



Tomas Bata University in Zlín

Centre of Polymer Systems

Doctoral Thesis

Stability Modification of Biodegradable Polyesters under Abiotic Conditions

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

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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 je 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 to them is they originate 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. This has led to research efforts being made to develop degradable biomaterials that would minimize environmental pollution, with the aim of eventually replacing traditional petroleum-based plastics. Biodegradable alternatives can be formulated from either natural or synthetic resins. Noteworthy examples of biodegradable polyesters that are now commercially available include polyhydroxyalkanoates (PHA), polyhydroxyhexanoates (PHH), polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), polylactic acid (PLA), polycaprolactone (PCL), polybutylene succinate (PBS) and polybutylene succinate adipate (PBSA) [2].

PLA has proven especially suitable in this regard. A biodegradable recyclable polyester, it is produced from renewable feedstock or waste products rich in polysaccharides, i.e. starch primarily sourced from the agricultural sector. Lactic acid as its precursor is produced by fermentation of glucose or sucrose and is refined to a high purity. 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].

It is also advantageous to target the end groups of PLA and chemically modify them. This approach allows the desired functionality to be introduced into the PLA macromolecules while maintaining the properties of the matrix. 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].

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. A proven means of combating these issues is to utilize specific additives and fillers. Another limitation relates to the rate of degradation, which transpires too quickly for some applications, examples being 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. The degradation mechanism of PLA tends to be dependent on the nature of the end

group and the external environment. 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].

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)

PLA represents one of the most common and commercially applied forms of bioplastic. Production of it is rising globally to meet significant growth in demand. At present, biodegradable plastics account for more than 64% (over 1.5 million tons) of related manufacturing capacity globally. Production of them is expected to ramp up to almost 5.3 million tons by 2026 in connection with the development of polymers such as PBAT (polybutylene adipate terephthalate) and PBS, as well as the greater demand for PLA [5].

The latter of these is a biodegradable polyester with a monomer of lactic acid. Obtained by fermenting carbohydrates from renewable crops like sugar beet, corn and other forms of biomass, lactic acid (2-hydroxypropanoic acid) occurs in two optically active configurations of D(-) and L(+) enantiomers. These can be produced either by bacteria or a chemical process, potentially giving rise to 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, while processing of it is relatively simple, requiring just standard equipment and technology to produce fibres, films or thin sheet 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].

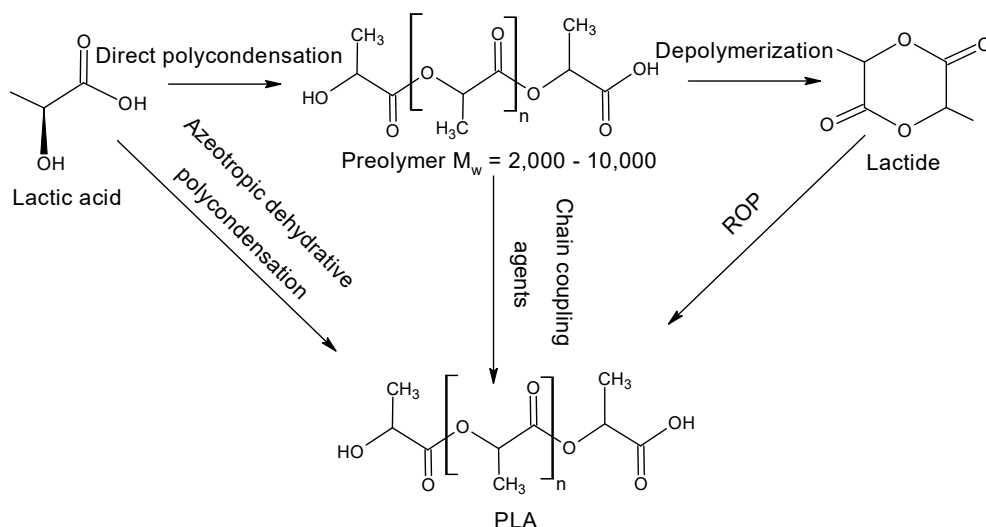


Figure 1. Methods for PLA synthesis [14].

The raw input material for the production of PLA is lactic acid, obtained either by bacterial fermentation or **chemical synthesis**. The latter involves the hydrolysis of lactonitrile into lactic acid in the presence of sulphuric acid. The lactic acid is esterified with methanol to give methyl lactate, which is distilled off and hydrolysed with water in the presence of an acid catalyst, resulting in lactic acid and methanol. During **fermentation**, anaerobic bacterial conversion of sugars takes place, e.g. by lactic acid bacteria, during which other products (acetic acid, ethanol) can be formed in addition to lactic acid [15], [16].

- **Direct polycondensation**

A relatively inexpensive option is direct polycondensation, bringing about PLA of low molecular weight (up to 10,000 Da). The hydroxyl groups (-OH) and carboxyl (-COOH) in the lactic acid permit direct conversion of the acid into polyester through a polycondensation reaction. Distillation of water is carried out, affecting the molecular weight of the product. The conditions required comprise high temperature (120 – 200 °C), a catalyst/initiator (often Tin (II) 2-ethylhexanoate (Sn (Oct)₂) or methanesulphonic acid (MSA)) and reduced pressure over an extended period [7], [17], [18].

- **Ring-opening polymerization (ROP)**

Applied on an industrial scale, ROP affords superior control over the reaction and produces PLA of high molecular weight. ROP synthesis involves the polymerization of lactide, cyclic dimer of lactic acid and ring-opening procedure. Three reaction mechanisms exist: anionic, cationic and coordination. The predominant of these is the latter, coordination polymerization, especially in the context of metal catalysts (e.g. alkoxides), which engender a product of high molecular weight with great optical purity. Anionic reactions prevent chain

propagation, while undesirable side reactions are likely to occur during cationic polymerization. An alternative to utilizing a metal catalyst in lactone ring-opening polymerization is application of a lipase catalyst instead. Findings reported in the literature describe the formation of PLA of high molecular weight (126 – 270 kDa) from *Candida antarctica* or *Pseudomonas fluorescens* [19], [20].

The properties of PLA resulting from a reaction are affected by these aspects:

- The purity of the lactide, as impurities in it diminish both the rate of polymerization and molecular weight.
- The conditions under which the reaction takes place (temperature, the catalyst used and time) which lead to racemization, i.e. the formation of variable stereoisomers.
- The content of lactide upon completion of the polycondensation reaction, triggering degradation in properties when processing the polymer [7], [20].

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. Materials that combine PLA with polyethylene terephthalate (PET) or polystyrene (PS) possess similar properties and have broad applicability. Figure 2 summarizes the preparation of PLA and its applications [21].

Referred to as a carbon-neutral life-cycle material, PLA can be produced not only from starch, but also food-related waste, such as fish, rice bran, sludge from winemaking, soy protein hydrolysates and unpolished, mature rice. 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 [22], [23].

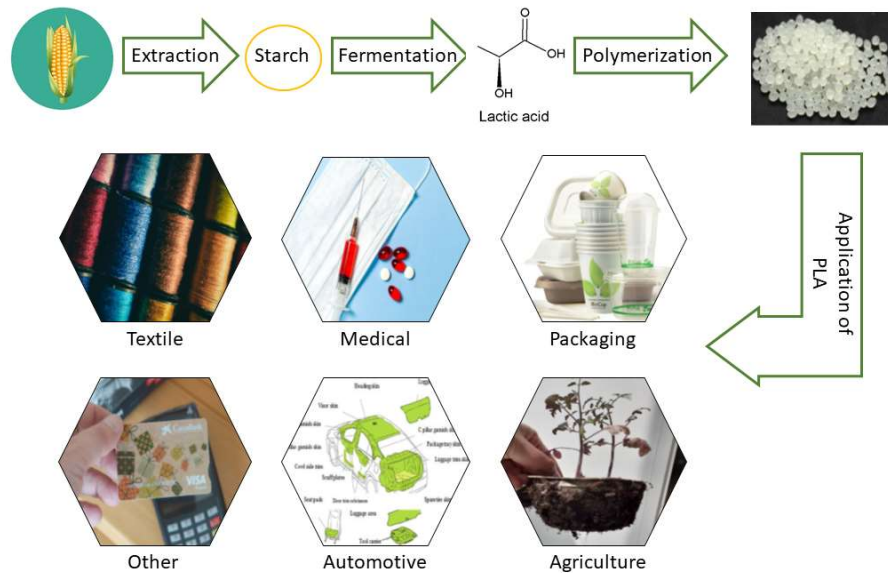


Figure 2. Schematic diagram of the general preparation of PLA and its most common applications [24].

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 (CO_2) released at the end point of its life cycle (e.g. by incineration or composting) equals the amount of CO_2 absorbed by the plants grown that constitute its raw materials. The greenhouse gas emissions for PLA (1 600 kg CO_2 /metric tonne) are sometimes far lower than for PET or nylon (4 140 and 7 150 kg CO_2 /metric tonne, respectively). Moreover, less water is needed for its manufacture [25], [26].

- **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 the regard, as up to 40% of packaging takes the form of disposable tableware items, including cutlery, foil and bags [27].

Biodegradable PLA clearly shows potential as an alternative to petroleum-based plastics, and it has been widely studied for use in food packaging. Showing excellent biocompatibility and good physical properties, such as high strength, thermoplasticity, processability and non-toxicity, it is considered by the Food and Drug Administration (FDA) as Generally Recognized as Safe (GRAS), paving the way for its application in food packaging. It does possess certain drawbacks that have limited its uptake in this regard, though, relating to low flexibility, poor dimensional stability and ineffective barrier properties [24],[27],[28].

Although the European Commission (EC) supports projects and activities that encourage the use of green materials, including PLA composites, a question mark hangs over the fate of oxo-biodegradable polymers. The core issue relates to associated recycling practices, as they usually end up dumped in landfill sites that lack suitable conditions for biodegradation, thereby significantly extending the duration of decomposition. Poor degradation in a marine environment is another reason, as fauna and flora in the oceans are impacted by their presence. A legislative regulation is currently being amended in EU that restricts or bans the use of disposable products made from biodegradable polymers. This forthcoming legislation will stipulate exceptions, yet customers and producers in the European market are already being discouraged from manufacturing such polymers [24].

- **Medical applications**

The aforementioned properties, including 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. The first study on the biocompatibility of poly (L-lactic acid) (PLLA) in rodents (guinea pigs and rats) was published as early as 1966 [29], [30]. Subsequent research has made substantial gains, and now 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 [31].

A notable use of PLA is as a pharmaceutical drug-delivery system. The FDA has approved fifteen products for direct human contact that employ a biological liquid PLA carrier for controlled administration of medication; e.g. anticancer, antidiarrhoeal, antipsychotic, antibiotic, anti-inflammatory and antidiabetic drugs and opioid antagonists. Controlled adsorption and drug release is facilitated by the adjustable pore size and pore connectivity of such PLA-based, solid scaffolds. The same principle governs the function of nanofibers, wherein greater thickness leads to rise in porosity. Disadvantages exist, however, as PLA exhibits reduced cell adhesion and a low rate of degradation, attributed to its hydrophobicity, biological inertness. As a result, inflammation can arise *in vivo*, which occurs in the presence of acidic degradation products. Bacterial adhesion, biofilm formation or even complications associated with necrosis also occur [32], [33], [34].

- **Agriculture**

Another key sector for PLA application is agriculture. With the aim of protecting the environment, it is important to deploy eco-friendly materials capable of being placed in soil and aqueous environments safely. In this context, PLA could replace high-density polyethylene (HDPE) plant protection structures, which serve as a non-chemical means of creating a physical barrier between pests

and crops [35], [36]. It has also found favour as part of a PLA with drugs for plant treatment system, whereby drugs are gradually released in earth, as well as in containers, flower pots and planters [37]. For the most part, such items employed in commercial cropping activities (made from polypropylene (PP), polyethylene (PE) or PS) comprise oil-based, disposable plant containers that excel in durability, size and shape. An alternative is to opt for a planter constructed from natural fibres (e.g. coconut), though these are structurally inferior to conventional plastic items and seep water through their side walls, hence higher costs are incurred when growing crops. Plant containers made of PLA have the advantage of possessing similar properties (thermal and mechanical) to petroleum-based plastic units, while also sharing the same infrastructure for manufacture by injection or blow moulding. Moreover, PLA is non-toxic and biodegradable. A downside of the material is poor biodegradation in soil, with the effect of slowing down the growth of plants. The roots are unable to penetrate the walls of the PLA container and cannot take in sufficient moisture and nutrients. In order to combat this issue, flower pots with modifications in their walling have been designed that permit parts to break off easily, thereby facilitating root growth and the action of biocomposites for accelerated decomposition of the container [35], [38], [39].

- **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. The most commonly employed polymers in the automotive sector comprise the following: PP, in items like bumpers and fuel systems; polyamide (PA), in seats and electrical components; poly (methyl) methacrylate (PMMA) and polyurethane (PUR), for lighting elements; and polycarbonate (PC), in bumpers, dashboards and trim sections for interiors and exteriors, usually in combination with acrylate butadiene styrene (ABS) [40], [41].

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. Deployment has since gone beyond upholstery components and ceiling mat surfaces, to encompass (in combination with PP) interior trim, air filters, engine covers and headlight elements. However, the applicability of the polymer in the automotive sector is hindered by certain disadvantageous mechanical properties, such as brittleness,

degradation at high temperatures and humidity and low chemical resistance [42], [43].

- **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. There has been a rise in the quantity of textile-related waste, i.e. polymeric materials consisting of synthetic fibres of polyester, nylon and polypropylene. Approximately one million tonnes of fabric for garments are produced in Europe annually, in which by spinning the yarn comprises natural fibres (e.g. cotton or wool) combined with synthetic fibres. Such combinations of fibres possess heightened properties but complicate recycling activities [44].

PLA fibres offer clear advantages over alternatives in textile applications. Moisture recovery is lower and moisture transport more rapid, similar to polyester. For example, even the process for manufacturing rayon generates toxins that present a threat to the natural environment. PLA fibres are produced in a non-toxic manner, in contrast, and retain a level of biological resistance, in addition to exhibiting good parameters in relation to fire retardation and UV resistance. Maintenance of clothing containing PLA fibres presents an issue, though, as such materials have a low glass transition temperature and poor impediment of hydrolysis, restricting their exposure to temperature and pH. In this regard, ironing garments at a high temperature risks damaging the fibres and causing the fabric to harden. Another limitation concerns washing conditions, recommended at temperatures of 35 – 55 °C and pH 8 or 10, and subsequent drying should not involve the use of a tumble dryer [44], [45].

- **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. This makes it ideal as a covering or insulation material for double-extruded 3D prints when used in conjunction with low-resistance conductive PLA, Nylon, PC or ABS fibres. Composites containing a conductive powder, based on carbon or metal (e.g. brass and copper), predominate in this context. Conductive PLA is a composite comprising a fundamental matrix of thermoplastic with black carbon particles [46], [47].

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 [24], [48], [49].

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. This is precisely why the polymer is commonplace today in items such as lunchboxes, bags, flower pots and non-woven fabrics. On the other hand, the SWOT analysis (strengths, weaknesses, opportunities, and threats) reveals (Fig. 3) that PLA also has undesirable properties, e.g. brittleness, poor melt strength and reduced stability at high temperature. Possible solutions exist to rectify these issues, however, including modifying PLA through techniques like copolymerization, blending, compounding and supplementation with additives [20], [50].

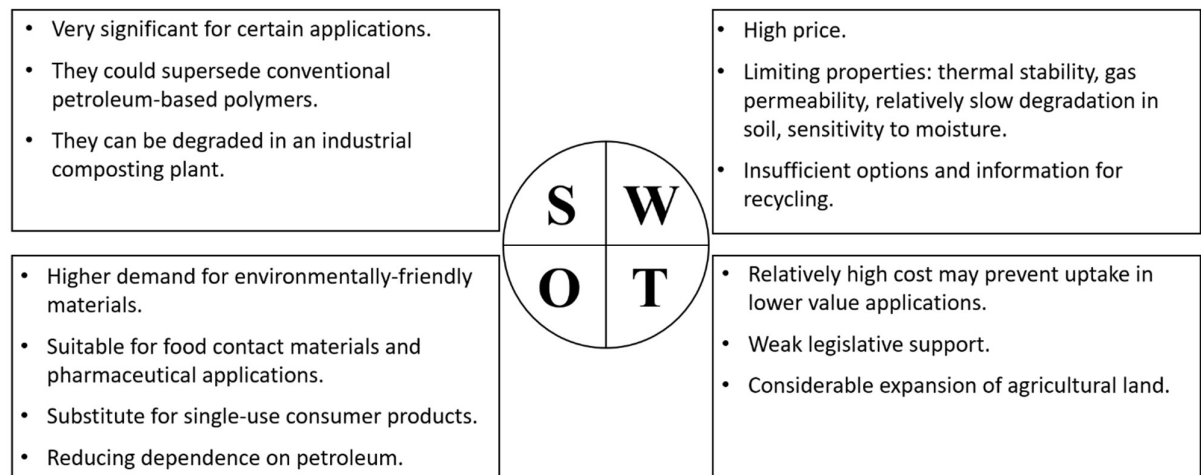


Figure 3. SWOT analysis of biodegradable polymers in packaging [51], [52], [53].

• Copolymerization

PLA modification methods are generally divided into chemical and physical forms. Chemical modification primarily consists of introducing various functional side groups (e.g. carboxyl, amine and hydroxyl) [54]. Under direct PLA polymerization conditions, it is possible to add in monomers that attach to the –OH or –COOH end groups.

Ring-opening polymerization produces a cyclic monomeric lactide, which undergoes coordination ring-opening polymerization upon reaction with a catalyst. It is assumed that propagation takes place by coordination of the monomer with active substances, and then by inserting the monomer into the metal-oxygen bond by rearrangement of electrons. 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 [55].

Intermolecular transesterification reactions modify the polylactide sequences, preventing the formation of block copolymers. The resultant products comprise

PLA copolymers of different types that vary structurally and in their given properties [55].

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) (see Fig. 4), as well as a type of poly(lactic-co-glycolic acid) (PLGA) [20]. Most of the copolymers mentioned herein possess a linear structure, yet specific branched structures also exist, e.g. star-shaped forms. Only a few reports in the literature describe the synthesis of star-shaped PLA by the polycondensation method. Such star-shaped polymers usually exhibit relatively low molar masses ($M_n < 4\,700\text{ g}\cdot\text{mol}^{-1}$), and these have attracted attention in various spheres of chemistry, biochemistry and engineering. Containing more chain ends than linear counterparts with the same molar mass, the greater quantities of terminal groups in them have the effect of heightening solubility and inducing differences in hydrodynamic volume. During the polycondensation of D, L-lactic acid with pyrimidine-2,4,5,6-tetramine (PTA), a star-shaped form of PLA was obtained (Fig. 5), which shows potential as a polymeric flame-retardant material [56].

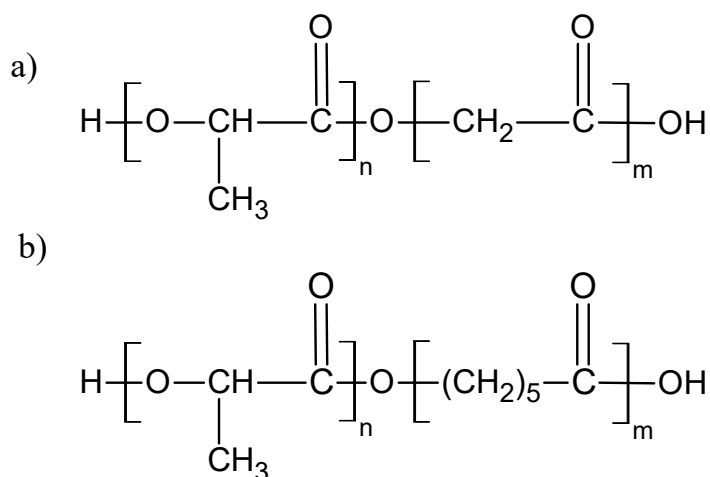


Figure 4. Linear copolymers of a) PLA-co-PEG and b) PLA-co-PCL [57].

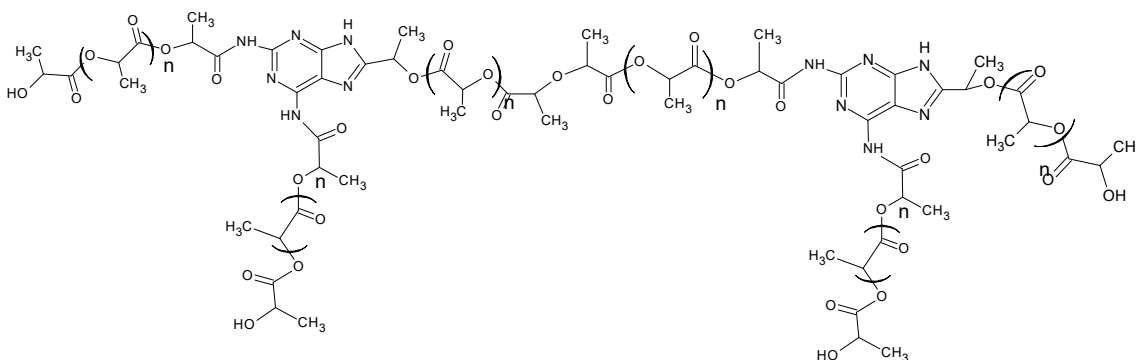


Figure 5. Star-shaped PLA [56].

Copolymerization facilitates the formation of block polymeric structures, i.e. macromolecules composed of two or more chemically different chains connected by covalent bonds. A variety of molecular architectures can be generated, e.g. AB diblock, ABA triblock and multiblock copolymers, which differ in structure and method of synthesis. The most common are diblock and triblock forms induced by polyethylene glycol (PEG) or poly(glycolic acid) (PGA). Such copolymers are synthesized with the aim of increasing the hydrophobicity of PLA or instigating faster degradation, properties desirable for drug delivery applications in the human body [50], [58], [59].

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”. In the “grafting to” method, the pre-synthesized terminal functional chains of PLA are chemically linked to another system via its amino or hydroxyl functional groups, whereas, in the “grafting from” method, ROP of the lactide monomer is performed in the latter from functional groups. The nature of the changes exerted in properties depends on the type of graft monomer utilized, the percentage and method of grafting, and the distribution of the grafted chain in the parent polymer. Polylactide graft copolymers are formed in combination with chitosan, cellulose, starch, PEG, vinyl-based polymers, lignin, dextran, methyl methacrylate, maleic anhydride and graphene oxide [20], [60], [61].

- **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.

The miscibility of mixtures is governed by the law of thermodynamics, wherein the free energy of mixing has to be negative. An aspect of this is that bio-based materials containing substances such as PE and low density polyethylene (LDPE) are formed, which enhance the mechanical properties of polylactide in terms of

elongation and reduction in brittleness. An economical and convenient strategy, blending PLA with other polymers improve the toughness and elasticity of the resultant material. For instance, adding the polymer polypropylene carbonate (PPC) into such a mixture has the effect of increasing elongation from 6% (0 wt%) to 173% (30 wt%) [62].

Bio-based materials suffer from the disadvantages of poor degradability and recyclability, though. A recent trend in research has been to prepare completely biodegradable materials containing PLLA, PDLA, hyaluronic acid (HA), PCL or PHA, with the intention of tackling these drawbacks. Other examples include elastomers, thermoplastic starch, PEG and tributyl citrate (TBC). However, in the case of low-molecular-weight plasticizers such as PEG or TBC, phase separation of the plasticizer occurs in proportion to the given temperature. It only takes a few days for an unwanted change to occur in the packaging, in connection with plasticizers being released onto the surface of the film. This impacts the foodstuffs within the packaging, not only since the plasticizers migrate in this way, but also because alterations transpire in relation to the barrier and shape of the material [9], [13], [20].

A targeted improvement in the thermal stability of PLA can be obtained by mixing two of its different optical isomer types, improves the extent of crystallization and consequently improving the heat resistance of PLA.

An alternative means of modifying PLA involves the preparation of composites, whereby two or more disparate components are combined. The matrix constitutes the main part of the binder, evenly distributing forces throughout the composite. It additionally contains reinforcing fibres and particles, which not only increase the stiffness and tensile strength of the matrix, but also contribute to reduction in the costs of the final product and enable alterations in physical, rheological, optical or other properties [9], [63]. Since an environmentally friendly system is still preferred, supplementary components of natural origin are incorporated in this kind of widely applicable PLA **biocomposite**, which preserve the properties of the given biomaterial [64].

The most commonly applied plant-derived bio-fibres in **biocomposites with natural, organic reinforcements** such as 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). Inorganic reinforcements like these support the crystallinity of PLA, while also enhancing antibacterial, barrier and thermal properties; however, heightened abrasiveness and poor dispersibility may be evident, too [63], [65], [66]. Table 1 details popular

fillers known to influence the behaviour of PLA and the properties associated with them.

Table 1. Examples of suitable fillers that form PLA biocomposites.

