Advances in Science and Technology
Research Journal

Advances in Science and Technology Research Journal 2021, 15(3), 9–29
https://doi.org/10.12913/22998624/137960
ISSN 2299-8624, License CC-BY 4.0

Received: 2021.06.14
Accepted: 2021.07.19
Published: 2021.08.01

Polylactide: from Synthesis and Modification to Final Properties

Joanna Aniśko[1*], Mateusz Barczewski[1]

[1] Poznan University of Technology, Institute of Materials Technology, Piotrowo 3, 61-138 Poznan, Poland
* Corresponding author's e-mail: joanna.anisko@put.poznan.pl

ABSTRACT
The article reports ways and trends in polylactide (PLA) modification methods concerning literature data. The paper consists of two parts and presents the process of polylactide production, and the connection of changes in its properties with the polymer structure obtained thanks to appropriate process conditions and methods of its final polymer properties improvement. Discussing both the most advantageous properties and disadvantages, the possibilities of increasing the scope of its applicability in reference to selected modification methods were presented and discussed. The presented research results related to various modification methods arrange the knowledge from the discussed scope, indicating the best possible effects and limitations. The most considerable emphasis is on the methods and results obtained from heterogeneous nucleation and incorporating various fillers in the PLA matrix. The other methods, like applying chemical interaction methods (crosslinking, using chain extenders), development of polymer blends, copolymerization, and plasticization, are presented synthetically. In summary, the review present and organizes the achievements in the possibility of modifying the most prospective biodegradable polymer, which is PLA.

Keywords: PLA, polylactide, modification, poly(lactic acid), composite.

INTRODUCTION

The growing interest in biodegradable polymers results from the growing consumption of reserves in fossil resources, including crude oil. The drastic decrease in the number of resources causes an increase in oil prices and their derivatives. The chemical industry uses only 10% of the crude oil, but any fluctuations in its price will affect the polymer industry. Therefore, an alternative is needed, which will be provided by polymers from renewable raw materials [1]. The interest in biodegradable polymers also results from the need to reduce the amount of polymer waste. The European Union imposes an obligation on the Member States to increase the amount of recycled plastic packaging. Directive (EU) 2018/852 assumes that by the end of 2025, the amount of plastics recycled is to be 50% by mass, and by the end of 2030 – 55% by mass [2]. Achieving this goal without innovative solutions may be extremely difficult. The solution to this problem may be the introduction of biodegradable polymers to the market. The cost of composting such polymers is about six times lower than the cost of recycling conventional polymers [9]. The best-known biodegradable polymer is polylactide, which has many advantages and the same amount of disadvantages. This paper provides a detailed description of ways to modification of PLA to eliminate these disadvantages.

POLYLACTIDE SYNTHESIS

Polylactide (PLA) is the best-known biodegradable polymer. It is made from lactic acid, and its other name is poly(lactic acid). Lactic acid can be obtained, e.g., as a result of lactic whey fermentation, which is a waste from cheese production. Whey is a perishable greenish liquid with an unpleasant odor. It constitutes 65–90% of waste from the production of cheese and curd. The production of this biodegradable polymer is based on recyclable materials, and therefore, it is even more ecological. PLA can also be made from corn, which is a cheap source of dextrose. Lactic acid is obtained from it by fermentation. The production of 500,000 tons of PLA constitutes less than 0.5% of the annual US corn crop. PLA was first obtained by scientists from DuPont in 1932 by heating lactic acid under very low pressure. It was patented in 1954, and in 1987, Cargill (USA) began working on the development of PLA. Today, Nature Works LLC produces many varieties of PLA with the trade name Ingeo™. The volume of this production is 150,000 tons per year. PLA has an excellent balance of environmental properties and benefits. The cost of PLA is approximately 4$ per kg. It is an attractive price but at the same time much higher than the price of conventional polymers obtained from petrochemical raw materials [3÷5].

