org/10.1038/s41598-022-16129-y>
6. DROHSLER, Petra, CISAR, Jaroslav, SOPIK, Tomas, SEDLARIK, Vladimir. Effect of an Antioxidant Based on Red Beetroot Extract on the Abiotic Stability of Polylactide and Polycaprolactone. *Molecules*, 2021, 26(17) 5190. <https://doi.org/10.3390/molecules26175190>.

7. KULTRAVUT, Katanyu, KUBOYAMA, Keiichi, SEDLARIK, Vladimir, MRLIK, Miroslav, OSICKA, Josef, DROHSLER, Petra, & OUGIZAWA, Toshiaki. Localization of Poly (glycidyl methacrylate) Grafted on Reduced Graphene Oxide in Poly (lactic acid)/Poly (trimethylene terephthalate) Blends for Composites with Enhanced Electrical and Thermal Conductivities. *ACS Applied Nano Materials*, 2021, 4(8), 8511-8519. <https://doi.org/10.1021/acsanm.1c01843>.
8. DURPEKOVA, Silvie, DI MARTINO, Antonio, DUSANKOVA, Miroslava, DROHSLER, Petra, & SEDLARIK, Vladimir. Biopolymer Hydrogel Based on Acid Whey and Cellulose Derivatives for Enhancement Water Retention Capacity of Soil and Slow Release of Fertilizers. *Polymers*, 2021, 13(19) 3274. <https://doi.org/10.3390/polym13193274>.

International conference contribution:

1. VÁLKOVÁ, Petra; CÍSAŘ, Jaroslav a SEDLAŘÍK, Vladimír. Eco-Friendly Composites Based on Lactic Acid with Improved Thermal Stability Suitable for Green Packaging. XI. Slovensko - Česká konference POLYMERY 2020, 5. – 8. 10. 2020, Bratislava, Slovenská Republika, p. 66-67. ISBN 978-80-89841-14-1.
2. VÁLKOVÁ, Petra; CÍSAŘ, Jaroslav a SEDLAŘÍK, Vladimír. Biodegradable Polylactide Composites with Improved Thermal Stability for Food Packaging. Polychar 27: World Forum on Advanced Materials, 14-17 October 2019, Naples, Italy, p.49.
3. VÁLKOVÁ, Petra; STLOUKAL, Petr; KUCHARCZYK, Pavel; SEDLAŘÍK, Vladimír. Effect of Polyacrylic Acid/Polylactic Acid Copolymer on Degradation of Polylactide under Biotic and Abiotic Conditions. 1st International Conference on Chemistry for Beauty and Health, June 13. – 16. 2018, Toruń, Poland, p. 52. ISBN 978-83-231-4027-6.

National conference contribution:

1. VÁLKOVÁ, Petra; STLOUKAL, Petr a SEDLAŘÍK, Vladimír. Komparativní studie plastifikátorů polylaktidu pro obalové aplikace. *Plastko: sborník příspěvků z konference*, 18. - 19. dubna 2018, Zlín, Česká republika, s. 86. ISBN 978-80-7454-727-0.

Other applied research outputs:

1. DRÖHSLER, Petra; HANUŠOVÁ, Dominika; PUMMEROVÁ, Martina; SEDLAŘÍK, Vladimír. Biodegradable compositions from secondary material from production applicable for direct growing applications. ID 43883740, 2022.
2. DRÖHSLER, Petra; HANUŠOVÁ, Dominika; PUMMEROVÁ, Martina; SEDLAŘÍK, Vladimír. Biodegradable polymer composition of a composite nature, utility model No. 36223 (Industrial Property Office of the Czech Republic), accepted: July19, 2022.
3. CÍSAŘ, Jaroslav; VÁLKOVÁ, Petra; KOLAŘÍK, Roman; SEDLAŘÍK, Vladimír. Biodegradable polymer composition, in particular for producing packaging films with increased barrier properties, and a method of producing films, patent No. 309087 (Industrial Property Office of the Czech Republic), accepted: December 09, 2021.
4. DRÖHSLER, Petra; YASIR, Muhammad; CÍSAŘ, Jaroslav; CRUZ FABIÁN, Dalila Rubicela; YADOLLAHI, Zahra; SEDLAŘÍK, Vladimír. PLA-based composite material with accelerated degradation mechanism under composting conditions. ID 43882757, 2021.
5. PUMMEROVÁ, Martina; DRÖHSLER, Petra; SEDLAŘÍK, Vladimír. Biodegradable composition for agriculture applications, ID 43882722, 2021.
6. PUMMEROVÁ, Martina; DRÖHSLER, Petra; KLABAN, Jakub; HANUŠOVÁ, Dominika; SEDLAŘÍK, Vladimír. Porous compositions based on a fully biodegradable polymer, especially for agricultural applications, utility model No. 35618 (Industrial Property Office of the Czech Republic), accepted: November 11, 2021.
7. CÍSAŘ, Jaroslav; VÁLKOVÁ, Petra; KOLAŘÍK, Roman; SEDLAŘÍK, Vladimír. Biodegradable polymer composition, especially for producing packaging films with increased barrier properties, utility model No. 34756 (Industrial Property Office of the Czech Republic), accepted: January 12, 2021.
8. CÍSAŘ, Jaroslav; VÁLKOVÁ, Petra; KOLAŘÍK, Roman; SEDLAŘÍK, Vladimír. Pilot plant test of the production of a single-layer thin film based on polylactide with increased barrier properties suitable for packaging applications, ID 43881355, 2020.
9. SEDLAŘÍK, Vladimír; CÍSAŘ, Jaroslav; VÁLKOVÁ, Petra. Production of a new generation of disposable biodegradable bowls with increased thermal stability suitable for microwave heating of food, ID 43881354, 2020.

10. VÁLKOVÁ, Petra; CÍSAŘ, Jaroslav; SEDLAŘÍK, Vladimír. Biodegradable polymeric lactic acid polymer composition for products with enhanced shape stability, utility model No. 33185 (Industrial Property Office of the Czech Republic), accepted: March 03, 2019.
11. PUMMEROVÁ, Martina; VÁLKOVÁ, Petra; SEDLAŘÍK, Vladimír. Biodegradable plasticizer for biodegradable polymers based on polylactide acid, utility model No. 32722 (Industrial Property Office of the Czech Republic), accepted: April 02, 2019.
12. PUMMEROVÁ, Martina; HAUSNER, David; VÁLKOVÁ, Petra; SEDLAŘÍK, Vladimír. A blown film based on modified polylactic acid with improved processing properties, utility model No. 32659 (Industrial Property Office of the Czech Republic), accepted: March 12, 2019.

Special-purpose publications:

1. VÁLKOVÁ, Petra.:The Possibilities of Whey Fermentation using *Kluyveromyces lactis* (Diploma thesis), FT UTB Zlín, 2017.
2. VÁLKOVÁ, Petra.: Characterization of Medicinal Plants Essential Oils and Their Properties (Bachelor thesis), FT UTB Zlín, 2015.

Ing. Petra Dróhsler, Ph.D.

**Modifying the stability of the course of biodegradation of
renewable polyester PLA**

Modifikace stability biologicky rozložitelných polyesterů za abiotických
podmínek

Doctoral Thesis Summary

Published by: Tomas Bata University in Zlín,

nám. T. G. Masaryka 5555, 760 01 Zlín.

Edition: published electronically

Typesetting: Ing. Petra Dróhsler, Ph.D.

This publication underwent no proof reading or editorial review.

Year: 2024

First Edition

ISBN 978-80-7678-290-7