Filler	Observed effect	Reference
Bio-fibres	Enhanced mechanical properties	[64]
Chitin		[67]
Starch	Accelerated degradation	[68]
Nisin	Antimicrobial agents	[69]
Chitosan		[70]
Clay	Enhanced thermal and mechanical properties	[71]
Silicates		[72]
CaCO ₃	Heightened crystallinity and enhancement in mechanical properties	[73]
Metal oxides	Antimicrobial agents	[74]

- **Modification of PLA by additives**

Lastly, supplementing PLA with additives results in alteration in the properties of the material. A wide assortment exists for this purpose, the most common of which rank as antioxidants, compatibilizers, heat stabilizers, plasticizers, dyes and pigments, blowing agents, biocides, flame retardants, hardeners or aroma/smell modifiers, and so on [75]. The prevailing forms of additives applicable for PLA are detailed below.

Additives include **a) antioxidants** as preservatives used in food, but also in polymers. Contribute to the inhibition or deceleration of oxidation reactions caused by free radicals, such as singlet oxygen, superoxides, peroxy radicals, hydroxyl radicals and peroxy nitrite. Although these tend to slow down the ageing process of the given polymer, consequent changes in its properties limit application somewhat. In polymers, the main representatives are butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), which have carcinogenic effects [76], [77].

Dyes referred to as **b) colourants** are employed in a wide variety of technical and industrial applications, including in lasers, organic light-emitting diodes (OLEDs), liquid crystal displays (LCDs), optical data storage and fluorescent labels. Widely used representatives among the large number of dye categories are triphenylmethane, azo, anthraquinone, perylene and indigoid dyes. Azo is frequently applied in PLA, since all colour shades are available and it has proven suitable for numerous applications, e.g. in dyeing fibres and food or drug packaging [78], [79].

c) Compatibilizers are effective at modifying the properties of morphologically immiscible polymer mixtures and improving their manipulation. They create adhesion between phases, reduce interfacial tension and stabilize

morphology. Comprising two constituent parts, both of these prove compatible with one or the other of two polymers undergoing compatibilization. They are either classified as reactive, i.e. those that combine with polymers, or non-reactive, which are miscible with polymers. A reactive compatibilizer performs the function of an acrylic, for instance, when maleic anhydride or glycidyl methacrylate is grafted onto a polyolefin. Non-reactive compatibilizers are copolymers of ethylene-ethyl acrylate, ethylene-butyl acrylate and ethylene methacrylate [80], [81]. A styrene-acrylic, multifunctional, epoxy copolymer is usually applied as a chain extender to increase the thermal stability of polyesters. The latter type constitutes a compatibilizer for PLA to a greater extent in PLA/PBAT blend systems in the fabrication of packaging or similar commodity items [82].

Added to plastics to provide protection against thermal stress during the processing stage of a product, as well as in its subsequent storage and use, **d) heat stabilizers** function as thermal stabilizers which safeguard polymers from the effects of chemical degradation at high temperatures, in addition to combatting decomposed products arising from oxidation. Heat stabilizers are primarily employed industrially in the production of polyvinyl chloride (PVC). Another important application concerns recycled materials, wherein they inhibit degradation and promote the restabilization of former plastic waste. Notable examples include metallic salts (barium-zinc and calcium-zinc) and organometallic (organotin) and non-metallic organic stabilizers (bisphenol-type epoxy resin and hydrolyzed polyvinyl) [83], [84]. Polycarbodiimide is particularly suitable for PLA, which reacts with the carboxyl group present to initiate chain formation and thus hamper the thermal degradation and hydrolysis of PLA. Common products manufactured in this way include containers, labels and forms of textile [85].

e) Plasticizers are low-volatile organic substances added to plastic compounds to enhance certain qualities, such as flexibility, extensibility and processability. They induce reductions in the melt viscosity, second-order glass transition temperature and modulus of elasticity of a polymer. Physical interaction with the polymer leads to release of the strength of intermolecular forces between the macromolecules, lending the macromolecules or related segments greater flexibility. Primary plasticizers exert the effect of gelling the polymer within the normal range of processing temperatures, but should not be excluded from the resultant plasticized material. Secondary plasticizers, which exhibit a lesser capacity for gelation and limited polymer compatibility. The most commonly utilized plasticizers comprise esters of phthalic acid (dioctyl phthalate). Emollients also exist, derived from adipic, sebacic and azelaic acids esterified with linear or branched monofunctional alcohols that are short to medium in chain length; e.g. dioctyl adipate (DOA; bis(2-ethylhexyl) adipate), diisononyl adipate (DINA) and di(n-butyl) sebacate (DBS) [83],[84], [86].

Plastic made with **f) blowing agents** has a foam-like appearance. Benefiting from reduced weight for convenient transportation, such materials are used as packing for the protection of items and as thermal insulators. Materials referred to as polyurethane foam (PUR) and polyisocyanurate foam polymer, and to a lesser extent extruded PS or phenolic foam, constitute important industrial commodities. There are two types of blowing agents, chemical blowing agents that release the blowing agent through a chemical reaction, or physical blowing agents, i.e. blowing agents that are released by evaporation or pressure release. The former of the two are either solid organic or inorganic compounds that emit a propellant gas, usually N_2 and/or CO_2 , at a specific processing temperature. Among the best known are the compounds of azodicarbonamide (ADC), 4,4'-oxybis(benzenesulfonyl hydrazide) (OBSh), 5-phenyltetrazole (5-PT) and sodium bicarbonate [84]. PLA can be produced as foam in several ways like PS (extrusion foaming, foam injection, bead foaming), with supercritical carbon dioxide attracting the most attention at present [87]. The stability and uniformity of such foam is enhanced by adding fillers that function as nucleating agents at the beginning of the process. Today, these PLA-based foam materials are gradually replacing PS foams alternatives since they represent an environmentally-friendly option in packaging, including of foodstuffs. The portfolio of commercial insulation materials for buildings has also broadened through their inclusion, while combinations of PLA and microcellulose fibrils (MCF) have been devised [88].

Eco-friendly additives applicable for use with PLA exist, too. Examples include the biodegradable emollients of citrate ester, ethyl acetate and triethyl citrate (TEC). These plasticizers integrate well with PLA via specific molecular interactions that arise through intermolecular hydrogen bonds, positively affecting the qualities of the material by raising the rate of crystallization and enhancing mechanical properties [89], [90].

Noteworthy alternatives are types of epoxidized vegetable oil and the epoxide esters of fatty acids (also called epoxide acids), which function as non-gelatinizing secondary plasticizers benefiting from the additional quality of migration resistance. They also have the purpose as heat stabilizers. Epoxidized soybean oil is widely deployed in industry as a stabilizer and plasticizer in PVC matrices. A highly common procedure to engender the epoxidation of vegetable oils is to utilize organic peracids in combination with mineral acids or enzymes as catalysts. A reaction takes place between the organic peracids and unsaturated fatty acids, with an oxygen atom being subsequently added into the double bonds ($C=C$) alongside the formation of epoxide groups (or oxirane rings) in the molecular structure of the fatty acid [91]. Vegetable oils show potential as renewable plasticizers since they are readily available, biodegradable and have low toxicity, making them suitable for PLA. A paper by Arkadiusz Zych et al. (2021) described adding a type of epoxidized soybean oil methyl ester into PLA to discern its suitability as a plasticizer in packaging applications. An

improvement in toughness and elongation at break was reported therein, as well as a reduced glass transition temperature, yet identical barrier properties were retained [92].

Consequently, we can also meet with additives exist based on essential oils (thymol, cinnamon) that have antibacterial properties, as do natural colourants from plants (turmeric, beetroot). Decelerating the ageing process of a PLA material is also possible with the aid of an antioxidant. For instance, the widespread utilization of BHT, a common synthetic compound, could be superseded by employing polyphenols from cinnamon, coffee or cocoa instead [20], [93], [94].

1.2. Degradation of PLA

One of the main properties of PLA, which is often disadvantageous, is its tendency to undergo degradation already during processing, especially when the material is not dried. This degradation leads to loss of properties. This degradation mechanism 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. Increase in the concentration of the carboxylic acid end groups in the degradation medium becomes a self-catalyzing, autonomous process. Degradation in amorphous regions is also preferentially accelerated, rather than in crystalline ones [95], [96].

- **Thermal degradation**

PET is one of the most common forms of thermoplastic polyester and boasts a wealth of applications. Consumer PET has become a global problem due to the immense volumes of it produced and the complexity involved in associated recycling and disposal processes, which is subject to thermal degradation even at high temperatures (300 – 1000 °C) and low pressure (1.01 bar). Products are formed at such temperatures, e.g. carbon monoxide (CO), CO₂, ethylene-acetylene, acetaldehyde, benzene, benzoic acid, vinyl benzoate, divinyl terephthalate, acetophenone and p-acetyl vinyl benzoate. Analogous to PET, PLA degradation typically occurs either by hydrolysis, thermal oxidation or photo-oxidation [97], [98]. The thermal degradation of PE takes place at high temperatures during pyrolysis. PE, together with PP and PS represent candidates for creating good calorific values and liquid oil yields. However, toxic gases are produced during incomplete combustion, much like other types of solid municipal waste. These gases contain dioxins (C₄H₈O₂), CO, hydrogen sulphide (H₂S), polycyclic aromatic hydrocarbons (PAH) and furans (C₄H₄O), and can cause serious health problems [99].

Thermal degradation is a highly controlled process that occurs in PLA during processing. It not only affects mechanical properties, but also reduces the ability of PLA to recycle. Structural changes in PLA become evident at T_g (60°C), which modify the mobility and volume of the polymer chains, but. The primary degradation temperature at processing temperature equals ca 190°C, though, when its molecular weight decreases by 70% in melt spinning and injection by 14 – 40 %. At 230°C or less, the cleavage of the polymer backbone in PLA mainly results from non-radical intramolecular transesterification, contributing to the formation of oligomeric rings, acetaldehyde and oxide units as by-products. At

270°C or above (not considered normal processing temperatures), cis-elimination and radical reactions occur, which promote the further development of carbon dioxide and methyl ketene. Thermal decomposition is affected by several external factors, e.g. residual metal catalysts, the processing temperature, moisture content, oxygen environment, duration of exposure to natural weathering and the surfactant present in the reinforcements. The thermal degradation of PLA is initiated by hydrolysis associated with moisture during processing. Prevention of this could involve supplementation with a chain extender, or precipitation and acid treatment to remove monomers, oligomers and residual catalysts from the matrix. Antioxidants typical for conventional polymers are also applied to stop degradation [57], [100], [101].

- **Photodegradation**

In the natural environment, PET can be degraded not only by thermal oxidation, but also by hydrolytic cleavage and photo-oxidation initiated by UV light. However, slow photooxidation in the environment most often occurs, and then they are accompanied by others. In addition, these processes are accelerated in an acidic and humid environment. Other representatives of frequently used polymers include polyolefin PE, which is inert and decomposes slowly in the natural environment (polyethylene lacks chromophores). PE-based films usually contain the antioxidant BHT, and this prolongs the rate of degradation. Furthermore, the bonds of this polymer are exclusively C–C, which are not easily hydrolyzed and resist photo-oxidative degradation. Small amounts of vinyl or vinylidene groups may be present in the material, however, and these are easily oxidizable. The free radicals formed during decomposition further react with oxygen to form peroxy radicals (RCOO·) followed by peroxides, which are converted into compounds in the decomposition process that support the decomposition and release of plasticizers and other additives into soil and water [97], [102].

This degradation of PLA normally occurs upon exposure to outdoor conditions. It is primarily strong solar radiation (around 245 – 400 nm), which includes invisible UV radiation of lower wavelengths and higher energy. In general, the carbonyl groups (C = O) in the PLA molecule absorb UV radiation of around 220–280 nm due to the transition of n- π^* electrons, and this energy can give rise to a chemical reaction in which double bonds of C–C and –COOH groups form through long-term exposure to UV radiation. Another possibility is the formation of anhydride groups or photolysis of the ester bond on the backbone, or the formation of hydroperoxide derivatives and their subsequent degradation into compounds containing carboxylic acid and diketone end groups. Figure 6 summarizes the products of both mentioned PLA degradation mechanisms. UV radiation also affects the mechanical properties of PLA undergoing photodegradation, much the same as in thermal degradation. Specifically, in this regard, tensile strength induces a reduction in the integrity of the polymer and eventually turns it into a brittle, white solid. Furthermore, changes in the M_w of

the polymer, reduction in stress and stress at break also take place. Heightened temperature and relative humidity (RH) in combination with UV radiation additionally cause significant reduction in the mechanical properties of the polyester and accelerate its degradation. Prolonged exposure to UV radiation impacts the ability of such materials to biodegrade, though [100], [103], [104].

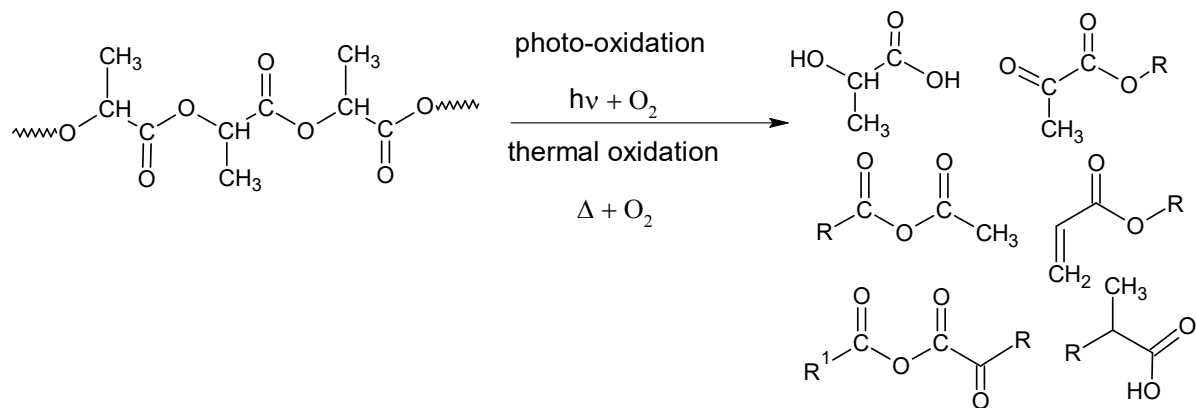


Figure 6. Simple schematic diagram of the photo-oxidation and thermal degradation of polylactic acid, alongside products typical of these processes (R and R^1 are polymer chains of different lengths) [98].

These degradation processes can be split into two main groups - abiotic hydrolysis and biodegradation. Abiotic and biotic processes often follow on from each other, with abiotic degradation converting larger molecules into smaller ones, which are subsequently mineralized by microorganisms and enzymes.

- **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. 7). 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 [57], [98], [105], [106], [107].

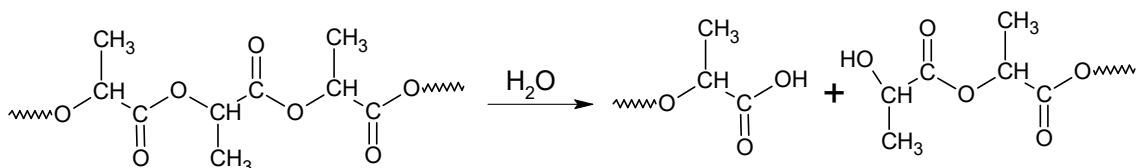


Figure 7. Hydrolytic degradation of PLA in the presence of water [108].

In large PLA chain, though, carboxylic acid groups are concentrated in the polymer at the end. This gives rise to a pH gradient (neutral) with consequent decelerated degradation of the surface of the polymer matrix compared to the centre. A level of critical osmotic pressure has to be created in the centre of the matrix first, followed by surface degradation [103].

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 [98].

- **Biodegradation**

As previously mentioned, PLA is a biodegradable polymer. The distinction between being “biodegradable” and “biodegradable plastic” has to be clarified in legislation. ASTM D883-12 determines the difference between these terms. 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 plastic material with a degradation mechanism induced by the actions of naturally occurring microorganisms such as bacteria, fungi and algae [109], [110].

PLA currently complies with this legislation and it is possible to compost it, although no composting facilities have yet been set up for this purpose. In connection with degradability in uncontrolled conditions, it takes far longer than under composting conditions, for example. The literature shows that simulations were performed at low temperatures by anaerobic biodegradation. The experiments were carried out under accelerated, optimal landfill conditions, and biodegradation was observed over a time frame of 100 years. These tests were performed at 21°C (390 days) and 35°C (170 days). The results showed that in the case of semi-crystalline PLA, a slight presence of biogas was recorded at up to 35°C, also appearing in small amounts at the same temperature in amorphous PLA [111], [112].

Recovering these polymers through recycling would be beneficial from an environmental perspective, but 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 and enzymatic activity in tandem [113].

In the case of PE, which appears to be an inert polymer with respect to biodegradability, as a consequence of the minimal reactivity of the C–C bond in the backbone and its high molecular weight. It is in widespread use, nevertheless, in all sectors from the food industry to agriculture. Buried in landfills in relatively high humidity, it undergoes a slight loss in weight over a period of 12 – 32 years. It exerts an impact against soil and water, though, causing deterioration in the quality of earth and nutrients, in addition to representing a threat to animals. Processes exist that can improve the microbial degradation of PE, thankfully. A well-known method involves nitric acid, which supports the fragmentation of PE films or thermo-UV pretreatment. Special species of microorganisms are also needed, belonging to genera like *Pseudomonas*, *Ralstonia*, *Stenotrophomonas*, *Klebsiella* and *Acinetobacter*; in addition to *Rhodococcus*, *Staphylococcus*, *Streptococcus*, *Streptomyces*, *Bacillus* and several genera of fungi including *Aspergillus*, *Cladosporium*, *Fusarium*, *Penicillium* and *Phanerochaete*. Even under favourable conditions, however, the extent of decomposition only reaches 1– 3 % in 40 – 60 days. It is also important to ensure suitable abiotic factors that increase efficiency, which is also negatively affected by any additives present in PE. Recent research on biodegradation has observed the effects of larvae of *Galleria mellonella* and *Plodia interpunctella*. These worms have the ability to metabolize beeswax, which possesses similarities to PE. It was found that approximately 100 *G. mellonella* worms caused weight within 12 hours by means due to mechanical combined with enzymatic digestion. It is not possible to comply with composting limits in relation to PE, unfortunately, and biodegradation in natural conditions takes place very slowly. In addition, the quality of the compost deteriorates and endangers the creatures in the immediate environment of polymer particles that bind to each other, e.g. polychlorinated biphenyls [114], [115].

Similar issues are posed by PET. Decisive factors in this regard comprise the flexibility of the polymer chain, crystallinity and surface hydrophobicity. Research has revealed that it is more efficient to utilize hydrolase enzymes for cleavage of the ester bonds. These enzymes contain cutinases that exhibit hydrolytic activities for both insoluble triglycerides (typical substrates for lipases) and soluble esters (substrates for esterases). Other known microorganisms boasting such degradation action include the filamentous fungi *Fusarium oxysporum* and *Fusarium solani*. One species of the genus *Ideonella*, namely *I. sakaiensis* 201-F6, shows promise and possesses a unique capacity for degrading PET as the main source of carbon and energy for its growth. While PET decomposition by hydrolases rarely occurs in microbial environment, it does serve as an inspiration for those in biotechnology [116], [117].

- **Microbial degradation of PLA**

Microbial activity against PLA commences once a polymer is fragmented into oligomers and has a molecular weight of ca 10,000, a process accompanied by biofilm formation on the surface of the material. The fragmented molecules are

then mineralized in compost to CH₄, CO₂ and H₂O. This process is amplified by a higher decomposition temperature (40 – 60 °C). The best environment for PLA biodegradation is provided at industrial composting plants. They function at the optimal temperature (58°C) and humidity (70%), thereby heightening the activity of aerobic microorganisms. Under these conditions, it is possible to observe loss in molecular weight over 17 days from 150 to 4.5 kDa [118]. Constituting the most abundant and recognized forms of microbial life in soil, are bacteria that are also able to degrade PLA, gram-positive bacteria of the order *Actinobacteria*. One of a few microorganisms with the potential to degrade the polymer, 26 species in 11 genera are known to exist. Most of these *Actinobacteria* belong to the family *Pseudonocardiaceae*, other taxa include members of the family *Micromonosporaceae*, *Streptomycetaceae*, *Streptosporangiaceae* and *Thermomonosporaceae*. The dominant form of PLA-degrading *Actinobacteria* comprise members of the genus *Amycolatopsis* (strains *HT-32*, *K104-1*, *HT-41* or *orientalis*) of the order *Pseudonocardiaceae*. Members of the genus *Amycolatopsis* are commonly found in dry soils, and discerned as the originators of secondary metabolites that could serve further biotechnological applications. Other known bacteria include *Bacillus brevis*, *Bacillus stearothermophilus* and *Geobacillus thermocatenulatus* [119],[120],[121].

Besides bacteria, fungi also have the potential to degrade PLA. Fungi help reduce the hydrophobicity of the polymer by forming various chemical bonds, such as carbonyl, carboxyl and ester functional groups. Characterized by their wide distribution and strong reproductive ability, fungi support the conversion and circulation of substances. Some are able to utilize polymer residues as a source of carbon. Very few fungal strains possess the capacity to biodegrade PLA, though. *Fusarium moniliforme* and *Penicillium roqueforti* are well-known for their ability to assimilate lactic acid and the racemic oligomeric products of PLA, but no degradable action has been observed against the polymer itself. *Tritirachium album* or *viride* is the only fungus ever reported to degrade PLA. Its efficiency increased after adding gelatin to the culture medium. The worst environment for PLA decomposition is seawater for reasons of low temperature and the presence of few bacteria. This reinforces the need to switch to PLA copolymers instead on an industrial scale, and adding a substance such as glycolic acid (PLGA) speeds up decomposition even more, with samples showing a complete loss of mass after just 270 days [112], [122].

- **Enzymatic degradation of PLA**

Biodegradation constitutes a more complex process as it involves enzymatic activity by microorganisms. An optimal presence of cations and coenzymes synthesized by microorganisms is also required. Enzymes help accelerate the degradation of PLA, and a wide range of them exists, e.g. lipases, serine proteases, cutinases, carboxylesterase and esterases. Enzymes function as biocatalysts and

attack amorphous regions first, followed by crystalline ones. Enzymatic activity is environmentally dependent, and lipases are highly versatile in this regard as they possess heightened resistance to external environments. They are also capable of synthesizing numerous substrates with high stereospecificity and enantioselectivity. The origins of lipases applied in polyester synthesis tend to be mammalian (porcine pancreatic lipase), fungal (*Candida antarctica* lipase B) or bacterial (*Pseudomonas cepacia*). Lipases are only able to catalyse PLA degradation to a limited extent, however, whereas proteinases seem more suited to this purpose [123].

The first report on enzymatic degradation by PLA proteinase K from *Tritirachium album* was published in 1981. Proteinase K prioritize the hydrolysis of ester linkages connecting L-lactyl units over D-lactyl ones. Another 56 commercially available proteases have appeared in the year since then. The most suitable of those appears to be alkaline, which produces a considerable amount of lactic acid from PLA, although its application is restricted for reasons of sensitivity to the natural environment. It is possible to hydrolyse PLA in two steps with the aid of an important enzyme - serine protease, a process which transpires in the presence of actinobacteria of the genus *Amycolatopsis*. In the first step, enzymes from microorganisms adhering to the surface of the PLA are released, and the substrate binds to the surface of the serine protease at the active site. The second step involves, cleavage of the bonds in the PLA occurs via a reaction of catalytic amino acids (Ser, Asp and His) in the presence of water [120], [124].

Lipases as well as polyurethane esterase have been investigated for the degradation of low-molecular weight PLA. A few enzymes have also been discovered with the capability of degrading high-molecular weight PLA, a recent group comprising purified enzymes. These enzymes are derived from the bacteria *Amycolatopsis orientalis* ssp. *orientalis* and are named PLAase I, II and III. Under optimal conditions (50 – 60 °C and pH 9.5 – 10.5), PLA was observed to degrade by 80% within 8 days; the high-molecular-weight, transparent, PLA film under test constituted the sole source of carbon [125], [126].

- **Biodegradation mechanisms of other biodegradable polymers**

In this work, it is also appropriate to mention the general mechanism of degradation of other biodegradable polymers such as polycaprolactone (PCL), polybutyl succinate (PBS) and poly-3-hydroxybutyrate (P3HB). All these aliphatic polymers are dominated by biodegradability, which is initiated by random chain scission and erosion, for which both abiotic and biotic hydrolysis is responsible [127].

Due to its semi-crystalline and hydrophobic nature, PCL is a slow-degrading polymer, typically requiring 2 to 3 years for complete degradation. PCL degradation is usually a two-step process like PLA. First, there is a degradation of the amorphous phase, which is accompanied by an increase in crystallinity, and then a degradation of the crystalline phase. Hydrolysis of PCL produces 6-

hydroxycaproic acid, which is subsequently metabolized. Acceleration is aided by an increase in temperature in the presence of air, when the oxidation of hydroxyl groups begins, but also by the presence of bacteria of the genera *Pseudomonas* and *Lactobacillus* and or fungi of the genera *Aspergillus*, *Candida*, *Mucor*, *Rhizopus* and *Thermomyces* [127], [128],[129].

PBS is a thermoplastic, synthesized from 1-4-butanediol and succinic acid, with properties similar to PP. It can naturally decompose into water and carbon dioxide. The decomposition time of PBS is similar to that of PLA. However, the onset is slower and even after 90 days the success rate of complete degradation is not 100%. To increase effectiveness, the fungi *Aspergillus fumigatus*, *Acidovorax delafieldii* or *Aspergillus oryzae* and their enzymes (lipases) can be applied [130], [131].