Receiving

Lactic acid (LA) is a weak organic acid that is soluble in water. It is in a liquid form at room temperature because its melting point is at 16.8 °C. Lactic acid has an asymmetric carbon atom (chiral center) in its structure. It can exist in the form of two enantiomers, i.e., dextrorotatory L (+) lactic acid and laevorotatory D (-) lactic acid. The preparation of both enantiomers or their racemic mixture (a mixture of equal amounts of enantiomers) is carried out using appropriate bacterial strains and process conditions (temperature, pH). Lactic acid can be obtained synthetically or by lactic fermentation of plant-derived carbohydrates. The synthetic process is the catalytic addition of hydrogen cyanide to acetaldehyde (or α-chloropropanoic acid) and the hydrolysis of the obtained cyanohydrin. Lactic fermentation takes place using bacteria such as cocci - streptococci (*Streptococcus*, *Lactococcus*, *Leuconostoc* types), tetrads (*Pediococcus*), and bacilli (*Lactobacillus* and *Bifidobacterium*). Due to the presence of Lactobacillus bacteria, fermentation occurs with high efficiency and speed of the process. The fermentation process includes sugars such as dextrose (from potato or corn starch), sucrose (from sugar beet or sugar cane), lactose (from whey), glucose and maltose. The fermentation process in the presence of bacteria can be divided into two methods: homofermentative or heterofermentative, depending on which bacteria are used. In the heterofermentative method, 1 mole of hexose (simple sugar) produces less than 1.8 moles of lactic acid and significant amounts of other metabolites (products of metabolism) such as acetic acid ethanol, glycerol, mannitol, and carbon dioxide. In the homofermentative method, however, 1 mole of hexose can also produce 1.8 moles of lactic acid on average, but with low levels of other metabolites. It means that every 100 g of glucose can produce more than 90 g of LA. The homofermentative method is more commonly used in industry due to its higher production efficiency and lower side product levels than the heterofermentative method. Chemically synthesized lactic acid gives a racemic mixture (50% of D and 50% of L). Lactic acid resulting from fermentation usually consists of 99.5% of the L isomer and 0.5% of the D isomer [6÷9]. The process of obtaining lactic acid (Fig. 1) is based on:

1. Photosynthesis,
2. Enzymatic hydrolysis,
3. Fermentation [9].

The largest producer of PLA (Nature Works LLC) begins producing the polymer with the cultivation of corn. As a result of photosynthesis carried out in maize cells, carbohydrates are produced, mainly sucrose and starch. All carbon, hydrogen, and oxygen in the starch molecule and the final polylactide molecule have their source in the water and carbon dioxide used for photosynthesis. After harvest, the maize is transported to a wet mill, where the starch is separated from the other constituents of the maize (proteins, fats, fiber, water). Starch is converted into dextrose by enzymatic hydrolysis. Nature Works LLC ferments the

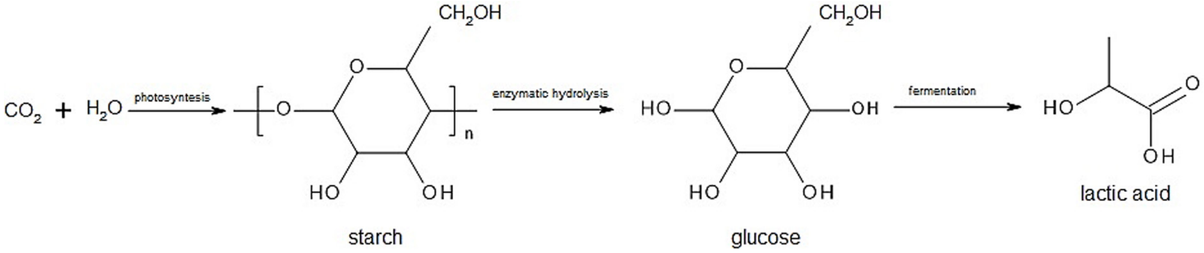

Fig. 1. Scheme of obtaining lactic acid

dextrose to lactic acid with an almost neutral pH by adding calcium hydroxide. The lactic acid solution is then acidified by the addition of sulfuric acid, which causes the formation and precipitation of gypsum. The gypsum is removed by filtration, and the lactic acid is concentrated by evaporation. After the final purification, lactic acid is transported to the PLA production process [5, 6, 10, 11].

In various parts of the world, locally available crops can be used as raw materials for PLA production, e.g., rice, sugar beet, sugarcane, wheat, and sweet potatoes. Total Corbion PLA uses sugar cane for this purpose. Total Corbion produces lactic acid by fermenting cane sugar. The entire process is the same as that used by Nature Works LLC, except that the sugar source, in this case, is from sugarcane. The pH of the fermentation is also controlled with calcium hydroxide, resulting in the formation of calcium lactate. It is then acidified with sulfuric acid to obtain the lactic acid. This step also causes the precipitation of gypsum, which is removed by filtration. The last stage is lactic acid purification, during which various impurities are removed [12].