P3HB is a thermoplastic polymer with thermal and mechanical properties similar to PP. P3HB is also very crystalline polymer and this reduces the degradation rate, for this purpose it is advantageous to copolymerize with 3-hydroxyvalerate. This is also helped by the formation of depolymerase, which can be secreted by some microorganisms, which hydrolyse ester bonds into water-soluble oligomers and monomers. A polymer modified in this way can easily degrade even under conditions where other biopolymers are almost resistant. In the marine environment, where approximately 40% weight loss occurs after 160 days. In an artificially created marine environment with microbial inoculum, even in 40 days by 70% [127], [132].

From the group of polyhydroxyalkanoates biopolymers, we can also mention the alternative poly(3-hydroxybutyrate-co-3hydroxvalverate) (PHBV). Diffusion of water in this polymer is a slow process and therefore surface erosion prevails. As with the other mentioned polymers, many factors matter here. However, it is known that the chemical nature of the chain, molecular weight and distribution are also important here. PHBV is characterized by a higher molar content of HV groups, which accelerate the hydrolysis process and reduce the crystallinity of the material. For that reason, enzymatic degradation is also faster than with P3HB homopolymers [133].

Although, each of the listed polymers has different optimal decomposition conditions, 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 [127].

- **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 its degradation products. In connection with this, conducting a life cycle assessment (LCA) method can be used, which can calculate 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 [134].

The ISO 14040:2006 and ISO 14044:2006 standards stipulate the principles and methodology required for carrying out LCA studies [135].

Studies in the literature have compared LCAs for conventional PET water bottles to PLA alternatives. Therein it was reported that PET bottles exerted a lesser environmental impact than PLA bottles, since agricultural burdens and issues are associated with the latter, i.e. growing suitable crops, the global warming potential (GWP), water, eutrophication, acidification, particulates and the inevitable land use. In light of the fact that non-renewable resources are dwindling and recycling processes are limited in their extent, it is only possible to view this finding as temporary. The studies also recommend optimizing the production of PLA, especially regarding fermentation, improving cultivation procedures and utilizing renewable energy sources. PLA demonstrates clear advantages over PET from a long-term perspective in terms of non-renewable resource consumption and issues surrounding global warming, but neither option is currently ideal [136], [137], [138].

The European Union is counting on the development of sustainable, recyclable plastics, while also addressing the opportunities and risks of such biodegradable materials. Research on biodegradable polymers has been on the rise for several years in connection with medical applications and foodstuffs. However, if we take the issue of plastics globally, where recycling processes are not developed and are disposed of in an uncontrolled manner, we still run into the problem of accumulation of plastic waste. In the environment, commodity plastic is going to accrue in the environment for decades (e.g. PET), and bottles made of it have an estimated life cycle of up to 93 years (at 100% relative humidity). This PET waste is particularly prevalent in locations where drinking water is not available, hence the latter is sold in bottled form. One way of tackling the issue may be to ban certain plastic products or supersede the commodity polymer with an alternative material, e.g. paper or a biodegradable polymer. On the other hand, the term "biodegradable" is used in many cases today without any evidence or degradation tests. Therefore, a necessary step shall be to perform degradation tests that encompass aspects like composting in a home setting or commercially composting tests. Simulating composting conditions in a laboratory is practically possible, with experiments encompassing a phytotoxicity test, wherein the growth of plants is determined in containers filled with a mixture of compost and decomposing bioplastic. Plants represent primary producers with a key role in regulating the functions of an ecosystem. In the case of plastics, ecotoxicological studies have been carried out *inter alia* on the effects of plastic particles on seed

germination, biomass growth (total biomass, root biomass, shoot biomass) and root elongation [139], [140].

Analyses of carbon and nitrogen content and associated ratio are also performed (C/N). Table 2 details some examples of waste commonly found in composting plants. The core technology for breaking down waste from biodegradable sources is composting, and commercial facilities turn out huge amounts of first-rate organic fertilizers and substrates. Spreading mature compost on agronomic soil contributes to greater crop yields, due to its high content of plant nutrients and moisture retention properties. Applying immature compost to soil can decelerate plant growth, conversely, for reasons of nitrogen deficiency, anaerobic conditions and the phytotoxicity of NH_3 and organic acids. The optimal C/N ratio for high quality compost is 25 – 30, although a lower C/N ratio of 15 is possible under certain, circumstances, e.g. lengthy durations of plant growth [141], [142].

Table 2. Average C/N ratio in composting materials [143].

Waste material	C/N ratio
City garbage	49–105
House refuse	30–75
Layer manure	4–12
Leaves	35–70
Grass clippings	10–30

A crucial aspect to determine is the quantities of hazardous substances present, e.g. heavy metals (As, Pb, Cd, Cu, Hg) and zinc (300 – 1200 mg/kg compost). Values for individual elements are set out in Decree No. 474/2000 Coll. “stipulating requirements for fertilizers”. Agricultural compost has to possess a wide ratio of C/N nutrients, a stable form of nitrogen, a primarily alkaline pH, soil microorganisms and also contains macro-elements of phosphorus (P), potassium (K), calcium (Ca) and magnesium (Mg), and other components. Phosphorus and potassium are essential for plant photosynthesis, seed maturation and crop yields. The former of the two facilitates the transport of energy and aids root development, while the latter heightens resistance to disease. Calcium contributes to the strong formation of shoots and roots, and acts as a signal when the plant is stressed. Mention should also be made of sulphur (S), which not only is a building block of other essential compounds, but also makes crops more resistant to cold, for instance. Minor amounts of iron (Fe), boron (B) and manganese (Mn) are also important for photosynthesis, the regulation of nutrients or help with metabolizing nitrogen [144], [145], [146].

1.3. Natural-based pro-degradation stability modifiers

PLA degradation follows a natural course, albeit somewhat inappropriate for any corresponding processing or storage. Conditions and influences affecting its properties have been described above in this text. 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. PLA can be supplemented with a host of additives of synthetic or natural origin, yet the impact such a mixture shall ultimately have on the environment has to be anticipated. Therefore, emphasis is placed on using as many environmentally-friendly and natural resources as possible.

- **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 crucial factors comprise what is expected of the material in terms of processing and mechanical (toughness, elasticity), thermal or barrier properties. Carrying out modifications to PLA with the aim of enhancing them may even turn out to have an opposing effect [147].

The primary means of preventing PLA degradation processes is to eliminate a hydrolytic reaction. Increasing the degree of crystallinity and crystallization is additionally necessary in order to reduce the amorphous phase, i.e. the cause of its low-thermal stability. Various 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** [147],[148], [149].

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 (TAIC) as a crosslinking agent (Fig. 8) [148], [150].

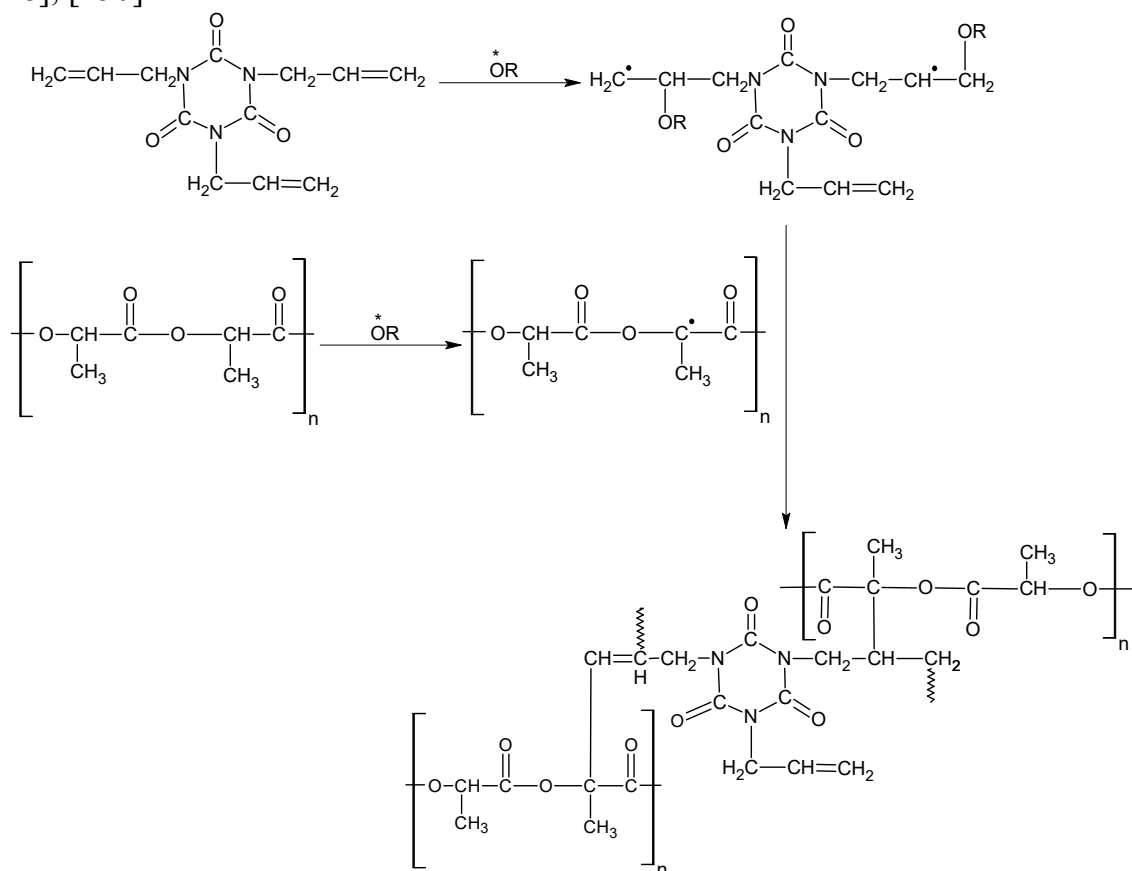


Figure 8. Schematic diagram of the chemical crosslinking reaction of TAIC for two PLA molecules [151].

Other common PFMs comprise trimethallyl isocyanurate (TMAIC), trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate (TMPTMA), 1,6-hexanediol diacrylate (HDDA) and ethylene glycol bis (pentakis (glycidyl allyl ether)) ether [152].

It is reported in the literature that the most optimal conditions for the introduction of crosslinking are ca 3% TAIC and an irradiation dose of 30–50 kGy. In the referenced study, crosslinked PLA films demonstrated superior thermal stability and mechanical properties. The irradiated PLA samples became harder and more brittle at low temperatures, yet rubbery, soft and stable at higher temperatures, even over 200°C. The degradation behaviour of the irradiated, crosslinked PLA samples was also significantly slower. Although this method is effective, there is the disadvantage of this method lies in its expense. Moreover, PLA samples can only be in the form of thin plates to ensure sufficient radiation

energy for the crosslinking reactions, severely limiting the practicability of this method [152], [153].

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. All such methods involve peroxide-induced radical crosslinking. Ensuring an optimal amount of peroxide and free radicals are just two criteria that have to be met to achieve the greatest efficiency. These are not only responsible for the crosslinking reaction, but also for cleavage of the chains, causing a loss in mechanical properties. These phenomena can be mitigated by utilizing organic peroxides (lauroyl peroxide or dicumyl peroxide) with multifunctional co-agents (epoxy natural rubber, triallyl trimesate). Treatment with peroxide has also had the effect of enhancing the compatibility between polymers [153], [154].

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. The procedure has other benefits, too - it does not involve the use of high temperatures, is safe for living systems and the associated costs are reasonable. First, PLA is functionalized at the chain ends by double bonds and then exposed to UV or visible radiation, inducing radical polymerization. Photoactive additives such as substituted phenylacetophenone (“Irgacure”, a so-called photoinitiator) or camphorquinone are then added to initiate free radical polymerization [152].

2) Chain extension

The chain length and its number of entanglements relate to the stability of the polymer under thermal stress. Alongside increase in these properties, a parallel rise is evident 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. Such multifunctional chain extenders contain epoxy groups that interact with the –OH and –COO groups of polyester chain ends. 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 (TNPP), polycarbodiimide (PCDI) and “Joncryl” (see below) [148], [155], [156].

The most commonly employed chain extender is the multifunctional, styrene-acrylic oligomer sold under the trademarked name of Joncryl. It was designed for post-industrial recycled or consumer recycled polyesters, such as PET, polybutylene terephthalate (PBT), polyamides (PA) and thermoplastic polyurethanes (TPU). 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). Figure 9 displays the structure of the Joncryl ADR chain extender and illustrates its reaction with PLA. Joncryl contains the groups R1-R5, i.e. H, CH₃ and higher

alkyl groups or combinations thereof, and R6, an alkyl group. Joncryl ADR is a low-molecular-weight oligomer ($M_n < 3,000$, $PDI > 3$) based on epoxy styrene acrylate. In addition to linear chain elongation, it is commonplace for branching and even crosslinking to occur [82], [155], [157].

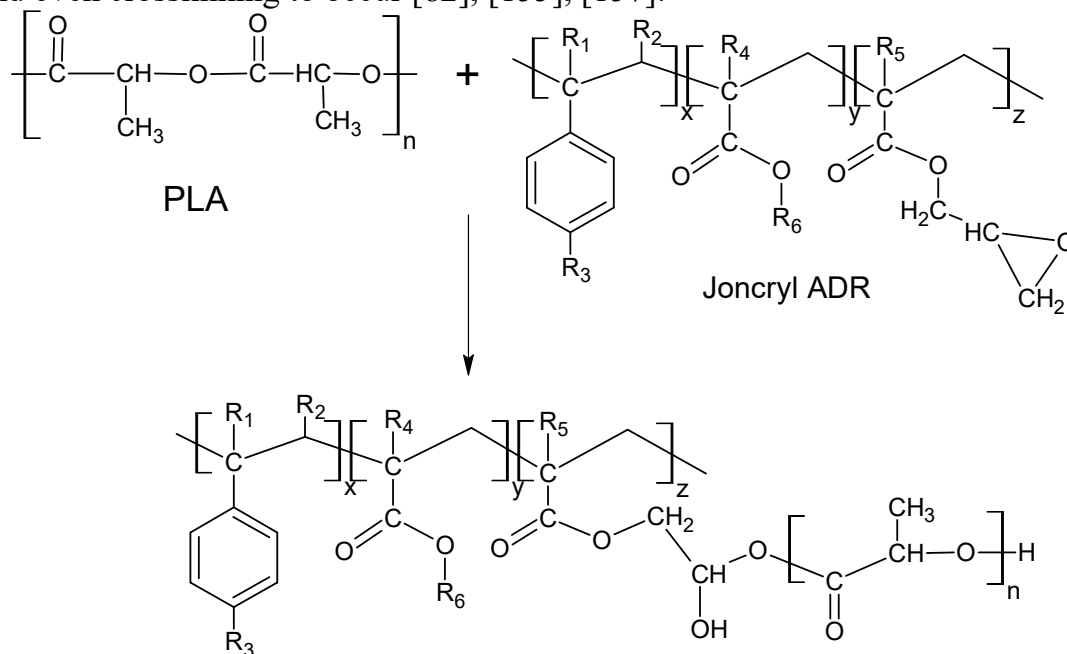


Figure 9. Reaction between the epoxy group of Joncryl and the terminal hydroxyl group of PLA [157].

3) Increase in the degree of crystallinity of PLA

A PLA monomer is characterized by its chirality, which exists in two forms – D- and L-, resulting in three configurations. By combining enantiomeric content, modifications are made that affect crystallization kinetics and thus other properties (mechanical, thermal and so on). The cohesiveness of the homopolymer bonds in the stereocomplex is brought about through Van der Waals forces. For higher operating temperatures, stereoblocks-PLA are applied, wherein these two forms are combined. Consequently, during the post-processing cooling stage, stereocomplexes develop that act as nucleating agents to support the crystalline regions. Crucial factors comprise the amount of D-form, 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 alpha form and γ -form grow, triggered by epitaxial crystallization [148], [158].

A more commonly used method involves the direct application of a nucleating agent within the PLA processing procedure. There are several types of nucleating agents, which are generally divided into **inorganic, organic or inorganic-organic hybrid materials** [159].

Of the common inorganic fillers, mainly mineral agents are used. Talc is a typical choice as it has a high efficiency (6% by weight, up to 500x increased nucleation density). The higher nucleation effect of talc has been reported as the formation of orthotropic crystalline textures caused by the presence of specific interfacial interactions between talc and PLA. Furthermore, common clay is also known to improve selected properties, and consists of calcium carbonate, carbon nanotubes or graphene oxide. Then there are organic compounds that are characterized by their good dispersion and miscibility in polymer matrices; e.g. derivatives of sorbitol, organic salts and compounds (sodium stearate and sodium benzoate), aromatic phosphonates and aromatic sulfonates. Polyhedral oligomeric silsesquioxanes and their derivatives have been employed, too, defined as hydride materials composed of an internal, rigid, siliceous cage structure surrounded by more flexible organic groups, such as PEG. Finally, nucleating agents can take the form of starch, lignin or nanocrystalline celluloses [159], [160], [161].

4) Antioxidants

The general role of antioxidants (AOs) is to balance reactive oxygen species (ROS) and nitrogenous substances (RNS). Free radical scavenging does not just concern biological systems, but also numerous industrial applications prone to oxidative degradation, including most polymers (PP or PE). The thermooxidative degradation of polyolefins pertains to an autocatalytic chain reaction of free radicals, constituting stages of initiation, propagation and termination. Alkyl, alkoxy, peroxy and hydroxyl radicals are all involved in these processes. 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), but not all exhibit the required action. The principle behind the antioxidant effect of polyphenols is the ability to donate a phenolic hydrogen to the generated free radical. The resulting phenoxyl radicals are resonantly stabilized and react with other free radicals. Stabilization packages added to the polymer contain polyolefins that function as a primary antioxidant and a secondary stabilizer, e.g. a hydroperoxide decomposer of phosphorus or sulphurous type, which significantly enhances the thermooxidative stability of the polymer melt. The purpose of secondary stabilizers is to reduce hydroperoxides to harmless alcohols. The incorporation of an antioxidant into materials takes place through hydrogen bonds, metal coordination or covalent interactions [162], [163], [164].

The foremost compound associated with polyphenols is α -tocopherol, while lignin has attracted the greatest attention of the phenolic varieties. Each year, 70 million tons of lignin are generated as a by-product of the pulp and paper industry. A biocompatible, high-molecular, polyphenolic, amorphous substance with antioxidant activity, lignin is capable of absorbing UV-light and functions as a barrier of such radiation. In a study by Boarino Alice et al. (2022), it was found

that just 1 wt.% of lignin particles could resist the penetration of 280 nm of UV radiation; notably, the transparency of the PLA film was maintained [165]. Figure 10 illustrates the antioxidant activity of lignin during UV-irradiation.

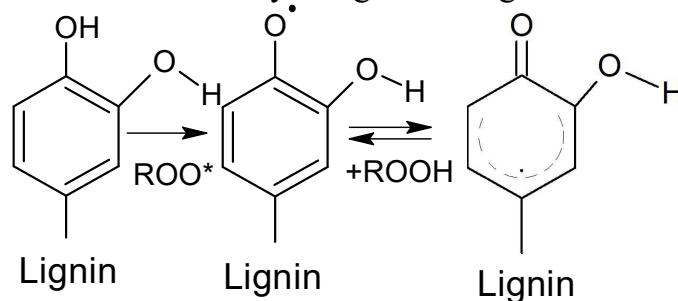


Figure 10. Antioxidant activity of lignin [165].

Related substances are extracted from red wine, green tea and citrus fruits, whereas ginger, pepper or fennel constitute sources of phenolic polymers. Lignin is present in the cell walls of vascular plants. There are also carotenoids in carrots, mint or sweet potatoes, and curcuminoids in turmeric. Lycopene, an extract of tomato, improves the processing stability of PP via the efficient capture of alkyl radicals. The extract increased the level of activation energy needed for the thermal decomposition of PP in nitrogen, yet significantly reduces it in an oxygen atmosphere. The last to feature in this list are tannins found in exotic fruits or grape skin and seeds. Natural antioxidants are less widely utilized than their synthetic alternatives for several reasons. A higher dosage is required for polymers and they are more prone to degradation, while price and availability also pose problems. As a consequence, the tendency is to use synthetic AOs include BHA, BHT and tert-butylhydroquinone (TBHQ) [164], [166].

- **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. Like any plastic material, it should be properly sorted and processed once it has served its post-consumption. The recommendation for consumers is to deposit it in brown organic waste bins, whereupon it goes to municipal composting facilities with optimal conditions for its decomposition. 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” [167].

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. Total homogenization of these in the polymer matrix is essential for accelerated hydrolysis. Beyond seeking ways of speeding up

degradation in soil or compost, researchers have been investigating the physiological environment for medical purposes. In connection with this, applying Mg in combination with PLLA accelerates the degradation behaviour of the composite; the mechanism involving the release of Mg in the physiological system, whereupon magnesium hydroxide ($Mg(OH)_2$) is formed in order to consume acidic PLA products [103], [168], [169].

Certain kinds of **plant-based matter** are also applicable, such as fibres (hemp, flax), wood flour or modified cellulose nanocrystals. Hemp fibres are finding favour in the automotive, construction and furniture-making sectors, serving as a substitute for glass or carbon fibre in the reinforcement of thermoplastic matrices. They have the advantage of being inexpensive, low in density, safe to handle and non-abrasive, so do not cause damage to mixing and moulding equipment. An issue arises with regard to vegetable fibres in manufacturing processes at high temperature, though. In combination with residual moisture and mechanical stress, degradation is promoted, hence mechanical performance is reduced [167], [170], [171].

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). Another example, a composition of PLA/PEG, serves as both a plasticizer and accelerator of degradation. The PEG in it induces degradation of the chain, which contains short segments of PLA, through the action of randomly cleaving the ester bonds along the PLA blocks. This is also the case with PBS in combination with PLA, the gaps between the PLA matrix and the dispersed PBS particles providing a path for water diffusion, thereby accelerated hydrolytic degradation. Supplementation with a polymeric additive such as poly(aspartic acid-co-lactide) (PAL) is also possible. PAL has a unique branched structure composed of polysuccinimide (PSI) and PLA segments, and can easily be converted into the hydrophilic copolymer poly(sodium aspartate-co-lactide) (PALNa) in a reaction with aqueous NaOH [172], [173], [174].

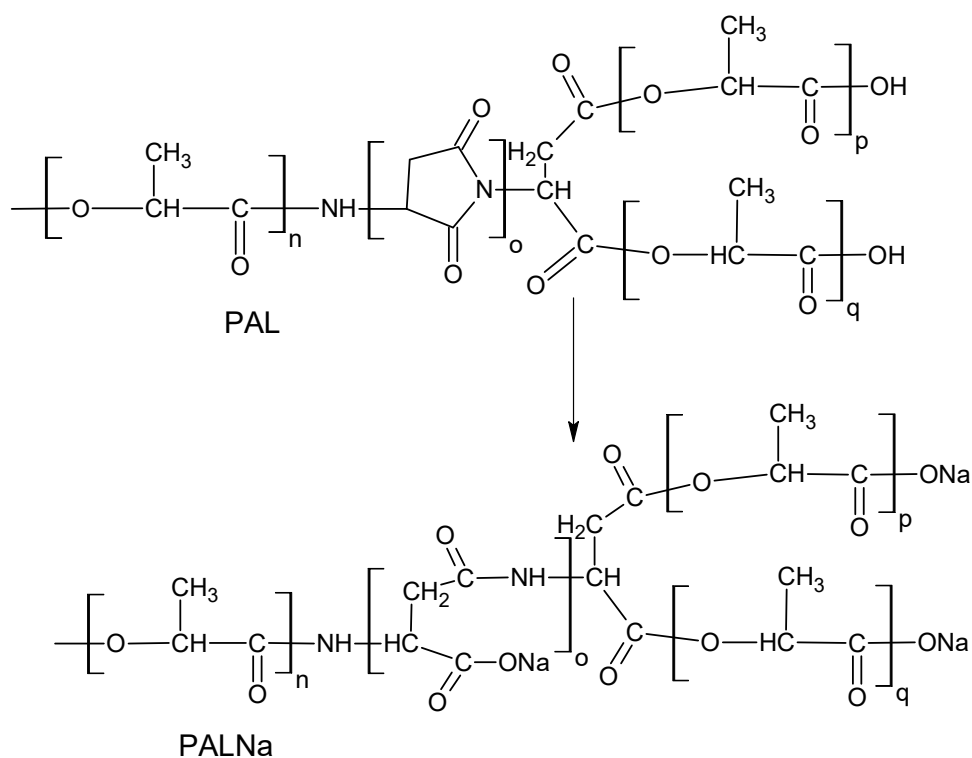


Figure 11. Schematic diagram of the structure of PAL and PALNa copolymers [174].

A further option is to utilize **microorganisms** that promote the degradation of PLA polymer. A study has reported on employing proteases, including proteinase K, pronase and bromelain, which increase the rate of PLA degradation. In this regard, the actinomycete *Amycolatopsis sp.* and fungus *Tritirachium album* are capable of being applied from 30°C [175].

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. The earlier sections of this manuscript detail such circumstances for both initial hydrolysis and microorganisms, whereby the complete disintegration of a sample is enabled [68].

2. AIMS OF THE 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.

3. 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 adopted industrially. 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 the material has to be processed in technical composting plants.

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

Material and chemicals

Commercial PLA (2003D) from NatureWorks (Minnetonka, MN, USA) and PCL from Sigma-Aldrich (Saint Louis, MO, USA) were employed in the experiments. Fresh red beetroot (BR) was obtained from a local farm (Ostrozka Nova Ves, Czech Republic). Bentonite was sourced from local wine producers at the particle size of $>20\ \mu\text{m}$. Ethanol (99.8%) was purchased from BC-Chemservis (Roznov pod Radhostem, Czech Republic). The acetone (99.88%) utilized was from Chromservis (Prague, Czech Republic). Folin-Ciocalteu's phenol reagent (2 M), gallic acid (97.5%), ascorbic acid (reagent grade), sodium carbonate (anhydrous, EmsureTMACS, ISO, Reag. Ph Eur), and 1,1-diphenyl-2-(2,4,6-trinitrophenyl) hydrazyl came from Merck (Darmstadt, Germany) and Sigma-Aldrich (Saint Louis, MO, USA). Tetrahydrofuran was supplied by Carl Roth Rotisolv[®] HPLC (Karlsruhe, Germany) and chloroform by Penta (Prague, Czech Republic). Water and Acetonitrile ChromasolvTM Plus solvents for HPLC and LC-MS were bought from Honeywell GmB (Seelze, Germany), and formic acid for LC-MS LiChropurTM obtained from Sigma Aldrich (Saint Louis, MO, USA).

Preparation of the beetroot extract and film

The authors lyophilized fresh BR, employing a CoolSafe 110-4 PRO freeze dryer for this purpose (Lyngø, Denmark).

There is a simple and efficient preparation of the extract, which is based on the preparation of 250 mg of homogenised and freeze-dried BR with 10 ml of extraction solvent (70% ethanol) was added into a centrifuge tube, and this homogenate then stirred on a Vortex device (IKA[®] MS 3 basic, Staufen, Germany) for 2 minutes at 500 rpm. The subsequent extract was centrifuged (Thermo ScientificTM, Heraeus Multifuge X1R, Osterode, Germany) for 15 minutes, at 9,000 rpm. The supernatant (7 g) was collected with a Pasteur pipette and applied to the bentonite (BE) (5 g) as a carrier. After mixing, the samples were lyophilized. Immobilization in this way simplifies handling of the additive and proves advantageous for technological processing.

Films were cast by dissolving the polymer and adding bentonite with the incorporated beetroot extract (BRE) (5% w/w, based on the weight of the polymer) in chloroform. The solution was stirred at room temperature for 8 hours to completely distribute the antioxidant in the polymer matrix. The polymer solution was then poured into Petri dishes of 140 mm diameter. Evaporation of the chloroform took place in a fume hood in darkness for 24 hours at 25°C. The resultant films were dried in a vacuum oven (Memmert VO400, Frankfurt, Germany) at 25°C for 5 hours to remove any residual solvent prior to being stored in a refrigerator. The eventual thickness of each film was $0.35 \pm 0.05\ \text{mm}$. Neat

PLA and PCL films and composites containing bentonite (BE 5% w/w) were prepared as reference samples for comparison with the BRE films. This procedure for formulating the polymer composites is illustrated in Figure 12, while the composition and names of the tested formulations are given in Table 3.

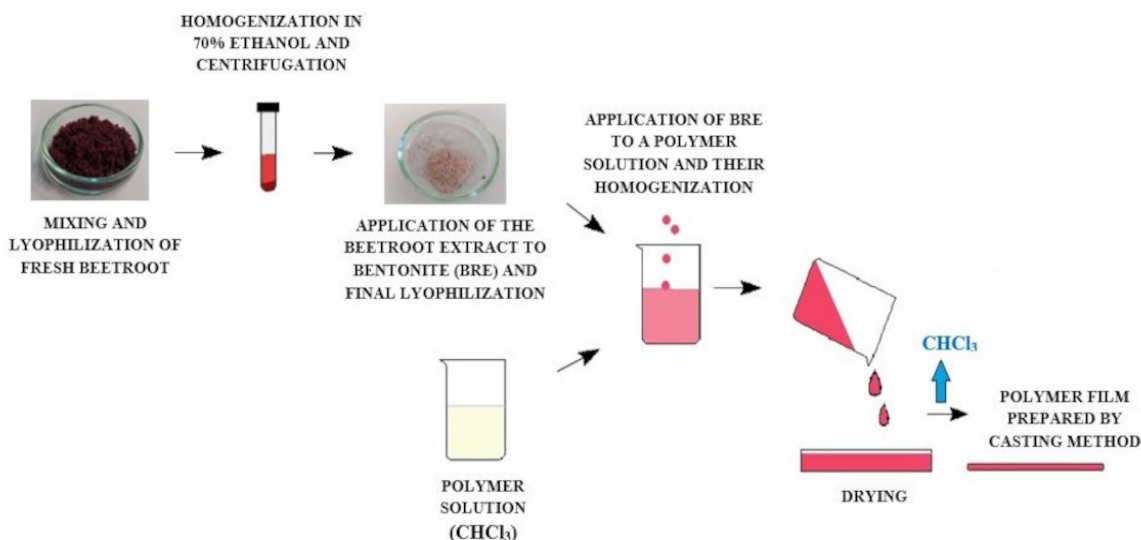


Figure 12. Method for fabrication of the samples.

Table 3. 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

Process for accelerated ageing

Accelerated ageing was performed in a climatic chamber (QUV UV tester, Westlake, USA) 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[176]. The chamber was fitted with 8 fluorescent lamps (UVB 313) of 313 nm in wavelength. Samples were placed directly under the lamps (perpendicular to the UV source) and, following the accelerated ageing test, denoted with the suffix -UV (added to the names in Table 3).

Antioxidant activity and polyphenol content of BRE

The Folin-Ciocalteu reagent method (FCM) was adopted to determine the polyphenol content in the BRE. The principle behind it is reduction of the Folin-Ciocalteu reagent (FCR) that contains a mixture of phosphotungstic acid and phosphomolybdic acid. This is reduced to a mixture of blue tungsten oxide(s) and molybdenum by oxidizing the phenols in the sample. The blue hue demonstrates maximum light absorption at the wavelength range of 750 – 760 nm, the intensity of this absorption being directly proportional to the total amount of phenolic compounds present. The resulting value is declared as the equivalent quantity of gallic acid.

The BRE supernatant at the amount of 0.1 ml was added into 1 ml of freshly prepared 10% FCR. The mixture was allowed to equilibrate for 5 minutes in darkness and then treated with 1 ml of 10% sodium carbonate solution. After incubation at room temperature for 15 minutes, the absorbance of the mixture was read at 750 nm, applying an appropriate solvent as a blank. The results were expressed as mg equivalents of gallic acid per 100 g of BR.

The antioxidant activity of BRE was determined by a basic method involving the scavenging of free radicals with DPPH. The principle behind it relates to the reaction of AOs (polyphenols) with the stable DPPH radical, thereby reducing the radical to form DPPH-H (2,2-diphenyl-1-picrylhydrazine). The reaction is observed by spectrophotometry at the wavelength of 515 nm, corresponding to the maximum absorbance of the radical, evidenced by intense change in its colour.

0.1 ml of BRE was mixed with 1 mL of 0.1 M acetate buffer (pH 5.5) and 1.9 ml of 0.2 mM DPPH. The sample was kept at room temperature in darkness for 60 minutes. A blank counterpart consisted of 1 ml of 0.1 M acetate buffer (pH 5.5), 1.9 ml of 0.2 mM DPPH and 1.9 ml of 70% ethanol, formulated for 60 minutes in darkness at room temperature. The results were expressed as mg equivalents of ascorbic acid per 100 g of BR.

HPLC-ESI-MS/MS analysis

HPLC analysis of the beetroot extract was performed on a 1260 Infinity LC system (Agilent Technologies, Santa Clara, USA). Chromatographic separation of the samples was carried out on a ZORBAX Extend C18 column (50 mm × 2.1 mm, 1.8 µm; Agilent Technologies, Santa Clara, USA) at a flow rate of 0.3 ml·min⁻¹ maintained at 35°C. The mobile phase consisted of 0.1% formic acid in HPLC grade water (eluent A) and acetonitrile (eluent B). The following gradient was applied: 0.0 – 1.0 min, held at 10% B; 1.0 – 2.0 min, linear gradient from 10% to 50% B; 2.0 – 6.5 min, held at 50% B; 6.5 – 10.0 min, linear gradient from 50% to 90% B; 10.0 – 17.0 min, held at 90% B; and the post-run lasted 3 minutes. The total running time was 17 minutes for each sample, for which the injection volume equalled 2 µl.

Detection was performed on quadrupole time-of-flight mass spectrometer (6530 Q-TOF, Agilent Technologies, Santa Clara, USA), employing a source of

electrospray ionization (ESI) set to positive ion mode. The mass spectrometer operated under the following parameters: capillary voltage 3500 V, nebulizer pressure 40 psi, drying gas 8 l·min⁻¹ and gas temperature 300°C. Mass spectra were acquired over the m/z 100 – 1,500 range at a scan rate of 3 scan·s⁻¹. Accurate mass measurements were obtained by means of a calibration solution, involving internal reference masses (purine (C₅H₄N₄) at m/z 121.050873, and HP-0921 [hexakis-(1H,1H,3H-tetrafluoropentoxy)-phosphazene] (C₁₈H₁₈O₆N₃P₃F₂₄) at m/z 922.009798). Data were recorded and processed in MassHunter software v.B.05.01 (Agilent Technologies).

Characterization techniques

Thermal properties

Thermal analyses were performed to discern the oxidizing capacity of the BRE polymer films, the techniques comprising differential scanning calorimetry (DSC) and thermogravimetry (TGA). The DSC tests were conducted to determine the glass transition temperatures (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m) and enthalpy change (ΔH_m) of all the materials; the device used was a Mettler Toledo DSC1 STARe System (Schwerzenbach, Switzerland) operated under a nitrogen atmosphere (at the flow rate of 50 ml·min⁻¹). The samples (~8 mg) were sealed in an aluminium pan and heated from -20 to 300 °C, then cooled to 20°C and reheated to 300°C at the same cooling-heating rates.

Further DSC measurements were obtained by analysing the thermal stability of the samples, conducted in the presence of an oxygen atmosphere at temperatures from 20 to 400 °C and the heating rate of 20 ml·min⁻¹. Temperatures from the DSC curves are referred to as initial degradation temperatures (T_{onset}), peak temperatures (T_{peak}) and internal enthalpy (ΔH).

Samples of 8 mg in weight were prepared for TGA measurement and investigated on a TA Q500 thermogravimetric analyser (TA Instruments, Delaware, USA), running TA Universal Analyser 2000 version 4.5A. software (TA Instruments —Waters LLC, Delaware, USA), set to a heating rate of 10 K·min⁻¹ from 0 to 800 °C under a nitrogen atmosphere. Data on temperatures at the maximum rate of weight loss of the samples (T_{max}) were collected.

Mechanical properties

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 (M350-5 CT Materials Testing Machine, Testometric, Lancashire, UK), under modified conditions based on EN ISO 527-3 [177]. Prior to this the specimens had been conditioned according to the ISO standard at 23°C and 50% humidity for 24 hours. Tensile testing was conducted at a constant rate of uniaxial deformation of 50 mm·min⁻¹ until the samples ruptured, with a minimum of 8 specimens from each group undergoing such observation. The factor of ageing

(A_f) was calculated concurrently for them based on Equation 4 below [179]:

$$A_f = (\sigma \cdot \varepsilon)_{\text{before ageing}} / (\sigma \cdot \varepsilon)_{\text{after ageing}} \quad (4)$$

where A_f is the coefficient for ageing (-), σ represents tensile strength (MPa) and ε corresponds to elongation at break (%).

Colorimetry

Optical examination of the samples by colour measurement was performed prior to and after the ageing test by on a portable spectrophotometer (Lovibond RT850i colourimeter, Tintometer Ltd, Amesbury, UK). The CIELab scale was applied to measure lightness, L^* , and the chromaticity parameters of a^* (red–green) and b^* (yellow–blue). Values for colour difference (ΔE), the whiteness index (W_i) and chroma (C_{ab}) were calculated according to Equations 5 – 7. These parameters afford estimation of change in the colour of the polymer after incorporating the natural AOs into the matrix of the polyester blend [181].

$$\Delta E = \sqrt{(\Delta a^2) + (\Delta b^2) + (\Delta L^2)} \quad (5)$$

$$W_i = 100 - \sqrt{a^2 + b^2 + (100 - L^2)} \quad (6)$$

$$C_{ab} = \sqrt{a^2 + b^2} \quad (7)$$

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared-attenuated total reflectance (FTIR-ATR) was employed to obtain spectra for all the polymer films (Nicolet iS5, Thermo Fisher Scientific, Waltham, USA). The unit was fitted a Ge crystal to determine structural alteration in chemical bonds under ageing conditions; it was set to the range of 600 – 4000 cm^{-1} and the resolution of 4 and 64 scans, with analysis in OMNIC software (Thermo Fisher Scientific, Waltham, USA).

Morphology

The cryo-fracture surfaces and the surfaces of the samples were gauged in a high vacuum environment at a test operating voltage of 10 kV by scanning electron microscopy. A Phenom Pro desktop scanning electron microscope (SEM) was employed for this purpose, fitted with a BSE detector (Phenom-World B.V., Eindhoven, Netherlands).

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

Materials and Reagents

Commercial PLA (Ingeo 2003D) from NatureWorks (Minnetonka, MN, USA) was deployed in the experiments. Halloysite (HNT) was purchased from Sigma-Aldrich (Germany). Tetrahydrofuran was obtained from Carl Roth Rotisolv® HPLC (Karlsruhe, Germany). The solvents acetone, methanol, acetic acid and ethanol (all analytical grade) were bought from PENTA s.r.o. (Prague, Czech Republic). Methanesulphonic acid (MSA, $\geq 95\%$), poly(acrylic acid) (PAA) 50% solution ($M_w = 2,000 \text{ g}\cdot\text{mol}^{-1}$) were supplied by Sigma Aldrich (Steinheim, Germany).

Synthesis of PLA-g-PAA

The procedure for polymer synthesis followed a method described by Kucharczyk *et al.* [180]. The process was performed as follows: 50 mL of L-LA was added to a 250 mL double-necked flask equipped with a Teflon stirrer. The flask was connected to a laboratory apparatus for distillation under reduced pressure and placed in an oil bath. Dehydration ensued afterwards in all instances (160°C , 200 mBar, 4 hours, 180 rpm). Once complete, the reactor was disconnected from the vacuum pump, and the appropriate amount (0.5 wt.%) of MSA and PAA (5 wt.%) were added dropwise under continuous stirring. After an hour, the pressure was lowered to 20 kPa (165°C ; with application of an oil pump) and water distilled out. An hour later the pressure was reduced to 1 kPa, and the reaction continued for a further 20 hours. The resulting product was allowed to cool down to room temperature and dissolved in acetone. The polymer solution obtained was precipitated into a mixture of chilled methanol and distilled water at the ratio of 1:10 (v/v) and filtered. Finally, the product was dried in an oven at 40°C for 48 hours. Table 4 summarizes the properties of the derived prepolymer in the form of a white powder.

Table 4. Characterization of the prepared additive PLA-g-PAA.

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

where M_w^a is the molecular weight and \mathcal{D}^b the polydispersity index ($\mathcal{D} = M_w/M_n$), as determined by gel permeation chromatography (GPC).

Preparation of samples

The PLA was dried at 60°C for 24 hours prior to being processed. Neat PLA and PLA composites were obtained by melt blending on a Brabender mixer (Plastograph® EC plus, Mixer 50EHT32, Duisburg, Germany). Samples were prepared under the following conditions: heat was applied at 190°C and the mixer set to an operating speed of 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 5.

Table 5. 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

Methods for characterizing the properties of the composite samples

The conditions for preparing the PLA-g-PAA additive via a direct polycondensation reaction were optimized through experimentation. Samples with various compositions were fabricated to discern improvement in the behaviour of the PLA modified with PLA-g-PAA and supplemented with HNT. The techniques described below were applied to select the best performing, optimized sample for the accelerated degradation experiment.

Gel Permeation Chromatography (GPC)

GPC analysis was conducted on a PL-GPC 220 chromatographic system (Agilent Technologies, Santa Clara, USA), equipped with dual detection system (refractive index and viscometric detectors). The samples were dissolved in THF (2 – 3 mg·ml⁻¹), stabilized with butylated hydroxytoluene (BHT) (125 ppm) and filtered by a syringe filter (0.45 µm). Separation was carried out on a series of gel-mixed bed columns (Polymer Laboratories Ltd., Amherst, UK), comprising 1 each of the following: a PLgel-Mixed-A bed column (300 × 7.8 mm, 20 µm), a PLgel-Mixed-B bed column (300 × 7.8 mm, 10 µm) and a PLgel-Mixed-D bed column (300 × 7.8 mm, 5 µm). The mobile phase contained the THF stabilized with BHT at 40°C, for which the flow rate of the mobile phase was set to 1.0

$\text{mL}\cdot\text{min}^{-1}$ and the injection volume equalled $100\ \mu\text{l}$. The GPC system was calibrated with polystyrene standards for molecular weight within the range of $580 - 6,000,000\ \text{g}\cdot\text{mol}^{-1}$ (Polymer Laboratories Ltd., Amherst, UK). The average molar mass (or molecular weight, M_w), number average molar mass (M_n) and polydispersity index ($\mathcal{D} = M_w/M_n$) of the tested samples were determined from peaks corresponding to the polymer fraction, in accordance with the universal calibration method. All data were processed in Cirrus software (Agilent Technologies, Santa Clara, CA, USA).

Scanning Electron Microscopy (SEM)

A Phenom Pro unit (Phenom-World BV, Eindhoven, Netherlands) was employed for SEM analysis, set to an electron accelerating voltage of 5 kV. Research focussed on the cryo-fractured parts of the neat PLA film and composites, with the aim of evaluating the degree of homogeneity and gaining insight into the internal structures of the composites.

Fourier transform infrared spectroscopy

The functional groups present in the thin polymeric films tested for robust degradation were determined by Fourier transform infrared spectroscopy (FTIR). A Nicolet iS5 unit (Thermo Fisher Scientific, Waltham, MA, USA) fitted with a Ge crystal was employed for this purpose. Analysis took place at ambient temperature and the settings of 64 scans, a resolution of 4 and measurement range of $600 - 4,000\ \text{cm}^{-1}$, with subsequent data processing in OMNIC software (Thermo Fisher Scientific, Waltham, MA, USA).

Differential Scanning Calorimetry (DSC)

The thermal properties of the materials were investigated on a DSC1 STAR System (Mettler Toledo AG, Analytical, Greinfensee, Schwerzenbach) under a nitrogen atmosphere ($50\ \text{ml}\cdot\text{min}^{-1}$). Samples of ca $8 - 10\ \text{mg}$ of material was testing in aluminium pans. Heating/cooling cycles occurred at the rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ and temperature range of $25 - 180\ ^\circ\text{C}$. The data obtained from the first heating cycle comprised the melting point temperature (T_m), region of glass transition temperature (T_g), melting enthalpy (ΔH_m) and the exothermic response to cold crystallization (T_c).

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out on a TGA Q500 device (TA Instruments, Wilmington, DE, USA) and analysed by a TA Universal Analyzer 2000 (version 4.5A, TA Instruments–Waters LLC, Wilmington, DE, USA). Samples of ca $10\ \text{mg}$ in weight were placed in a platinum pan and, following equilibration, exposed to temperatures ranging between 25°C and 600°C . Analysis took place in a nitrogen atmosphere, at the heating rate of 10

$\text{K}\cdot\text{min}^{-1}$ and constant flow rate of $100\text{ ml}\cdot\text{min}^{-1}$. A data set was calculated from the percentage of additives remaining in each tested film after processing.

Tensile testing

Mechanical properties were investigated on a universal tensile testing device, the M350-5 CT Materials Testing Machine (Testometric Company, Lancashire, UK). This was set to the crosshead speed of $10\text{ mm}\cdot\text{min}^{-1}$ in accordance with the standard EN ISO 527-3 [177]. Specimens with specific dimensions ($100 \times 10 \times 0.5\text{ mm}$) were cut from the various compression moulded films. Prior to testing, the samples were kept under the conditions of 22°C in temperature and 50% relative humidity for 48 hours. A minimum of eight specimens from each group were investigated.

Contact angles

Values for the contact angles of the neat PLA and their composites were determined on a Surface Energy Evaluation System (SEE System, Advex Instruments, Brno, Czech Republic). A set of seven samples was tested with three liquids (water, ethylene glycol and diiodomethane), drop of $5\text{ }\mu\text{l}$ in volume. Each contact angle was measured approximately a second after the drop had fallen from the micropipette. The free surface energy of the samples was gauged according to the Owen-Went model, and the arithmetic means of five measurements were calculated.

Abiotic Hydrolysis (TOC-L, GPC)

The rate of PLA hydrolysis was observed for 60 days at a steady temperature of 58°C . For this experiment the PLA film samples (50 mg) were cut into $0.5 \times 0.5\text{ cm}$ specimens and suspended in 50 ml of sodium phosphate buffer (Na-PB, $0.1\text{ mol}\cdot\text{l}^{-1}$, pH 7) amended with a microbial growth-inhibiting substance (NaN_3 , 0.2 wt.%). Testing was carried out in triplicate for each type of sample. The supernatants were analysed for dissolved organic carbon on a TOC-L Analyzer (Shimadzu, Kyoto, Japan). In parallel, at appropriate intervals, the materials were also evaluated by GPC. Three parallel measurements for each sample were performed.

Biodegradation under Composting Conditions

The composting test was performed according to ISO 14855-1:2012 [178], a standard applicable for determining the ultimate aerobic biodegradability of plastic materials. The amount of carbon dioxide (CO_2) released is measured, along with the degree of decomposition of the given material at the end of the assessment period. Study was made herein of the CO_2 released from PLA samples placed in a 500 ml reagent bottle equipped with septa mounted on the stoppers. In

addition to a sample (50 mg), each bottle contained natural compost (5 g of dry weight) and perlite (5 g). The flasks were incubated at 58°C for 48 days. Headspace gas was sampled at appropriate intervals through the septum with a gas tight syringe (100 µl), and then injected manually into a Agilent 7890 GC instrument (Agilent Technologies, Santa Clara, CA, USA) equipped with a Porapak Q (1.829 m length, 80/100 MESH) and 5A molecular sieve (1.829 m length, 60/80 MESH); the apparatus also comprised packed columns connected in series and a thermal conductivity detector (carrier gas helium, flow 53 ml·min⁻¹, column temperature 60°C). From the data gathered, it was possible to calculate the percentage of biodegradation, representing the theoretical quantity of CO₂ produced and the amount of oxygen consumed in each flask. From the CO₂ concentration thus determined, the percentage of mineralization related to the carbon content in the initial sample was calculated. The initial extent of carbon content in the samples was determined on a TOC-L Analyzer (SSM-5000A, Shimadzu, Kyoto, Japan).

Degradation kinetics

Komilis (2006) developed a first-order mathematical model based on Monod kinetics to describe the course of degradation of solid carbon into carbon dioxide under composting conditions (Eq. 8), which is also applicable for calculating hydrolysis kinetics [182]. Some modification to it was necessary to describe merely the first phase of the degradation process, i.e. the conversion of dry solid carbon to water-soluble transition carbon. The rate constant k_{aq} (day⁻¹), expressing the mineralization of water-soluble carbon into carbon dioxide, was excluded as a consequence (Eq. 9). The process for change in molecular weight (M_w) during abiotic hydrolysis was modelled via an existing first-order kinetics equation (Vieira et al., 2011). Equation 10 expresses an analytical solution for the model [183], [184], [185].

$$C_{T,t} = \left\{ C_{aq,0} \cdot (1 - e^{-k_{aq}(t-c)}) + \left[C_{h,0} \cdot \left(1 - \frac{k_{aq}}{k_{aq}-k_{hr}} e^{-k_{hr}(t-c)} + \frac{k_{hr}}{k_{aq}-k_{hr}} e^{-k_{aq}(t-c)} \right) \right] \right\} \quad (8)$$

$$C_{aq,t} = C_{aq,0} + C_{h,0} \cdot (1 - e^{-k_{hr}(t-c)}) \quad (9)$$

$$M_{w,t} = M_{w,0} \cdot e^{-ut} \quad (10)$$

Finding a solution to Equation 11 permits calculation of total CO₂ production (in per cent, $C_{T,t}$ or $C_{aq,t}$) at time t (days); $C_{aq,0}$ relates to the initial percentage of water-soluble carbon and $C_{h,0}$ the solid carbon content at the outset. The kinetic parameter k_{hr} (day⁻¹) represents the rate constant of first-order solid carbon

hydrolysis. Parameter c denotes the dwell time (in days) of the initial decomposition phase, prior to the commencement of CO₂ production [183], [185].

In the kinetics equation pertaining to mechanical degradation exerted by change in M_w , $M_{w,t}$ and $M_{w,0}$ constitute values for final and initial means of M_w at time t ($t = 0$). The rate constant for abiotic hydrolysis is denoted in the equation by the parameter u (day⁻¹).

The assumed mathematical constraints needed to derive a valid model are given below:

$$\begin{aligned} C_{C,0} &= C_{aq,0} + C_{h,0} \\ C_{C,final} &= C_{aq,final} + C_{h,final} \end{aligned} \quad (11)$$

All the parameters are positive

$$C_{h,t}, C_{aq,t} \text{ and } C_{T,t} = 0 \text{ for } t \leq c$$

where $C_{C,0}$ and C_C are percentages for the total and eventual initial carbon present [183], [185].

Evaluations of data from degradation processes were investigated by applying appropriate kinetic models. Parameters for all the models were optimized in the solver utility program of MS Excel, thereby minimizing the sum of squares of residues between the measured data and the interpolated values provided by the models. Their adequacy was compared by the coefficient of determination (R^2). An analytical solution pertaining to the proposed model was reported by Stloukal *et al.* [183].

Hydrolysis

Water-soluble carbon was observed during abiotic hydrolysis by TOC analysis and was recorded at the same time changes in the molecular weight (M_w) of the solid sample. The kinetic model for M_w describes the mechanism of random cleavage during hydrolysis. First-order kinetics were applied to discern M_w , wherein $C_{aq,0}$ (%) is the initial percentage of water-soluble carbon, $C_{h,0}$ (%) represents the initial content of hydrolyzable solid carbon, k_{hr} (day⁻¹) denotes the rate constant of first-order hydrolysis for the hydrolyzable solid carbon, and c is the duration of the lag phase (days) during the initial phase of biodegradation before the onset of CO₂ production. The rate constant k_{hr} was excluded for mineralization in an aqueous medium. The parameters for change in M_w in the aquatic environment are $M_{w,0}$ (g·mol⁻¹) is average initial weight at time $t = 0$ and u (day⁻¹) stands for the rate constant of abiotic hydrolysis.

Biodegradation

The kinetic model was adjusted according to the biodegradation conditions and evaluated from the amount of organic carbon released from the solid sample. The related parameters, wherein $C_{r,0}$ (%) represents the initial content of hydrolyzable

solid carbon and $C_{aq,0}$ (%) is the initial percentage of water-soluble carbon. The kinetic parameter k_{hr} (day^{-1}) represents the respective rate constant of first-order hydrolysis for the hydrolyzable solid carbon; k_{aq} (day^{-1}) expresses the rate constant for the mineralization (biodegradation) of water-soluble carbon to carbon dioxide; and c is the duration of the delay (days) in the initial phase of biodegradation prior to the commencement of CO_2 production.

Composting test

The experiment on the disintegration of samples under composting conditions was performed according to ISO 20200:2015 [186]. The plastic reactors were equipped with a composting medium mixed with water at the ratio of 45:55, the former comprising 40% sawdust (sourced from a local carpenter), 30% rabbit feed (Versele-Laga, Deinze, Belgie), 10% ripe compost (Central Composting Plant, Brno, Czech Republic), 10% corn starch (RUF Lebensmittelwerk KG, Essen, Germany), 5% sugar (Tereos TTD, České Meziříčí, Czech Republic), 4% sunflower oil (Bunge, Chesterfield, MO, USA) and 1% urea (Ing. Petr Švec – PENTA s.r.o., Prague, Czech Republic). Samples were prepared (25 mm x 25 mm, thickness ≤ 5 mm) and buried approximately 2 cm below the surface. The reactors (PP boxes, 9.0 x 26.0 x 19.5 cm) were placed in a climatic chamber (Climacell 440, BMT Medical Technology Ltd., Brno, Czech Republic) wherein conditions were set to 58 ± 2 °C and RH 80%. During the 45 days, which the test was performed, the reactors were weighed and the pH and temperature inside the reactor were measured, then more water was added. Some reactors were also set aside to be sampled for GPC and DSC analysis and photographs were taken. At the end of the test the composting media from the reactors were dried, sieved and the remaining content of polymer residue weighed. Determination was made of the ash present in the composting medium, and the quantities of C/N and elements stemming from the leachate were gauged by elemental analysis (TOC-L, Shimadzu, Kyoto, Japan) and EDX (ARL QuantX ED-XRF spectrometer, Thermo Scientific, Ecublens, Switzerland).

According to the stated standard, the degree of decomposition (D) is determined by the percentage of particles trapped on a 2 mm sieve, which are washed and dried to constant weight. Loss in weight is expressed according to Equation 12:

$$D(\%) = \left(\frac{m_i - m_r}{m_i} \right) \cdot 100 \quad (12)$$

where m_i corresponds to the initial dry weight of the samples, and m_r represents the dry weight of pieces of the samples obtained by sieving.

The test also requires the decrease in content of volatile solids (R) to be determined, relating to the difference in amounts of original synthetic waste and

compost obtained at the close, which has to equal or exceed 30%. R was calculated according to Equation 13:

$$R(\%) = \left[\frac{(m_i \cdot DM_i \cdot VS_i) - (m_f \cdot DM_f \cdot VS_f)}{(m_i \cdot DM_i \cdot VS_i)} \right] \cdot 100 \quad (13)$$

where m_i is the initial mass of the wet synthetic waste matrix, DM_i is the initial dry mass of the synthetic waste matrix and VS_i is the initial content of volatile solids in the synthetic waste matrix. M_f , DM_f and VS_f represent the final weight, dry weight and volatile solids of the compost, DM and VS are expressed as a percentage divided by 100.

Upon completion of the composting test, the extent of phytotoxicity was gauged to determine the properties of the compost for plant growth and development. An experiment was conducted to calculate the germination index (IK), wherein leachate from the compost was applied (1 ml) to filter paper in a Petri dish (diameter 5 cm) with a distribution of watercress seeds (*Lepidium sativum*). Incubation occurred at 28°C in the dark for 24 hours. Each sample was replicated and investigated 10 times (80 seeds in total), alongside a blank (distilled water). This phytotoxicity test of degraded samples in compost with watercress seeds was developed by the RIAE (Research Institute of Agricultural Engineering in Prague), where it is regularly carried out for analytical purposes [187].

$$IK(\%) = 100 \cdot \frac{k_v \cdot l_v}{k_k \cdot l_k} \quad (14)$$

Where k_v represents the germination of a watercress seedling (%) and k_k is the germination of the control plant (%), while l_v corresponds to the mean length of the roots of the watercress seedling (in mm) and l_k the mean length of the roots of the control specimen (in mm).

4. RESULTS AND DISCUSSION

The results given herein are presented in accordance with how topics appear in the chapters above. Each part summarizes research efforts relating to the introduction, results and discussion sections, and conclusions. The various findings originate from the entire period of the doctoral study, and have either been published in relevant professional journals or as contributions to projects detailed in patents or utility models.

The section is entitled as follows:

- Effect of an antioxidant based on red beetroot extract on the abiotic stability of polylactide and polycaprolactone
(published in *Molecules*, 2021, 26, 5190)
- Comparative degradation study of a biodegradable composite based on polylactide with halloysite nanotubes and a polyacrylic acid copolymer
(published in *Materials Today Communications*, 2022, 33, 104400)

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

Motivation

Beetroot (*Beta vulgaris* subsp. *vulgaris conditiva*) belongs to the family Chenopodiaceae and is an herbaceous, flowering, biennial plant. Its root is utilized as both a foodstuff and a source of a natural dye. Originating in the Middle East, numerous colour variations now exist globally [188]. The betacyanins and betaxanthins (betalains) present in it - heterocyclic, hydrophilic, nitrogen-based pigments - lend the tuber of the vegetable its characteristic colouring. Its earthy, mushy taste and aroma stem from geosmin, a volatile, bicyclic, tertiary alcohol. Other than the role it plays in the food industry, beetroot has recently been adopted in the production of biodegradable, edible, smart, active, intelligent packaging films. Beetroot (BR) extract in polymer films serves as a natural additive and alters certain properties (modulated physical, mechanical, functional, barrier and structural). The primary benefit is the antioxidant activity exhibited, caused by phenolic compounds, betanin, betacyanins and betaxanthins, which help scavenge free radicals and chelate metal ions [189], [190].

These bioactive compounds also help to combat bacterial contamination by fungi and mesophilic aerobic or anti-colloidal bacteria, aiding extension of the shelf life of a product. Besides these antibacterial and antioxidant properties, BR contains natural betacyanin (a red-purple pigment) that ranks alongside betaxanthins (yellow-orange pigments) as dyes of plant origin referred to as betalains, which change colour in reaction to pH. It is possible to apply substances such as synthetic or natural antimicrobial agents or antioxidants to packaging materials, e.g. nisin, chitosan, herbal essential oils, rosemary (*Rosmarinus officinalis*), oregano (*Origanum vulgare*), sage (*Salvia officinalis*), rose hips and medicinal and aromatic plants. Tocopherol (vitamin E) is the most common antioxidant, adopted by the food industry as a preservative and as a component in packaging materials, with the aim of prolonging the shelf life of packaged foods. A multitude of commercially available synthetic AOs have been developed, and limited amounts of them are deployed for packaging purposes, especially in active packaging; popular examples include BHA, BHT and TBHQ [191], [192], [193].

Furtherance in the production of plastic materials continues to be led by manufacturers of packaging for foodstuffs. Several polymers have proven suitable for this application, namely petroleum-based ones (PE, PS, PP and PET). While these possess physical and mechanical properties highly suited to this purpose, they have obvious drawbacks. Fossil fuel resources are unsustainable, their utilization exerts a carbon footprint, exacerbated by inadequate recycling practices, and such polymers do not biodegrade naturally. Therefore, efforts are being made to supersede them with suitable biodegradable alternatives. Starch

and cellulose constitute options in this regard, though PLA and PCL are common, widely applicable and possess favourable properties [192], [194].

A growing awareness exists amongst consumers about caring for the environment, stimulating the demand for biodegradable polymers. A clear preference for PLA has emerged, attracting attention for its short life cycle, transparency, high modulus and stiffness at room temperature, biocompatibility and non-toxicity. Unlike PET, which is similar in relation to certain properties, PLA requires only a small amount of energy for its manufacture, being derived biochemically from renewable sources like sugar, starch and cellulose [195], [196]. PCL is a biodegradable polyester with two stages of fabrication. Therein, carbohydrates are converted to ethanol and acetic acid by fermentation, followed by the transformation of ethanol into cyclohexanone by chromic acid, resulting in a product which undergoes Bayer-Villiger oxidation to give caprolactone [197], [198]. Hydrolysis of PLA and PCL occurs through the ester bonds. Unfortunately, these polymers are subject to premature and undesirable degradation processes, restricting their practicability. For example, abiotic factors arise under storage conditions, e.g. light, temperature, UV radiation and, notably, oxygen, which act synergistically with humidity. This affects the physical and chemical integrity of the materials, altering their mechanical, thermal, barrier and optical properties. Stabilizers and AOs are employed as countermeasures to prevent such abiotic processes. The function of an AO is to eliminate reactive oxygen and nitrogen species by providing hydrogen to them from a hydroxyl group [25], [199].

Natural antioxidants (e.g. carotenoids and betalains) are influenced by various conditions, not only storage, manifested by loss in colour caused by UV radiation and oxygen, and a subsequent reaction with peroxides and the chemical quenching of singlet oxygen [164].

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). PLA and PCL polymer composites were mixed with the stabilized AO, and subsequently characterized for their thermal, chemical and structural stability under abiotic conditions, especially UV radiation and temperature.

Results and discussion

Determination of antioxidant activity and polyphenol content in the extract of BR (BRE)

DPPH is a principal and common method for determining the antiradical activity of pure and mixed samples. The main attribute of an AO concerns the absorption of radicals, i.e. their ability to provide hydrogen. The reducing ability of DPPH radicals was determined spectrophotometrically at an absorbance of 517 nm, the result being indicated by the discolouration of the solution. Ascorbic acid was employed as a standard. Subsequent measurements revealed that the antioxidant activity of the BRE corresponded to 114 mg per the equivalent amount of 100 g of ascorbic acid. The value for such antioxidant activity by BRE, herein converted to the amount of ascorbic acid, is variously influenced by aspects relating to BR, e.g. the type of storage, the given conditions, the environment of its cultivation and the technique for preparing the extract. This explains the wide variance reported in the literature, i.e. from 20 to 170 mg (expressed in mg as the ascorbic acid equivalent per 100 g of BRE) [200], [201], [202].

The Folin–Ciocâlteu spectrophotometric method (FCM), also referred to as the Gallic acid equivalent (GAE), is normally used to assess the sum of phenolic compounds in plant extracts and juices. Gallic acid serves as the standard. Herein, the polyphenol content of the extract was quantified by FCM, an assay being performed for the entire BR bulb. The data obtained were evaluated in accordance with the prepared calibration series and application of the gallic acid standard. The extract was derived in 70% ethanol, which actually contained 93 mg (expressed in mg as the gallic acid equivalent per 100 g of BRE). The content of polyphenolic substances in the BRE reached similar values as those reported in the literature. The BRE remained stable during storage at low temperature (4–8 °C) in darkness for at least one month, without exhibiting any significant change in polyphenol content [203], [204].

Determination of AO by HPLC analysis of the BRE

Figure 13 shows a representative, total ion chromatogram (TIC) for the BRE determined by mass spectrometry in positive ion mode. Upon integration, the TIC exhibited several peaks evaluated as ms/ms fragmentation obtained as a consequence of collision-induced dissociation. 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 14, part A) stated in references [205], [206]. 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 14, part B) typical for betanin or isobetanin (2.61 minutes) [205], [206], [207]. 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). Provisional identification also revealed feruloyl glucose at 3.55 minutes ($[M+H]^+ = 357.1175$), 5,5',6,6'-tetrahydroxy-3,3'-biindolyl at 3.74 minutes ($[M+H]^+ = 297.0874$), betavulgarin at 5.35 minutes ($[M+H]^+ = 313.0704$) and cochliophilin A at 6.23 minutes ($[M+H]^+ = 283.0604$) [205], [206].

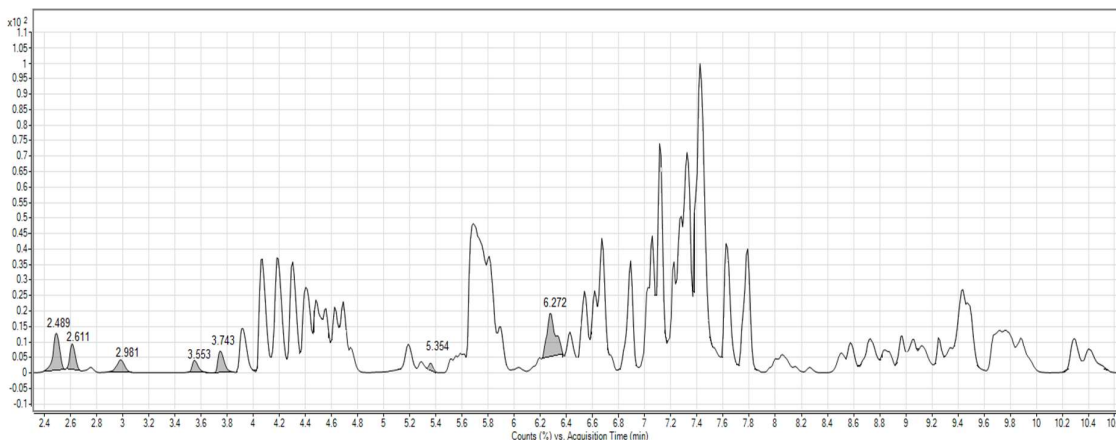


Figure 13. Representative TIC of the diluted BRE; the retention times were attributed by mass spectrometry analysis.

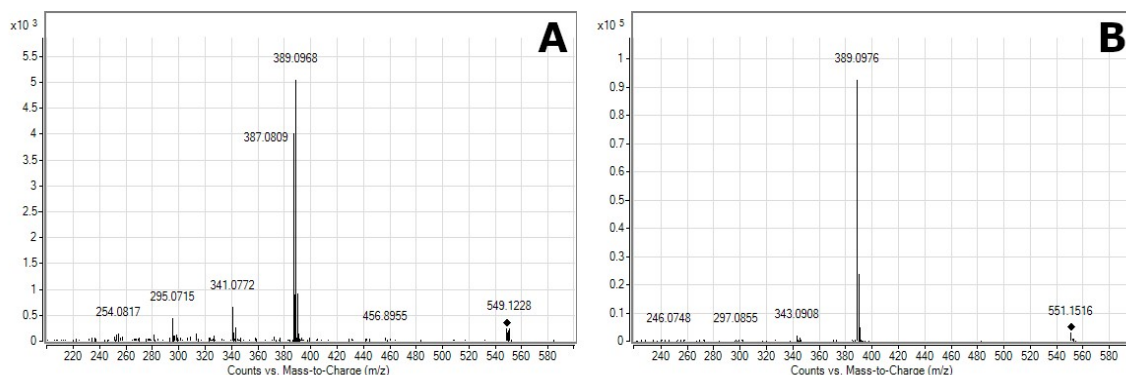


Figure 14. Positive electrospray tandem mass spectra for (A) neobetainin and (B) betainin or isobetainin.

Thermal analysis

Incorporating an inorganic filler in the polymers and introducing a polyphenol, such as an AO, has the capacity for altering a multitude of properties, an example being thermal stability. DSC and TGA analyses were conducted to gauge the thermal properties of the prepared PLA and PCL samples with natural BRE anchored on bentonite (BE); comparison was made to neat polymers and samples without BRE, concurrently. The effects exerted by artificial ageing in a UV chamber were monitored for 720 hours. Significant changes were observed in the T_g of the PLA samples and its composites (see Table 6). As a result of accelerated

ageing, a clearly noticeable decrease in T_g values was observed for the neat PLA sample, potentially caused by two phenomena. Firstly, low-molecular-weight compounds may have formed new macromolecules in the process of degradation, giving rise to plasticizing properties and lowering the glass transition temperature of the polymeric materials. Secondly, the macromolecules could have been shortened by breaking the polymer backbone. Short macromolecules are known to have low glass transition temperatures and encourage a plasticizing effect. The ageing experiment for the semi-crystalline PCL revealed that it was not possible to technically compare the glass transitions of the materials (-60°C). Analysis of the PCL samples permitted evaluation of data on T_m , with the neat PCL and PCL-BE samples showing two melting peaks (Table 7). The absolute values for cold crystallization and enthalpy of melting of these samples were virtually identical, since ageing PCL often exhibits double-melting behaviour, i.e. a stable melting structure at high temperatures and a less stable melting structure at lower ones [208].

Table 6. DSC data for the neat PLA and PLA composites with bentonite and AO before and after the UV ageing test.

Sample	T_g [$^\circ\text{C}$]	T_m [$^\circ\text{C}$]	ΔH_m [J/g]	T_{onset} [$^\circ\text{C}$]	T_{peak} [$^\circ\text{C}$]	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	-	-

Table 7. DSC data for the neat PCL and PCL composites with bentonite and AO before and after the UV ageing test.

Sample	T_{m1} [$^\circ\text{C}$]	T_{m2} [$^\circ\text{C}$]	T_{cc} [$^\circ\text{C}$]	ΔH_{cc} [J/g]	ΔH_m [J/g]	T_{onset} [$^\circ\text{C}$]	T_{peak} [$^\circ\text{C}$]	ΔH [J/g]
PCL	65	-	34	2.7	88.3	245	312	3168
PCL-BE	65	-	34	2.5	86.4	240	314	2254
PCL-BRE	66	-	35	2.7	90.1	236	281	1157
PCL-UV	39	66	26	2.6	91.5	215	286	254
PCL-BE-UV	38	64	36	2.8	99.2	216	288	307
PCL-BRE-UV	-	64	30	1.4	92.5	208	265	143

Visible changes were observed merely in T_{peak} thermal stability values in the presence of oxygen. DSC analysis showed that samples with the carrier (bentonite) and carrier with AO exhibited faster thermal degradation than those

containing the pure polymers. The primary difference between the polymers was the notably low internal enthalpy (ΔH) of the PCL samples (1157 J/g). Figure 16 and Table 7 illustrate that the thermal degradation of the PCL-BRE samples was slower than for the PCL samples. In the case of PCL-BRE, the antidegradant ceased to act as a disruptor of the chain autooxidation reaction, causing the formation of free radicals from the macromolecular chain. The thermal decomposition of polymers can be caused by various factors, primarily factors such as temperature, humidity, UV and the presence of oxygen. Another important aspect is the formation of free radicals, which affect thermal stability. The thermal degradation of polymers is considered an inevitable effect under normal conditions, e.g. in melt processing. Such degradation can be prevented or slowed down by adding an inorganic filler or AO, a phenomenon more pronounced for the given PCL samples [209], [210].

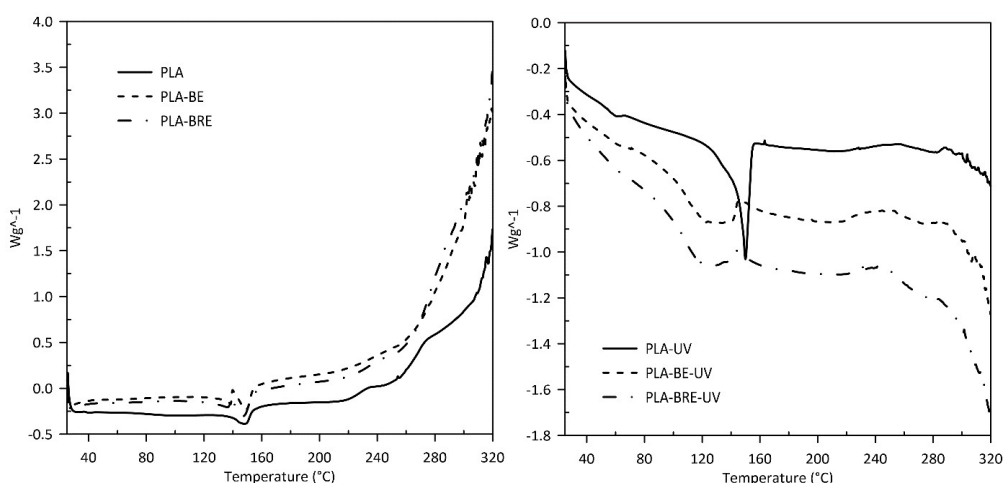


Figure 15. DSC degradation test for the PLA samples under an oxygen atmosphere.

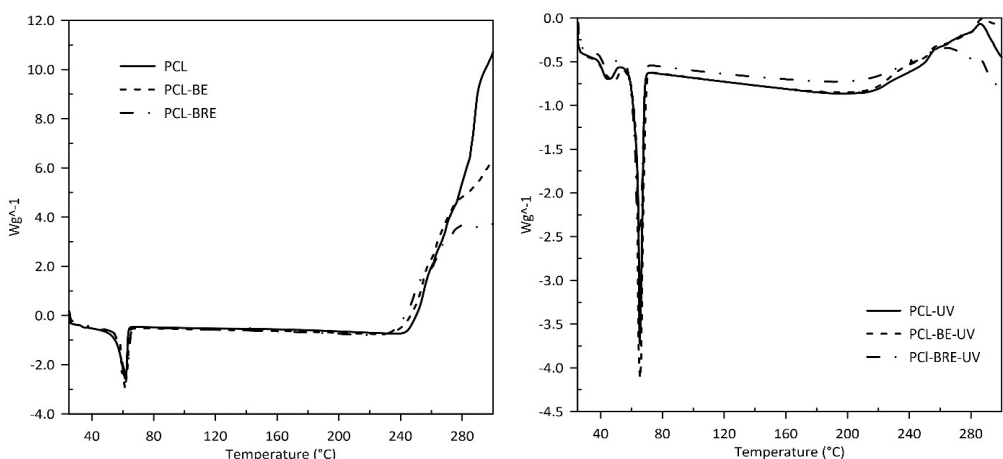


Figure 16. DSC degradation test for the PCL samples under an oxygen atmosphere.

Regarding the results of TGA analysis, the respective curves highlight that an influence was exerted by solar ageing on the stability of the PLA and PCL with additives. The PLA curves of the samples depicted in Figure 17 begin with the normal, initial release of moisture and volatiles. This is followed by thermal degradation, with a faster course in neat PLA. Upon ageing in the UV chamber, the T_{onset} of neat PLA is higher (354°C) than for its composites (343°C and 347°C), although the degradation process itself is slower. This is especially evident for the PLA-BRE-UV sample, as the temperature at point T_{10} starts at 175°C , indicating a slower mass loss (see Table 8). The TGA curves in Figure 18 describe the degradation of the PCL materials. The effect of bentonite is obvious, reducing the temperatures of the degradation rate for PCL-BE-UV to 367°C and PCL-BRE-UV to 360°C , with that for PCL-UV at 335°C . However, the influence of the AO on this sample cannot be demonstrably claimed from this method [211], [212].

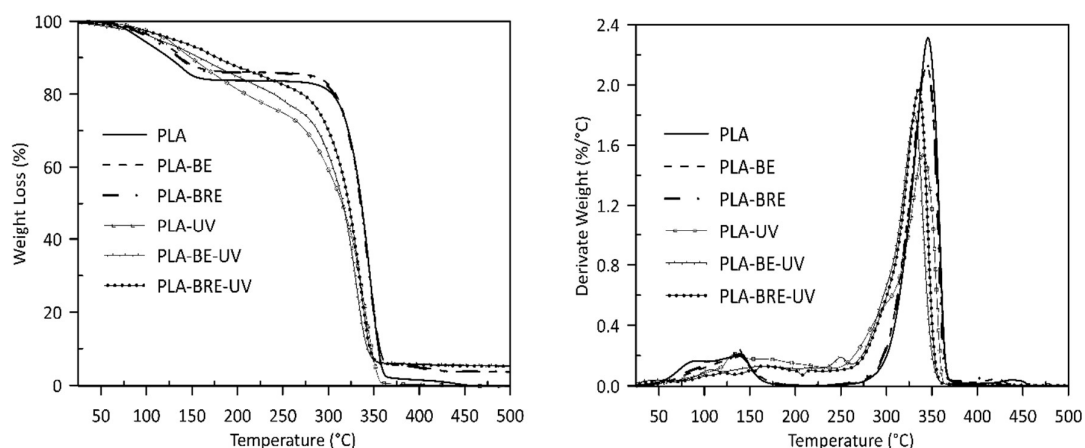


Figure 17. Thermogravimetric response of PLA-bentonite with the AO alongside reference samples.

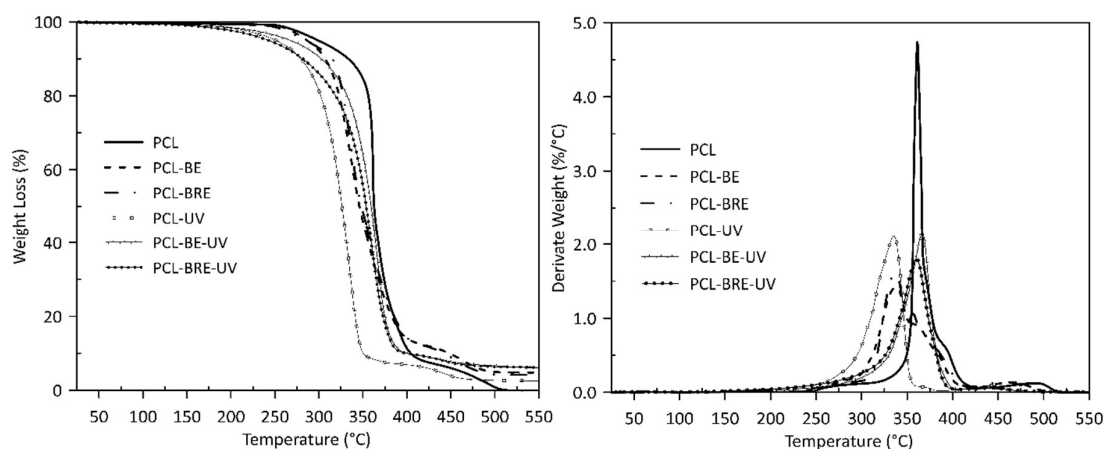


Figure 18. Thermogravimetric response of PCL-bentonite with the AO alongside reference samples.

Table 8. 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

Mechanical properties

The mechanical properties of the PLA, PCL and their composites were observed prior to and following the artificial ageing test. The first of the parameters was monitored by applying Young's modulus (Figure 19). Increase in this parameter 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. This difference was less significant in the PCL samples since a slight photodegradation process occurred. The point of maximum stress of the materials was also researched (Figure 20). A slight increase in this parameter was observed for the composites

with bentonite, as the latter acted as a nucleating agent. Another important parameter concerned elongation at break (Table 9). For the PLA- and PCL-based systems, adding a natural AO heightened the elastic modulus. The slight rise in elongation at break in all the AO-supplemented systems was attributed to a plasticizing effect initiated by stabilization of the molecules. It is known that low-molecular-weight molecules dispersed in polymer matrices have the capacity to further the free volume of the system and reduce friction between the macromolecules.

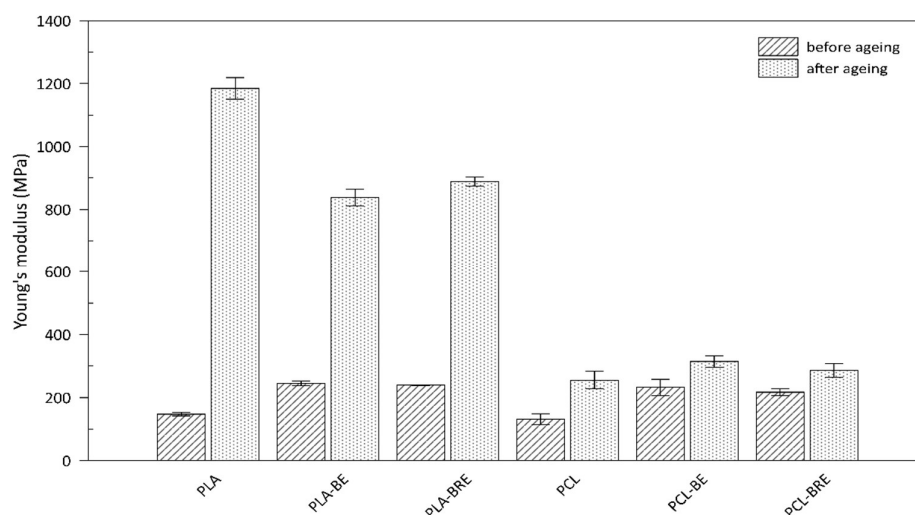


Figure 19. Mechanical properties of the PLA and PCL samples as per Young's modulus.

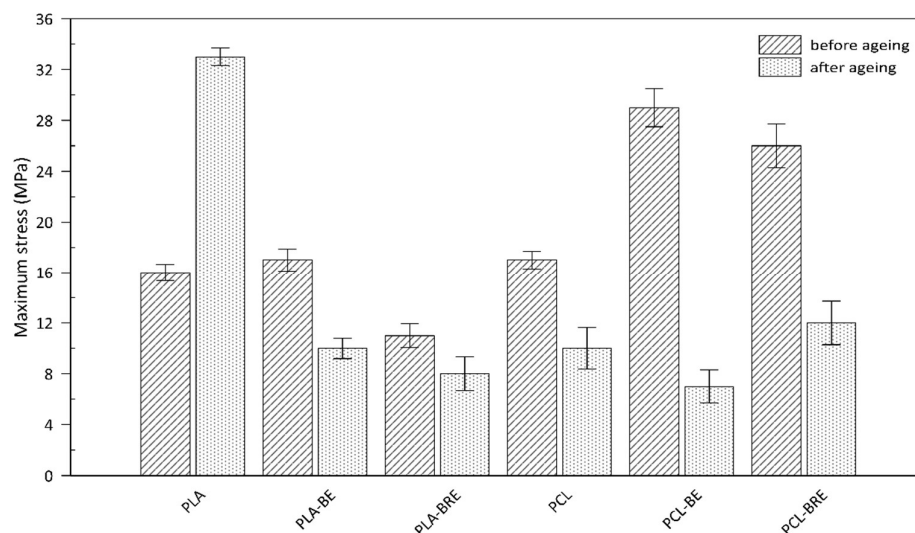


Figure 20. Mechanical properties of the PLA and PCL samples as per maximum stress.

According to the results in Table 9 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 ageing factor. This study demonstrated the limited effect of the natural AO derived from BR. In this regard, BRE proved capable of reducing the amount of synthetic AO in the degradable polymer formulations, especially those based on PCL. The literature states that hydrolytic degradation of the chains in PLA takes place primarily on the surface and preferably in amorphous regions [212], [213].

Table 9. Comparison of the mechanical properties of the PLA and PCL composites prior to and following ageing; the ageing factor (A_f) was calculated according to Equation 4.

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

Colour measurement

As mentioned above, a polymer is influenced by numerous factors that aid degradation and affect its properties. In the case of smart packaging, dyes are used to visualize such changes, indicating alterations related to the freshness of the foodstuffs and in the properties of the polymer. The overall appearance is thus affected and an associated effect made on consumers. In particular, UV light can trigger undesirable photooxidation processes, bringing about either potentially rapid loss in quality or deterioration in the packaged foods. This could occur during transport and storage, ultimately giving rise to unwanted deviation from the original colour [214]. In this context, it is important to investigate the effect of the additives on the various properties of the materials. The results presented herein reveal the influences of the given additives (natural bentonite and extract additives) on the biopolymers (Figures 21, 22).

The natural phenomenon of ageing is manifested through change in hue, as visible in every film tested herein. In the case of the neat matrices, the alteration was from transparent PLA and milky white PCL to a shade of yellow. In the PLA films, the most pronounced shift in hue was demonstrated by the sample containing merely bentonite. The colour change index (ΔE) for this specimen was 29, i.e. the same value as for the neat PCL sample (Figure 21). In contrast, the lowest values were evident for the samples with BRE, the colour change index

equalling 17 in both instances. During the ageing test, a significant alteration became apparent in the chroma (C_{ab}) of the biopolymer samples supplemented with bentonite only. The whiteness index (W_i) increased in all the samples, which in the PLA materials pertained to a shift in their transparency, and a slight haze appeared during the ageing experiment. For these reasons, incorporating such natural dyes into the polymers would permit a visual indication as to the degree of degradation and even afford them the potential to serve as indicators (Figure 22).

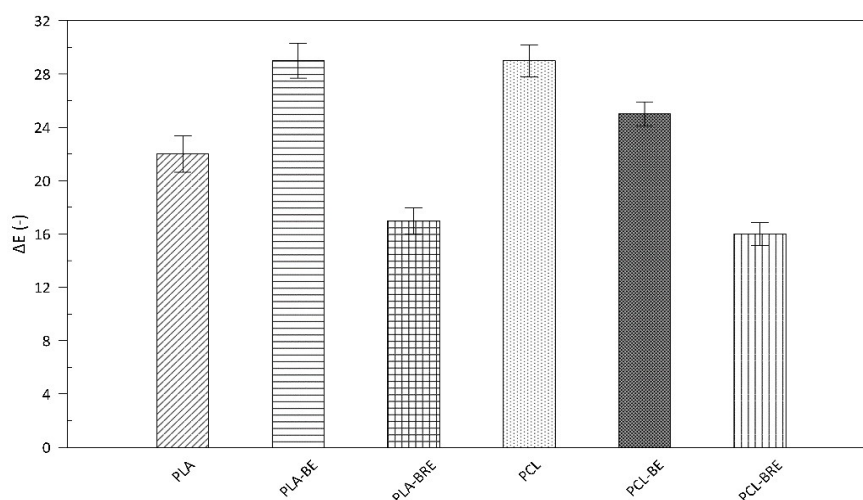


Figure 21. Colour change (ΔE) in the PLA and PCL composites with bentonite and the natural AOs, in comparison with the references of neat PLA and PCL; calculations were performed according to Equation 5.

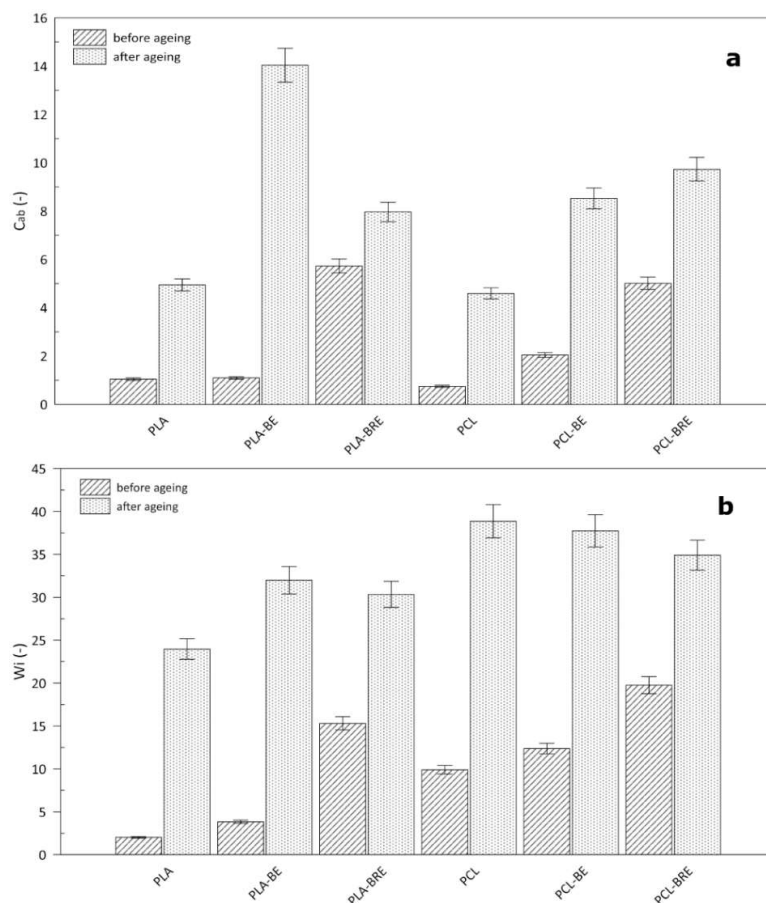


Figure 22. Impact of solar ageing on (a) the chroma (C_{ab}) and (b) whiteness index (W_i); calculations were performed according to Equations 6 and 7.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was carried out to record certain changes, mainly in chemical structure, as this is affected when polymeric PLA and PCL films age. Figure 23 shows the spectra for PLA before and after UV exposure. As regards the PLA and its composites, changes occurred through exposure to UV radiation, evident in alteration in the intensities of characteristic peaks, such as at 1756 cm^{-1} , corresponding to (C = O) carbonyl groups. The ether groups (C-O-C) of PLA in the bands at 1088 cm^{-1} and 1183 cm^{-1} also proved sensitive to UV ageing. A peak was additionally formed in the PLA-UV sample in the region of 1654 cm^{-1} , indicating the formation of anhydride groups during degradation. In conclusion, the samples of neat PLA demonstrated a significant decrease in their characteristic bands instigated mainly through photodegradation, though thermal degradation of the polymer structure might have played a contributory role [215], [216].

In the case of the PCL films (Fig. 24), the main characteristic peaks appear primarily in the regions of 2865 cm^{-1} and 2945 cm^{-1} , which represents a symmetrical and asymmetrical expansion of the -OH groups. A peak at 1724 cm^{-1}

¹ pertains to carbonyl ester vibrations, while C-O-C bands are denoted by peaks at 1187 cm^{-1} and 1241 cm^{-1} . Degradation was observed after exposing the PCL samples to the UV chamber, resulting in increased peaks for the carbonyl groups and indicating the formation of radicals in the PCL macromolecules. In the instance of PCL-UV, the main peak widened to 1724 cm^{-1} . All the samples exhibited partial degradation, affected somewhat by the higher temperature of the UV chamber. Relatively demanding conditions were set for the materials over a relatively long period of time, hence it was not possible to directly discern the clear influence of the AO under the circumstances [217], [218].

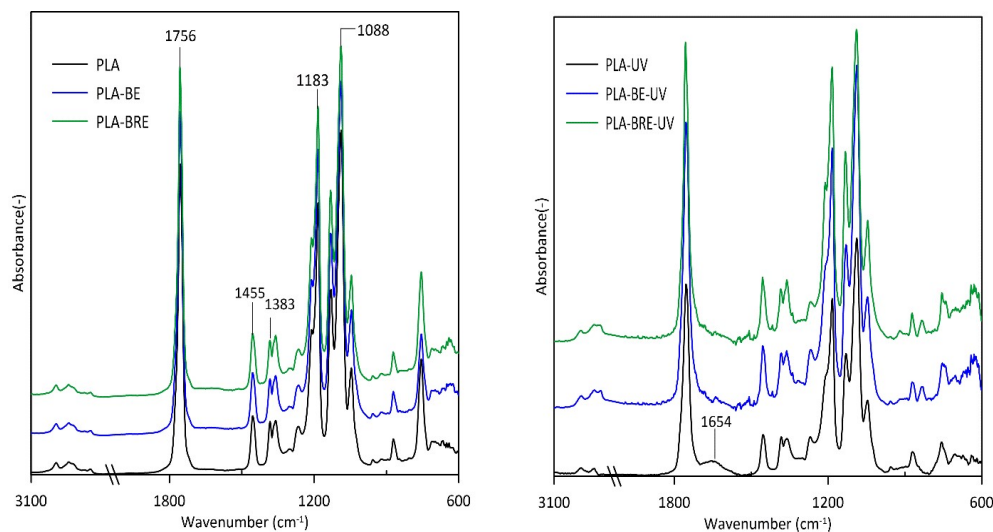


Figure 23. FTIR spectra for the PLA and PLA composite films prior to and following exposure in a UV chamber.

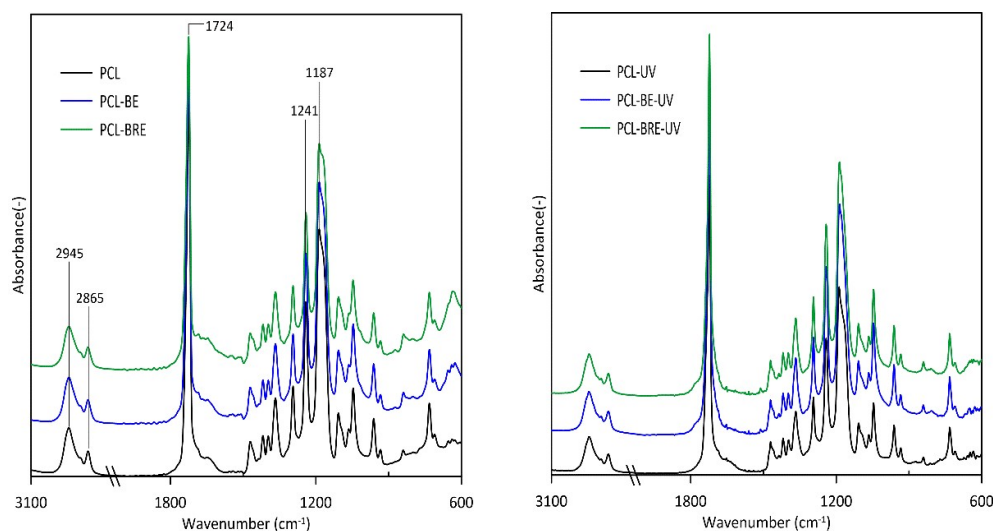


Figure 24. FTIR spectra for the PCL and PCL composite films prior to and following exposure in a UV chamber.

Scanning Electron Microscopy (SEM)

This optical method with mobile electron beam imaging was used to obtain images of the refractive surfaces of the PLA and PCL samples (Figure 25 and 26; A–F), taken before and after exposure in the UV chamber, as well as the surfaces of the samples after the UV chamber (G–I). This facilitated detailed observation of the influence of the UV chamber environment on both materials. Thus, it was possible to recognize stratification in the films and the homogeneity of the filler present in the PLA, PCL and their composites.

The degradation process was evidently underway after four weeks in the UV chamber, with cracks, cavities and flaking fragments visible in the materials. 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.

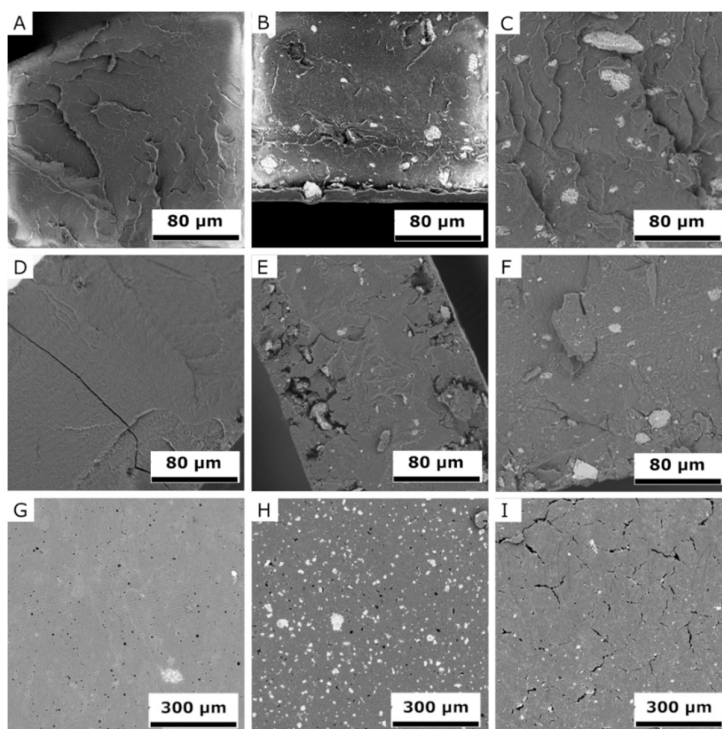


Figure 25. SEM images detailing change in the PLA samples prior to and following exposure in a UV chamber, comprising the fracture surfaces of samples (A) PLA; (B) PLA-BE; (C) PLA-BRE; (D) PLA-UV; (E) PLA-BE-UV; and (F) PLA-BRE-UV; and the surfaces of the samples (G) PLA-UV; (H) PLA-BE-UV; and (I) PLA-BRE-UV.

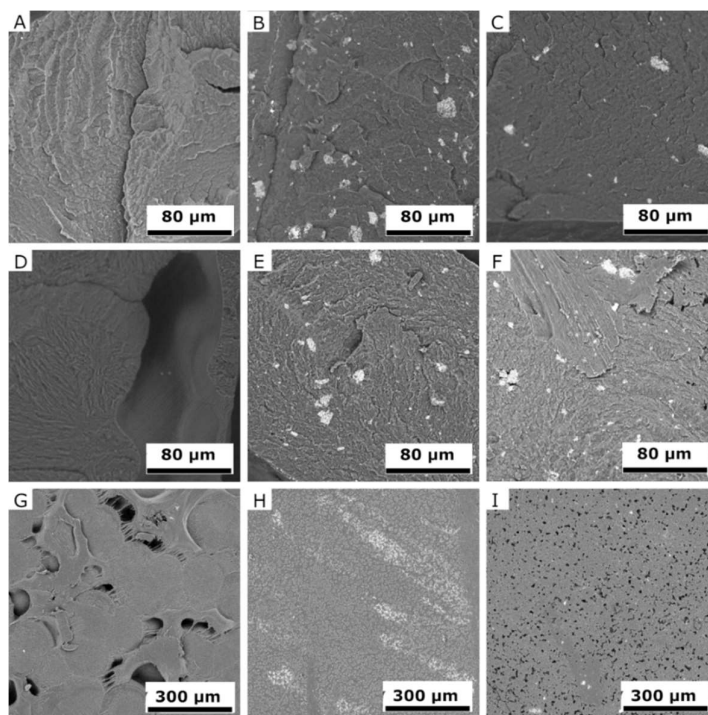


Figure 26. SEM images detailing change in the PCL samples prior to and following exposure in a UV chamber, comprising the fracture surfaces of samples (A) PCL; (B) PCL-BE; (C) PCL-BRE; (D) PCL-UV; (E) PCL-BE-UV; and (F) PCL-BRE-UV; and the surfaces of samples (G) PCL-UV; (H) PCL-BE-UV; and (I) PCL-BRE-UV.

Conclusions

A heightened interest is discernible in the adoption of alternative polymeric materials that are environmentally-friendly. Another trend concerns incorporating natural additives in such polymers without exerting any impact on their overall concept and integrity. Accessible, inexpensive fillers and additives are needed that would be applicable for the foodstuffs and packaging industries, for example. Research focused on designing a simple method for preparing biodegradable polymers, namely polylactide (PLA) and polycaprolactone (PCL), filled with a natural ingredient with antioxidant and colouring effects. Emphasis was placed on superior incorporation of BRE in polymer films for extended AO efficiency. The effect of the AO additive was demonstrated during experiments, manifested by reduced colour change, which was detected by spectrophotometry. Determining the thermal stability of the samples by DSC analysis revealed that the BRE in the PLA sample neither affected T_g after being aged in the UV chamber, nor reduced the onset of degradation in an oxygen atmosphere. In relation to TGA, the thermal degradation of the PLA-BRE sample commenced at a higher temperature (175°C) prior to and following exposure to UV. The PCL sample supplemented with the AO component exhibited stable intrinsic enthalpy,

as confirmed by DSC. Mechanical tests detected the effect of bentonite on the brittleness of the material. wherein the filler-free samples showed high values for Young's modulus after ageing; for neat PLA and PCL, the increase was 90% and 50%, respectively. However, bentonite diminished the total strength of the specimens during a stretching test. The elongation at break indicated a possible antioxidant effect for the PCL sample, which equated to 375% compared to the others at ca 10%. The presented findings suggest that the additive derived from beetroot shows potential as a natural antioxidant capable of increasing thermal stability and colour fastness in packaging materials, as required in the food industry and elsewhere.

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

Motivation

Biodegradable polymer-based materials have the potential to replace the current range of mainstream, petroleum-based plastics, thereby contributing to reduction in the amount of plastic waste generated. The best known biopolymer presently deployed by manufacturers is PLA, since it possesses unique properties such as biocompatibility and biodegradability, and breaks down into the final decomposition products of CO₂ and H₂O. It also has similar properties to PS, although PLA is produced from agricultural raw materials [219]. Drawbacks exist, however, that hinder further adoption, e.g. high production costs and slow degradation. Regardless of the future commercial use of PLA various areas, it shall become paramount to tackle the environmental burden will eventually be considered due to the slow rate of degradation of many products that do not allow chemical recycling [171]. Consequently, it is necessary to improve the development and application of PLA in connection with raising its performance and accelerating its degradation. The rate of degradation processes in the composting medium should be comparable to the rate of other forms of biodegradable matter, and no residues should be apparent [220], [221].

The rate of PLA degradation depends on many aspects, an example being molecular weight, as low-molecular-weight polymers degrade faster than high-molecular-weight ones. Abiotic factors (e.g. mechanical, light, thermal and chemical substances) also influence the initiation of the biodegradation process [222]. Temperature is crucial, since it significantly accelerates degradation in parallel with high humidity. The optimal temperature for PLA is 58°C, which is identical to its glass transition temperature. During this process, high-molecular-weight chain fragments decompose, then shorter fragments are further digested and mineralized by microorganisms into essential elements [103], [222]. However, this phase lasts several days compared to a normal composting process, resulting in insufficient depolymerization of the chains of the given material. The ability to accelerate depolymerization during composting is reasonable, i.e. to reduce the time required for biodegradation to ensure compatibility of the material with surrounding organic by-products.

Several approaches can be used to treat PLA to promote biodegradation and significantly alter the rate of hydrolysis. Examples include copolymerization [223] and grafting various monomers onto polymer chains [224], [225], blending PLA with extremely biodegradable additives and modifying properties such as crystallinity [226]. Nevertheless, improving the biodegradability of PLA could lead to unintended deterioration in the properties of the material (e.g. mechanical, thermal stability and transparency) [227]. Nanocomposites and multiphase

materials made up of two or more parts constitute suitable options for adjusting the initial characteristics of PLA [228]. For instance, deploying certain nanoparticles affects the mechanical properties of PLA and, dramatically, its biodegradation behaviour. Clays, zinc oxide, TiO₂, graphene oxide, metal oxides and natural polymers such as chitosan and nanocellulose are known to accelerate the decomposition of PLA. The development of PLA-based nanocomposites often involves a trade-off between the performance of such composites and their degradability at the end of their life cycle. They improve selected properties of a given biopolymer, in terms of strength and heat resistance, while also lending stability to the structure. This is because incorporating a nanofiller leads to the formation of effective interfacial hydrogen bonds between the components. Another advantage of nanofillers is their low cost [103].

A well-known form of nanoclay, halloysite nanotubes (HNT) show real potential since they are non-toxic in nature, biocompatible and dispersible. They also have a high cation-exchange capacity, hence the formation of hydrogen bonds is likely, arising through the hydrogen atoms in the PLA interacting with oxygen atoms in the HNT [195], [229]. This marks the material out as a particularly suitable additive for the biopolymers of PLA and PLA-g-PAA (polylactic acid)/poly(acrylic acid). It also disperses well in a matrix, which is crucial for optimizing the properties of a nanocomposite film. The additive in PLA-g-PAA facilitates superior dispersion in the matrix, thereby enhancing the properties of the nanocomposite film. It also helps to accelerate the biodegradation of PLA during hydrolysis, caused by enrichment of the PLA matrix by ester groups. These groups are the first to be released and help convert oligomers to monomers [103], [185].

The characteristics of the PLA biopolymers are affected by the dispersion of an HNT nanofiller in their matrices, the chemical bonds between them and the mean molecular weights of the resulting materials, which in this regard could be achieved by suitable concentration of both chosen fillers. Although the influence exerted by HNT on the properties of PLA has previously been investigated by researchers, the emphasis was on specific characteristics, so a more detailed and thorough investigation was absent [228]. Indeed, an accelerated degradation experiment has never been published that addresses the effect of the environment of a municipal composting facility on PLA-g-PAA/HNT nanocomposites [230]. The authors believed it necessary to fill the gap in knowledge on effective nanocomposite PLA-g-PAA/HNT films by researching the topic in connection with different environments, including data processing and the application of kinetic models.

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.

Results and discussion

Surface morphology of the PLA and modified nanocomposite films

Figure 27 illustrates the surfaces and fracture surfaces of the PLA (a, a'), modified films (b, b' – g, g') and HNT (h). The surfaces of all samples are very similar to each other. The presence of additives was observed in the fractured cross-sections. The HNT nanoparticles were observed as white particles in Figure 27 b', c', e', f', as highlighted by the blue arrows. These white spots are absent from Figure 27 a' for neat PLA and in Figure 27 d' and g' merely for the PLA-g-PAA variant (without HNT). Despite the presence of the additives in the PLA matrix, even at higher concentrations, the surfaces of the film samples remain smooth and crack-free, indicating good homogeneous dispersion enabled by significant interaction between the components. The structure of the HNT provides negatively charged oxygen atoms that interact with positively charged PLA hydrogen atoms via hydrogen bonds. Similarly, hydrogen bonds are also formed between the siloxane groups in the HNT and the hydroxyl groups of the PLA. 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 [230]. 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 [185].

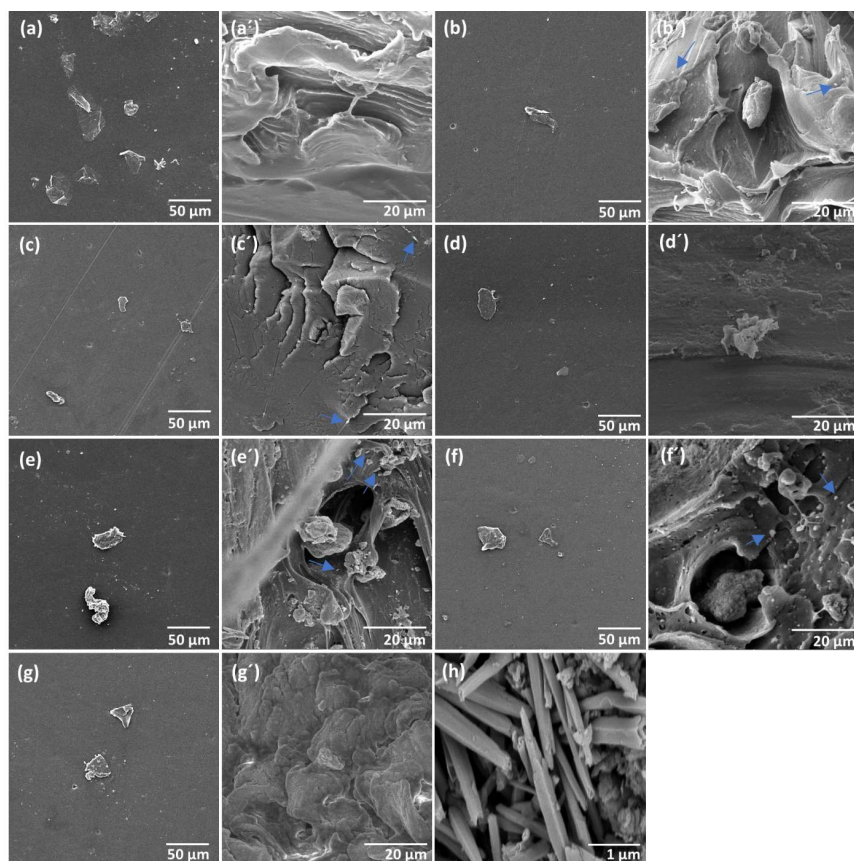


Figure 27. Electron micrographs of the surfaces and fractured surfaces of the thin films: (a, a') PLA; (b, b') PLA/5H; (c, c') PLA/5H/20PLA-g-PAA; (d, d') PLA/5PLA-g-PAA; (e, e') PLA/20H; (f, f') PLA/20H/20PLA-g-PAA; (g, g') PLA/20PLA-g-PAA; and (h) HNT; (blue arrows indicate HNT particles).

FTIR spectra for powders of the neat PLA, HNT, PLA-g-PAA and modified films

The FTIR plots in Figure 28a depict separate spectra for the PLA matrix and the additives in order to facilitate the identification of functional groups. Characteristic absorption bands of the HNT filler appear at 3695 cm^{-1} and 3624 cm^{-1} , indicating the stretching vibration of the O–H bond with aluminium and implying internal and surface stretching. The IR bands at 1029 cm^{-1} and 912 cm^{-1} correspond to the symmetric stretching of the Si–O–Si bond and the bending vibrations of Al–OH. The peaks observed at 1008 cm^{-1} are formed by absorption/in-plane stretching of Si–O in the HNTs [230]. The slight humps at 1117 cm^{-1} , 793 cm^{-1} and 746 cm^{-1} are caused by in-plane Si–O stretching, Si–O–Si symmetrical stretching and Si–O–Al perpendicular stretching, respectively [231].

The spectra in Figure 28a for the PLA-g-PAA powder and neat PLA look similar, with a clearly visible broad peak starting at 1720 cm^{-1} , attributed to an

increase in the concentration of $-\text{COOH}$ and a parallel rise in the amount of PAA. The PAA signals, i.e. $-\text{CH}$ and $-\text{CH}_2$, essentially overlap others from this part of the PLA polymer, otherwise there no significant qualitative changes are apparent in the spectra [232].

The characteristic peaks observed for PLA at 1756 cm^{-1} , 1269 cm^{-1} and 754 cm^{-1} for $-\text{C}=\text{O}$ relate to its strength vibration, bending vibration and torsion vibration, respectively. The peak located at 955 cm^{-1} corresponds to the $\text{C}-\text{C}$ group, while the spikes at 1132 cm^{-1} , 1045 cm^{-1} and 869 cm^{-1} belong to $\text{C}-\text{O}-\text{C}$ groups for strength vibration. The peak at 1454 cm^{-1} signifies $-\text{CH}_3$ bending, whereas those expressing symmetrical and asymmetrical strength vibrations of the $-\text{CH}$ bond are indicated at 1360 cm^{-1} and 1383 cm^{-1} [233]. For the PLA/HNT films, a shift in the lower wavenumber from 1756 cm^{-1} to 1752 cm^{-1} for the $-\text{C}=\text{O}$ bond is visible, owing to strong interactions between the hydroxyl groups of the HNT and carbonyl groups of PLA [234].

Adding HNT into the PLA triggered a rise in intensity to 1045 cm^{-1} for the PLA/HNT films, resulting from the overlapping of shifted peaks for the HNT at 1029 cm^{-1} and 1008 cm^{-1} (see Figure 28b). The peaks at 869 cm^{-1} and 754 cm^{-1} pertain to amorphous and crystalline regions present in the PLA [230].

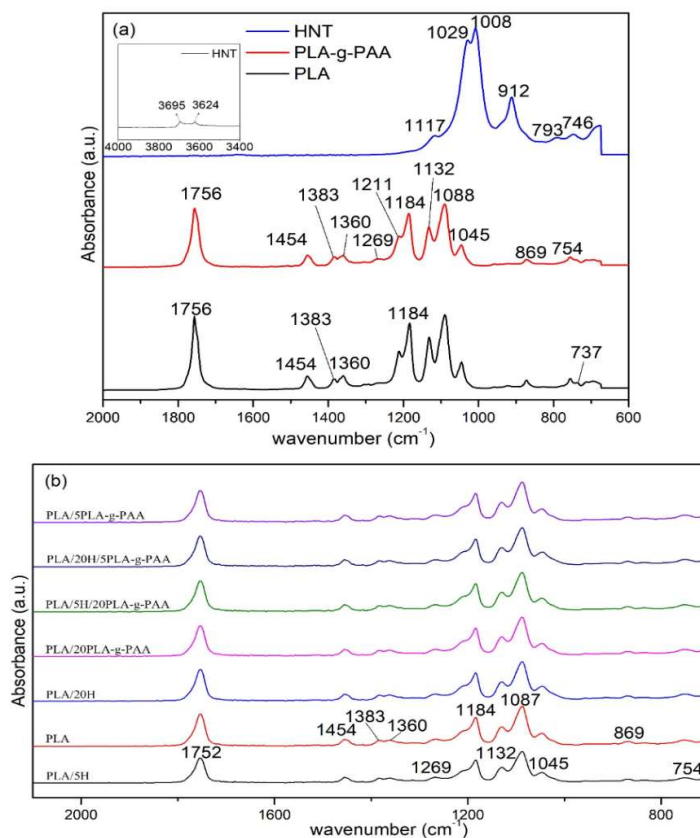


Figure 28. FTIR spectra for attenuated total reflectance (ATR) samples of PLA, PLA-g-PAA and HNTs in (a) powdered form and (b) as pristine PLA and modified films.

TGA

The thermogravimetric properties of thermal decomposition in an inert atmosphere (nitrogen) are given in Table 10. The main parameters that characterize the thermal stability of the PLA samples and composite specimens with the HNT and PLA-g-PAA additives comprise temperatures for degradation onset (T_{onset}) and maximum degradation (T_{max}). The former, T_{onset} , was affected by increase in HNT concentration, dropping by up to 8% (in the case of 20 wt.%), alongside a significant reduction in the degradation maximum by up to 9% (30°C). This decrease in thermal stability was attributed to the catalytic role of the HNT on the pyrolysis of PLA, with the existence of Si-OH and Al-OH acidic sites on the outer surfaces of the HNT nanoparticles [235]. The thermal stability of samples containing lower percentages of PLA-g-PAA was not notably influenced. Although a drop in thermal stability was evident, no corresponding dip in temperature occurred that would disrupt or interfere with the thermal processing of the PLA matrix.

Table 10. Effects of the copolymer and nanofiller on thermal stability.

Sample	T_{onset} (°C)	T_{max} (°C)	Mass loss (%)
PLA	317	350	100
PLA/5H	301	332	94
PLA/20H	293	319	78
PLA/5PLA-g-PAA	313	348	100
PLA/20PLA-g-PAA	311	342	100
PLA/20H/5PLA-g-PAA	298	321	82
PLA/5H/20PLA-g-PAA	299	331	94

Mechanical testing

Table 11 shows the Young's modulus (E), elongation at break (ϵ) and tensile strength (σ) of the neat PLA and its composites with different contents of both additives. Mechanical properties are key to determining the suitability of materials for most applications, acting as a basic indicator in production, storage, transport and handling. 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 HNT composites exhibited a strong effect in connection with PLA-g-PAA, as values for the modulus were reduced compared with neat PLA or the PLA/HNT composites. This phenomenon could be attributed to PLA-g-PAA (with its shorter chains) and how it was incorporated into the polymer matrix. The consequent reduction in intermolecular binding and greater chain mobility in the polymer matrix heightened the flexibility of the films and contributed to the loss of rigidity [236]. 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. A higher concentration of HNT filler can also reduce the elongation of PLA, and the opposite was the case with a lower concentration of PLA-g-PAA.

Table 11. Mechanical properties of the neat PLA and PLA composites.

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

Contact angles

The wettability of the PLA samples was measured by the static water contact angle (W), ethylene glycol (EG) and diiodomethane (DIM) methods. The mean values with the standard deviation are given in Table 5, and the mean values were processed using Tukey's test and recorded in the upper index in lower case letters. Contact angle measurements revealed that incorporating HNT nanotubes did not significantly affect wettability in the case of water. However, in the case of ethylene glycol, a phenomenon was manifested that was the opposite of expectations, namely that the hydrophobicity of samples containing HNT increased with the increasing content of this filler. This phenomenon could be due to the hydrophobic nature of HNTs with a low number of hydroxyl groups, which led to a decrease in water absorption capacity, or also to the well-dispersed HNTs in the mixed matrices, which could use some free -OH to form hydrogen bonds

between them [237]. The surface free energy (SFE) varies with the amount and type of filler added to the PLA matrix. For samples containing PLA-g-PAA, these changes are not striking, but in the case of composites containing 20 % HNT, there is a slight increase, which could be caused by a slight agglomeration of this filler in PLA [238]. As confirmed by SEM analysis, every sample was smooth, and cracks were absent that could affect the contact angle.

Table 12. Values for contact angle discerned for liquids (water, ethylene glycol and diiodomethane) and the surfaces of the various samples.

Samples	Contact Angle Values (°)			Total SFE (mJ·m ⁻²)
	W	EG	DIM	
PLA	68 ± 4 ^a	34 ± 6 ^a	42 ± 6 ^a	45 ± 1 ^a
PLA/5H	62 ± 4 ^a	43 ± 4 ^b	37 ± 3 ^a	45 ± 1 ^a
PLA/20H	62 ± 3 ^a	47 ± 4 ^b	37 ± 2 ^b	48 ± 0 ^b
PLA/5PLA-g-PAA	67 ± 3 ^a	41 ± 2 ^a	42 ± 4 ^a	45 ± 0 ^{a,c}
PLA/20PLA-g-PAA	65 ± 3 ^a	41 ± 1 ^a	40 ± 2 ^a	45 ± 1 ^c
PLA/20H/5PLA-g-PAA	64 ± 3 ^a	47 ± 3 ^b	36 ± 3 ^b	48 ± 0 ^b
PLA/5H/20PLA-g-PAA	60 ± 4 ^b	38 ± 4 ^a	38 ± 2 ^a	45 ± 1 ^c

* Variations are given in parentheses. Samples with different letters are significantly different at 95% confidence interval of probability according to Tukey's tests.

Abiotic hydrolysis

Abiotic hydrolysis is a process of initial degradation that is essential to determining the stability of materials. It is also necessary for the course of subsequent biodegradation by microorganisms. The aim of the two given additives was to accelerate the initial stages of the protracted abiotic hydrolysis of the PLA matrix, a procedure primarily influenced by temperature and humidity. The hydrolytic behaviour of neat PLA and its composites was observed herein under the influence of abiotic factors, i.e. a high temperature of 58°C and in aqueous medium (0.1 M Na-PB). During the process, changes associated with dissolved organic carbon (TOC-L) and molecular weight (GPC) were analysed, as detailed in Table 13 and Figures 29 and 30. Experimental data obtained from the dissolved organic carbon tests were subsequently processed by applying mathematical kinetic models and coefficients of determination (R²), mainly in relation to the first phase of degradation.

The 60-day experiment revealed the course of abiotic hydrolysis of PLA and its composites, and the experimental data agreed with the kinetic models. The adequacy of the model was also evident from the resulting coefficients of determination, with a level of significance exceeding 0.99.

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 that expressed the initial phase of hydrolysis, i.e. the amount of carbon dissolved in the aqueous medium; this represented a step preceding the final stage of microbial carbon mineralization during biodegradation. 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.

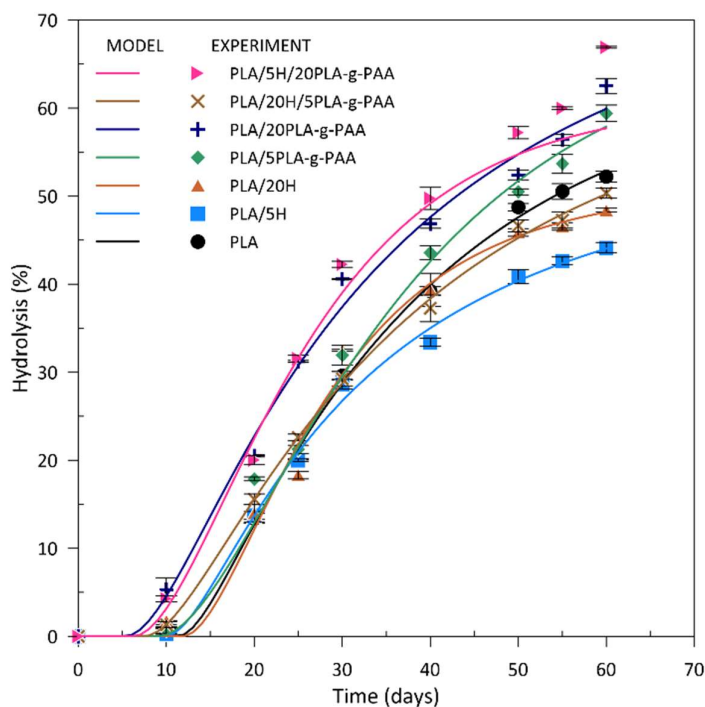


Figure 29. Carbon content of the neat PLA and PLA composites during abiotic hydrolysis, in 0.1 M Na-PB ($\text{pH} \sim 7$) at 58°C .

Table 13. 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.

Investigation at a molecular level by GPC was carried out to discern the behaviour of the materials during hydrolysis. Agreement with previously recorded data was seen for molecular weight and findings on the degradation of the neat PLA and composites. Figure 30 details a marked decrease in M_w in the first 10 days for all the PLA samples. The rate increased significantly in the presence of PLA-g-PAA, this more rapid onset and course of biodegradation most likely instigated by the presence of PAA, which catalysed the hydrolysis of ester bonds. 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 (Table 14).

The full course throughout the period of 25–60 days, according to the measured data, is detailed in the bar graph (see Figure 31) of molecular weights gauged during abiotic hydrolysis. The molecular weight of PLA decreased by 76% after 10 days in the abiotic environment (from approximately 201 kg·mol⁻¹ to 48 kg·mol⁻¹). The PLA/5PLA-g-PAA and PLA/20PLA-g-PAA samples decreased by 90% (from approximately 170–174 kg·mol⁻¹ to 22–11 kg·mol⁻¹), whereas the

PLA/5H and PLA/20H composites reduced by 72% from the baseline (from approximately 195–191 kg·mol⁻¹ to 49–55 kg·mol⁻¹), respectively. All the samples showed a 99% reduction from their original molecular weights after 25 days.

The results confirmed the rapid onset and course of degradation of PLA supplemented with PLA-g-PAA in combination with a limited amount of HNTs (5 wt.%). Heightened acceleration of abiotic hydrolysis is desirable, whereby the rapid fragmentation of long chains occurs alongside the potential mineralization of soluble oligomers, the latter then being broken down by microorganisms [183].

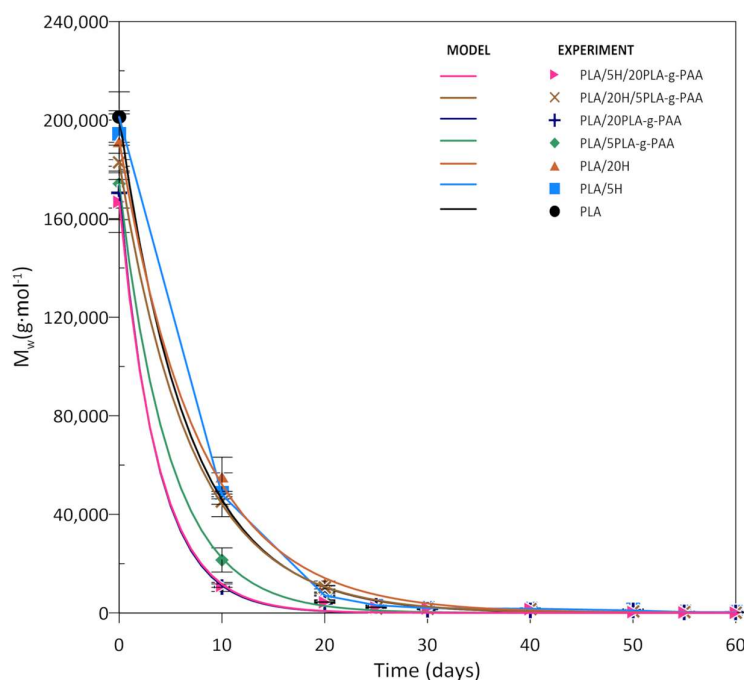


Figure 30. Reduction in molecular weight during abiotic hydrolysis of the neat PLA and various composites with additives, according to the kinetic model.

Table 14. Parameters of the first-order kinetic model and coefficients of determination (R^2) for random scission of the PLA and PLA composites.

Sample	$M_{w,0}^a$ (g·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.

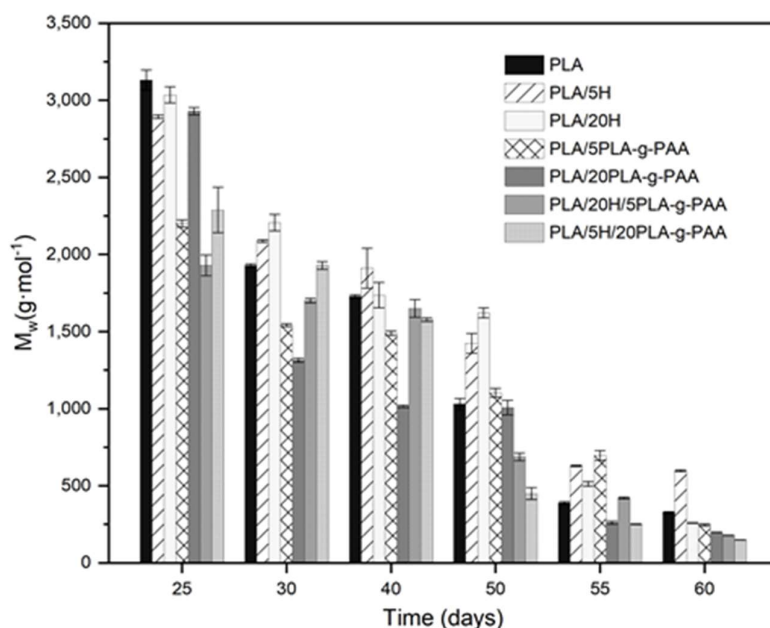


Figure 31. Course of abiotic hydrolysis during 25–60 days.

Biotic degradation test

Aerobic composting (AC) on a laboratory scale made it possible to monitor the biodegradation of the material by gauging the amount of CO_2 released from the test samples [239]. Composting conditions were set at 58°C after 48 days, since control pieces of the cellulose films degraded by more than 70% within 48 days of incubation.

Parameters of the kinetic model and the coefficient of determination (R^2) were determined from the findings, as detailed in Figure 32 and Table 15. Calculation of the kinetic model was performed in order to predict the course of biodegradation, and the values plotted are in general agreement with the experimental data obtained from all experiments. The resulting coefficients of determination are remarkable, with significance levels 0.99 for each material.

Analysis revealed that both degradation factors (abiotic and biotic) acted on the samples, with each one reaching approximately 40% mineralization after 48 days of incubation, thereby confirming their biodegradability in the composting medium. All the samples, except for composites with a higher HNT content, 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.%. Adding 5 wt.% of the HNTs into the PLA matrix also exerted a positive

effect. Rate constants for biodegradation comprised 0.0238 day^{-1} for PLA, 0.0307 day^{-1} for PLA/5PLA-g-PAA and 0.0364 day^{-1} for PLA/20PLA-g-PAA. The highest value for rate constant (0.0397 day^{-1}) was discerned for the PLA/5H/20PLA-g-PAA composite.

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. This finding is consistent with reports in the literature on acid-catalysed hydrolysis of PLA ester bonds in the presence of high carboxyl groups, with the structure of the HNTs also aiding water binding and accelerating PLA degradation as a consequence [174], [180], [185].

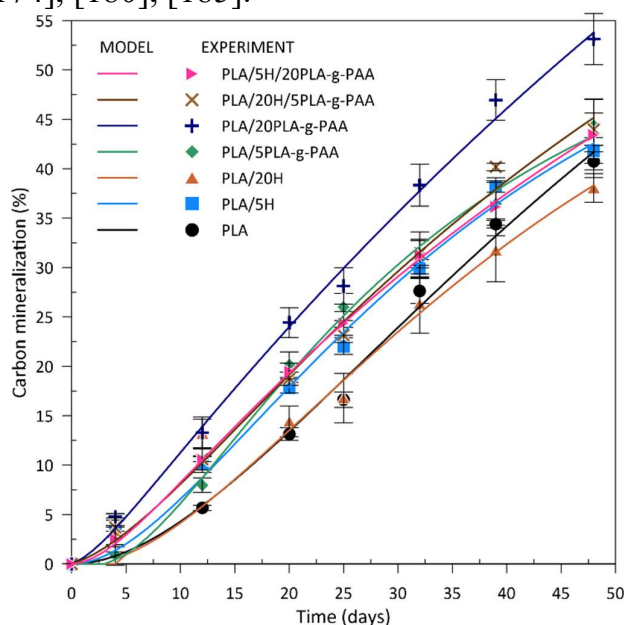


Figure 32. Biodegradation of the PLA, PLA with HNTs and PLA-g-PAA/HNT nanocomposite films, as converted to carbon during mineralization.

Table 15. 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.

Composting test

The composting process has the potential to convert biodegradable plastic waste matter into environmentally-friendly products. Investigation was made as to the degree of degradation (decomposition of the material over time) exhibited by the produced nanocomposites in a composting environment. This study of the biocomposites over a period of time was performed under laboratory conditions that simulated circumstances at a municipal composting plant. Degradation of the samples was observed in terms of change in M_w (Figure 33) and crystallinity (Table 16); note that a high M_w can impede this process. Supplementing PLA with certain additives greatly impacts its thermal stability and crystallization, and thus its subsequent biodegradation. In this context, DSC analysis was performed to determine alteration in the behaviour of the polymer and its composites during the composting process.

M_w dropped by approximately 50% in the first 4 days, and in the PLA/20PLA-g-PAA and PLA/5H/20PLA-g-PAA composites by up to 62%, a phenomenon related to the hydrolytic degradation of ester groups [185]. After 7 days, the other composites had degraded by approximately 61%, although samples containing PLA-g-PAA had decreased by up to 95%. The HNTs were expected to accelerate the degradation of PLA, caused by binding that in turn permitted the rapid binding of water. An opposite effect of the HNTs was found in relation to molecular weight under composting conditions, potentially through an increase in the crystalline phase, which subsequently hindered such degradation. Based on these findings, it was concluded that the HNTs decelerated the degradation process, in comparison with neat PLA, since they were inorganic in nature. However, as other authors have reported [240], supplementation with a limited amount of HNTs may promote the breakdown of the polymer matrix. According to the results, maybe in a concentration of less than 5%.

After less than a month, however, the M_w of all samples equalled ca 3,000 g·mol⁻¹ and it was not possible to detect such values after 28 days.

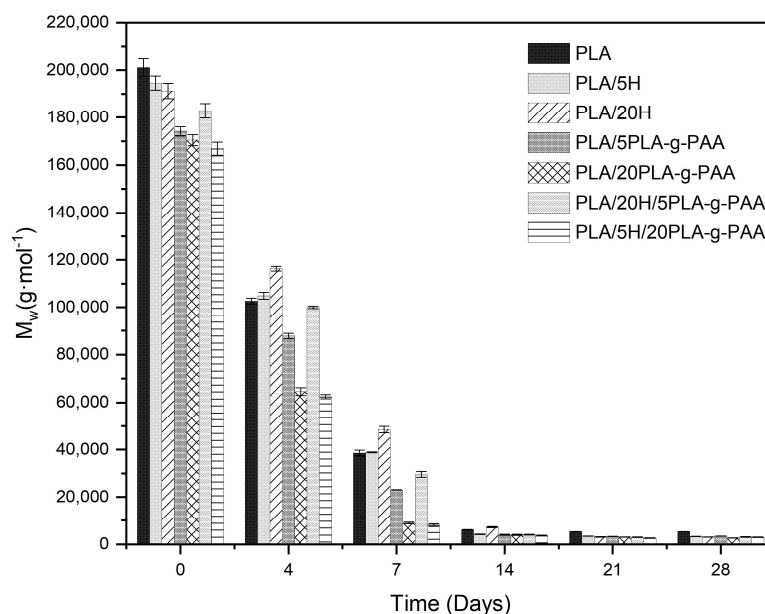


Figure 33. Values for the molecular weights of the PLA and PLA composites during degradation under composting conditions.

The capacity of PLA is generally quite poor and the crystallinity of the prepared films was low. When initially exposed to the composting environment, each sample contained an amorphous polymeric material. The duration of the composting experiment was 45 days, and values for enthalpy of melting (ΔH_m ; the content of the crystalline phase in the polymer) are summarised in Table 16. Biodegradation under the given composting conditions (58 ± 2 °C and 80 % RH) was influenced by various factors, especially temperature and humidity. Temperatures can up to 60 °C in this environment, meaning they align with the range for the glass transition of PLA, thus cold crystallisation occurs in the material [112]. Biodegradation transpired the quickest during the first and second weeks of exposure. The high temperature in the reactors caused a decrease in molecular weight alongside an increase in melting enthalpies, i.e. crystallinity. Such a drop in molecular weight is associated with the chain length being shortened and the formation of lactic acid oligomers, which crystallize efficiently [241]. The results compare the PLA composites with the neat PLA matrix. In the initial phase of degradation (7 days), the PLA/5PLA-g-PAA and PLA/20H/5PLA-g-PAA composites resembled neat PLA. The sample containing the experimentally prepared additive PLA/5PLA-g-PAA was similar to neat PLA in this respect at the end of the test. Differences in biodegradation became more pronounced after 35 days had passed. The PLA samples lost the ability to cold crystallise during the second heating scan, although melting enthalpy increased, indicating that the amorphous parts of the tested samples had biodegraded, leaving merely a crystalline portion. There was also a noticeable loss in melting point associated with chain separation and a reduction in molecular weight for all the

samples. Thus, the separation of multiple crystalline chains into semi-crystalline or amorphous portions could have contributed to the microbial degradation of the polymer [242].

Table 16. DSC results for the neat PLA and composites during degradation under composting conditions.

Sample	Amorphous materials; after cold crystallization		Crystalline materials					
	T _g ^a (°C)	ΔH _m ^b (J/g)	ΔH _m ^b (J/g)					
	amorphous	crystalline	7	14	21	28	35	45
			(days)					
PLA	66	18	54	84	77	80	76	-
PLA/5H	60	2	39	83	87	77	61	-
PLA/20H	58	13	78	57	48	40	29	-
PLA/5PLA-g-PAA	58	35	56	97	89	95	84	-
PLA/20PLA-g-PAA	58	4	38	94	85	83	93	-
PLA/20H/5PLA-g-PAA	58	13	50	64	60	31	14	-
PLA/5H/20PLA-g-PAA	57	30	77	84	68	60	25	-

^a Glass transition temperature determined by DSC.

^b Melting enthalpy determined by DSC (from the 1st heating scan) of the studied material.

Samples were reported at particular intervals until the end of the composting test at 45 days. Figure 34 shows the changes that occurred in the surfaces of the neat PLA and composites during the composting process in the laboratory setting. Not only did the materials become brittle after 7 days, but also alteration in colour was evident. In the first phase, yellowing primarily affected the composites with PLA-g-PAA. An organic segment formed over time, and the samples turned a shade of brown. Those containing up to 20% of PLA-g-PAA reached 98% of biodegradation after 45 days, even when they contained 5% HNTs. Remnants were visible solely through the presence of the mesh. As for the compost, no evidence of any residual PLA polymer was discerned in it after sieving.

Measurements were taken of the pH levels and temperature in the reactors during the biodegradation experiment. At time 0 until day 3, pH equalled 6–8 and the temperature 58°C. Then the pH rose sharply to 10–12 and the temperature to 60–62 °C, which remained unchanged until day 10, when both of these gradually diminished; by the 35th day, pH values had dropped to about 9 and the temperature back to 58°C. This phase, reported as lasting 3–4 weeks, is referred to as “active”, wherein the temperature could rise to 70°C, depending on the material. Compost is hygienized in this phase, a process in which pathogenic organisms are destroyed by the high temperature and organic matter is decomposed into basic raw materials. Thermophilic microorganisms at such temperatures facilitate the degradation of complex organic matter, and the conversion of nitrogen into ammonia occurs, raising the pH of the compost. It is possible for the process to end after 35 days, depending on temperature and pH, by which time a mesophilic phase of polymer degradation has occurred and fungi are visible to the naked eye. At the end of the composting process, it can be assumed that biodegradation has transpired, wherein the decomposing polymer is processed into a humus complex while the compost benefits from a high fertilizing effect [243], [244].

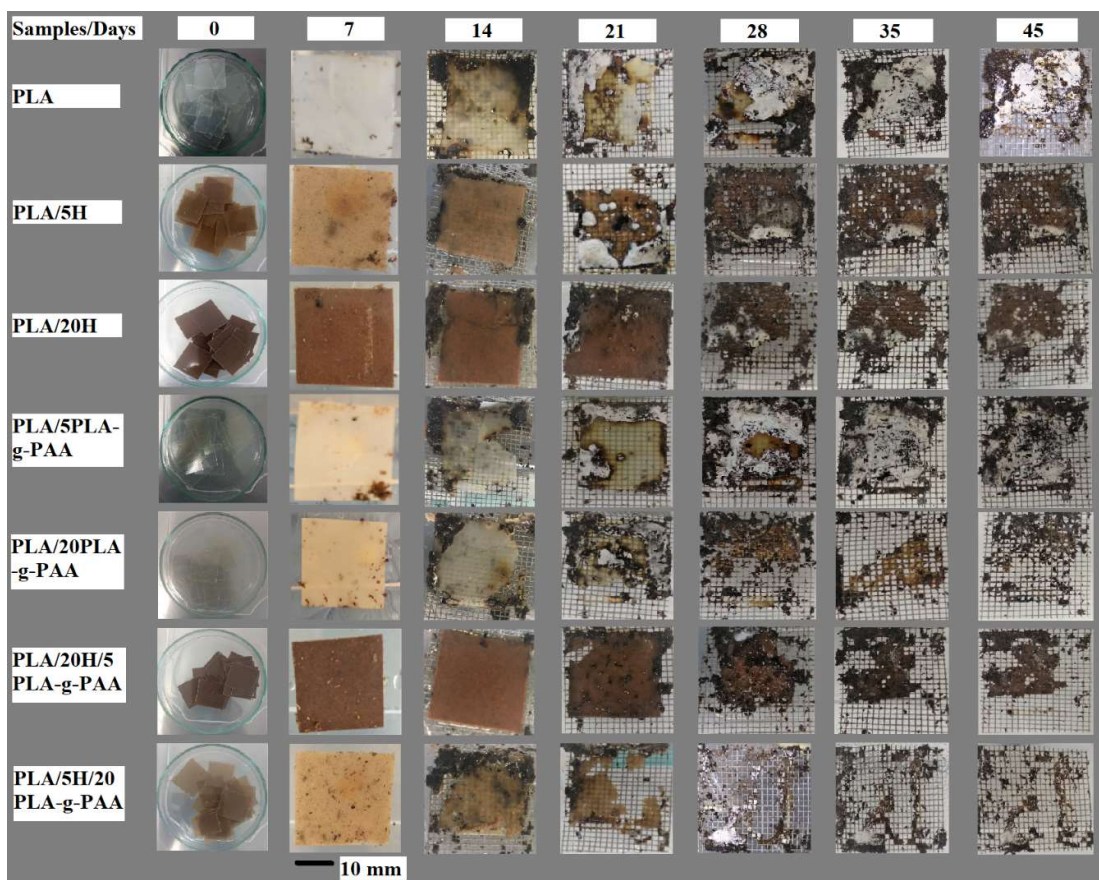


Figure 34. Images showing the course of biodegradation of the neat PLA and PLA composites during the composting experiment.

Approximately 10 g of dried compost was required to prepare the extract. Sampling was performed from each reactor, including a blank. This amount was supplemented with 200 mL of distilled water, shaken for 24 h, and then the samples were filtered. An initial quantity of technical waste was prepared for the samples at the beginning of the composting test. The filtered extracts were first analysed from an elemental perspective, revealing changes that occurred during the composting experiment and the possible presence of dangerous or toxic elements.

The extracts did not contain hazardous elements such as As, Cd, Hg, Cu and Pb, i.e. those strictly controlled in drinking water and landfill sites. On the contrary, common elements were found instead, including potassium, chlorine and calcium (see Table 17). As expected, the chlorine concentration did not differ significantly, ranging from merely 0.02 to 0.03%. The presence of calcium was observed only in small amounts. Two samples (PLA/5PLA-g-PAA and PLA/20H/5PLA-g-PAA) showed a slight decrease in potassium, from 0.08% to 0.06–0.04 % [245]; such a trace amount was at the detection limit of the device. Potassium is an essential nutrient for plants, though, necessary for their proper development. It is also a positive mobile ion with the potential to interfere in

nutrient uptake (fungi) or mineralization at the concentrations listed herein. Each such disruption is followed by spontaneous stabilization of itself [246].

Table 17. Energy-dispersive X-ray spectroscopy (EDX) analysis of all samples.

Sample	Element (wt.%)		
	K	Cl	Ca
Synthetic waste	0.078	0.022	-
Blank	0.074	0.026	-
PLA	0.071	0.029	-
PLA/5H	0.075	0.025	-
PLA/20H	0.073	0.027	-
PLA/5PLA-g-PAA	0.040	0.027	0.053
PLA/20PLA-g-PAA	0.072	0.028	-
PLA/20H/5PLA-g-PAA	0.060	0.027	0.013
PLA/5H/20PLA-g-PAA	0.075	0.025	-

Table 18 presents the decomposition values of the samples (*D*), the percentages of reduction in volatile matter (*R*), the C/N ratios after composting and the results of the phytotoxicity test (*IK*). Every composted sample degraded by more than 90%, and each one adhered to the given standard. However, neat PLA showed the lowest values, while samples containing 20% of PLA-g-PAA reached almost 100%, as confirmed by Figure 34 above. The content of volatile matter in the samples and blanks also decreased universally by more than 70%, indicating that they also adhered to the standard, with the final result exceeding 30%. The C/N ratio is a key factor that affects both the composting process and the related quality. The act of composting triggers inevitable losses in nitrogen (N) and carbon (C) through the mineralization of organic matter by microorganisms, which causes the release of dozens of gaseous metabolic products. A C/N ratio at the range of 20–30 is considered optimal for composting. This ratio is often affected by the composition of the compost, as plant components increase this ratio, while manure and food residues reduce it. The results showed that the compost reached a C/N ratio of 8–9 in all cases, including the blank, after 45 days of incubation. Therefore, the samples did not impact the characteristics of the compost. In practice, the properties of compost are modified by mixing fillers (e.g. straw, leaves and woody material) [247], [248], [249], [250].

In order to evaluate the overall quality of compost, its phytotoxicity was tested, which is important for determining its maturity, i.e. the effect it has on the overall growth and development of plants. Percentages indicating germination indices

(*IK*) include good compost maturity between 80% and 100%, partially mature at >60% and immature at <60%. The effect on germination of PLA-bound seeds and their composites after 45 days of composting (the minimum duration) was insufficient in all the samples; indeed, *IK* values were measured of about 50%. However, the samples of PLA and its composites did not affect the composting process, as the same result was obtained for the comparison blank. It can be assumed that a longer maturation time after 90 days could improve the properties of the compost, as described in the literature [251], [252], [253].

Table 18. Biodegradation of the PLA and PLA nanocomposite materials under composting conditions in reactors.

Samples	<i>D</i> (%)	<i>R</i> (%)	C/N ratio*	<i>IK</i> (%)
Blank	–	75.7 ± 0.7 ^{a,d}	8.6 ± 0.2 ^a	48.7 ± 3.2 ^a
PLA	93.2 ± 3.8 ^{a,b,c}	73.9 ± 0.5 ^{a,b,c}	8.8 ± 0.8 ^a	54.8 ± 4.0 ^a
PLA/5H	94.1 ± 3.9 ^{a,b,c}	74.3 ± 1.0 ^{a,b,c,d}	9.1 ± 0.8 ^a	56.7 ± 5.1 ^a
PLA/20H	97.8 ± 0.3 ^b	74.9 ± 0.5 ^{a,d}	8.3 ± 1.7 ^a	46.2 ± 3.8 ^a
PLA/5PLA-g-PAA	94.9 ± 3.0 ^{a,b,c}	73.5 ± 0.6 ^{a,b,c}	8.1 ± 1.1 ^a	49.3 ± 1.6 ^a
PLA/20PLA-g-PAA	99.4 ± 0.9 ^{b,c}	73.4 ± 0.1 ^{b,d}	9.3 ± 0.4 ^a	51.1 ± 3.3 ^a
PLA/20H/5PLA-g-PAA	96.8 ± 0.3 ^{a,b}	73.1 ± 0.2 ^c	8.3 ± 1.0 ^a	52.4 ± 4.4 ^a
PLA/5H/20PLA-g-PAA	99.8 ± 0.4 ^c	76.0 ± 0.2 ^d	9.3 ± 0.8 ^a	49.6 ± 4.1 ^a

D – degree of disintegration according to Equation (12)

R – decrease in the content of volatile solids according to Equation (13)

IK – germination index according to Equation (14)

*Results obtained from the TOC-L total organic carbon analyser.

** Mean values were processed using Tukey's test, and different letters in the same column indicate significant differences ($p < 0.05$).

Conclusions

Initially, two additives (HNTs and PLA-g-PAA) were incorporated into the PLA matrix at various concentrations (5% and 20% w/w) by heat extrusion followed by compression into films. Furthermore, the films were characterised by mechanical (tensile properties), thermal (effect on thermal degradation), wettability and overall homogenisation of additives in PLA (optical method) which is important for processing applications. PLA-g-PAA had a plasticiser property when the HNT filler was added, and it increased the strength and

stiffness without any significant effect on the thermal stability of the material. The influence of individual additives and their composites was monitored, the inclusion of which effectively supported the degradation of the PLA material. In the case of abiotic hydrolysis, it was noted that the fast lag phase was achieved with composites containing 20 % PLA-g-PAA additive, where the quickest course was achieved by PLA/5H/20PLA-g-PAA composite, reaching disintegration by about 30 % in 60 days (compared to neat PLA (TOC-L analysis)). Similar results were obtained for molecular weight disintegration and biotic test where degradation was almost twice faster than pure PLA because the additive containing acrylic acid provide chains with a high concentration of terminal carboxyl groups capable of catalysing the random cleavage of ester bonds in the PLA matrix. In the case of composting, the results of these composites confirmed an accelerating effect on PLA degradation, manifested by almost 100 % disintegration in 45 days without adversely affecting the compost properties that could prevent plant germination. The optimally designed combination of both components in the sample led to the desired biodegradation of PLA, especially under conditions ideal for composting plants. The results indicate that the composite could be potentially usable in materials that cannot be fully recycled.

SUMMARY OF WORK

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.

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LIST OF SYMBOLS AND ABBREVIATIONS

ΔH	Reaction enthalpy
3D	Three dimensional
5-PT	5-phenyltetrazole
ABS	Acrylonitril butadien styren
AC	Aerobic composting
ADC	Azodicarbonamide
$A_{(t)}$	Ageing factor
Al_2O_3	Aluminium oxide
AO	Antioxidant
APP	Ammonium polyphosphate
Asp	Aspartic acid
BE	Bentonite
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
BRE	Bentonite with beetroot extract
$CaCO_3$	Calcium carbonate
CH_4	Methane
DBS	Dibutyl sebacate
DIM	Diiodomethane
DINA	Diisononyl adipate
DOA	Dioctyl adipate
DPPH	2,2-diphenyl-1-picrylhydrazyl
DSC	Differential scanning calorimetry
EC	European Commission
EDX	Energy-dispersive X-ray spectroscopy
EG	Ethylene glycol
ESI-MS/MS	Electrospray ionization tandem mass spectrometry
FCM	Folin-Ciocalteu method
FCR	Folin – Ciocalteu reagent
FDA	Food and Drug Administration
Fe_2O_3	Iron(III) oxide
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatograph
GPC	Gel permeation chromatography
GRAS	Generally Recognised as Safe
GWP	Global warming potential

H ₂ S	Hydrogen sulfide
HA	Hyaluronic acid
HDDA	1,6-hexanediol diacrylate
HDPE	High-density polyethylene
His	Histidine
HNT	Halloysite
HPLC	High-performance liquid chromatography
LC	Liquid crystal
LCA	Life cycle assessment
LDPE	Low-density polyethylene
MCF	Microcellulose fibrils
(Mg(OH) ₂)	Magnesium hydroxide
M _n	Number average molecular weight
MSA	Methanesulfonic acid
M _w	Molecular weight
Na-PB	Sodium phosphate buffer
OBSH	4,4'-oxybis(benzenesulfonylhydrazide)
OLED	Organic light-emitting diodes
PA	Polyamide
PAA	Polyacrylic acid
PAH	Polycyclic aromatic hydrocarbons
PAL	Poly(aspartic acid-co-lactide)
PALNa	Poly(sodium aspartate-colactide)
PBAT	Polybutylene adipate terephthalate
PBS	Polybutylene succinate
PBSA	Polybutylene succinate adipate
PBT	Polybutylene terephthalate
PC	Polycarbonate
PCDI	Polycarbodiimide
PCL	Polycaprolactone
PE	Polyethylene
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PFM	Polyfunctional monomers
PGA	Polyglycolic acid
pH	Potential of hydrogen

PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PHH	Polyhydroxyhexanoate
PHV	Polyhydroxyvalerate
PLA	Poly(lactic acid), Polylactide
PLGA	Poly(lactic-co-glycolic acid)
PMMA	Poly (methyl methacrylate)
PP	Polypropylene
PPC	Polypropylene carbonate
PS	Polystyrene
PSI	Polysuccinimide
PTA	Pyrimidine-2,4,5,6-tetramine
PVC	Polyvinyl chloride
PUR	Polyurethane
Rh	Relative humidity
RNS	Reactive nitrogen species
ROP	Ring-opening polymerization
ROS	Reactive oxygen species
SEM	Scanning electron microscopy
SFE	Free surface energy
Ser	Serine
Sn(Oct ₂)	Tin(II) 2-ethylhexanoate
SWOT	Strengths, weaknesses, opportunities and threats
TAIC	Triallyl isocyanurate
TBC	Tributyl citrate
TBHQ	Tert-butyl-hydroquinone
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
TMAIC	Trimethallyl isocyanurate
T _{max}	Temperature at the maximum rate of weight loss of samples
TMPTA	Trimethylolpropane triacrylate
TMPTMA	Trimethylolpropane trimethacrylate

TNPP	Tris (nonylphenyl) phosphite
TOC-L	Total Organic Carbon Analyze
T _{onset}	Initial degradation temperatures
T _{peak}	Highest temperature peak measured at O ₂
TPU	Thermoplastic polyurethanes
UV	Ultraviolet
ZnO	Zinc oxide

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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.

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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: July 19, 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.
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5. PUMMEROVÁ, Martina; DRÖHSLER, Petra; SEDLAŘÍK, Vladimír. Biodegradable composition for agriculture applications, ID 43882722, 2021.
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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.
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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.