Three different methods can be used for the production of PLA. Each one of the methods gives a product with different properties and structures. The direct method is based on the direct polycondensation of lactic acid. The obtained product has a low molecular weight Mn = 10,000–20,000, worse mechanical properties than the one obtained in two stages, and contains impurities, e.g., unreacted monomer. This process is not conducive to the production of copolymers and homopolymers of various molecular weights. Thanks to special catalysts and process conditions, it is possible to obtain PLA with a high molecular weight. One such method is the use of antimony (III) oxide as a catalyst and dipentaerythritol as a branching agent. Both of these factors must be present. Polycondensation of lactic acid only with the Sb_2O_3 catalyst does not allow obtaining a polymer that has a high molecular weight [9, 13].

The two-step method is based on the polymerization of lactide previously obtained from lactic acid. In this case, ionic ring-opening polymerization is used. This reaction produces PLA with a molecular weight of more than 50,000 and favorable mechanical properties. The first step in this method is the depolymerization of lactic acid oligomers. Thus, a lactic acid dimer (lactide) is obtained. There are two chiral centers in its molecule, and therefore, there can be three different diastereoisomers. They differ in how the atoms are arranged in space, but they follow the same order in which they are connected. These diastereoisomers are (Fig. 2):

- D, D - Dilactide [(3R)-cis-3,6-dimethyl-1,4-dioxane-2,5-dione],
- L, L - Dilactide [(3S)-cis-3,6-dimethyl-1,4-dioxane-2,5-dione],
- D, L - Dilactide (meso-lactide) [(3S)-trans-3,6-dimethyl-1,4-dioxane-2,5-dione].

The next step is the Ring-Opening Polymerization (ROP). It can follow three mechanisms. The differences between them are the place of ring-opening and the used initiator:

1. Anionic – the bond breaks between the carbon of the acyl group and oxygen. The initiators of this mechanism are generally alkali metal alkoxides or butyllithium, e.g., potassium alkoxide. In effect a PLA with good mechanical properties and a molecular weight within a narrow range is obtained. The growing PLA chain has a negative charge located in the oxygen molecule, which prevents the change from L to D and vice versa. Partial racemization is possible. The anionic mechanism occurs quickly and with high efficiency due to the low participation of unwanted side reactions [7, 9, 13].
2. Cationic – breaks the bond between the carbon of the alkyl group and the oxygen in dilactide. The mechanism is based on the substitution of a monomer at the chiral center, which allows the formation of mixtures of enantiomers

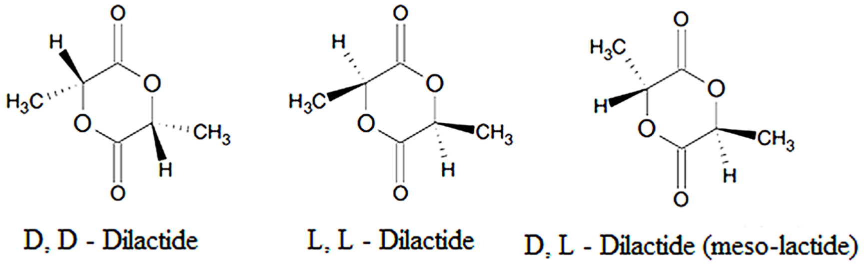

Fig. 2. Diastereoisomers of lactide [7]

(racemization). Lewis acids are the initiators of this reaction. A stereochemical change in the substituent position may occur, leading to a system with a different L-, D- PLA configuration. This change occurs because the positive charge is on the chiral carbon atom. The method allows obtaining a polymer with a low molecular weight, therefore was not used on an industrial scale [7, 9, 13].

3. Coordinating – is the breakdown of the aryl - oxygen bond and the combination of lactide with the initiator. These initiators can be alkoxides or carboxylates containing covalent bonds between oxygen and copper atoms or those with free p or d orbitals. The most known initiators are those formed by alcohols or phenols with metal ethanols: zinc, aluminum, titanium, tin (IV). The use of zinc or aluminum alkoxides makes it possible to obtain polylactides containing appropriate ester groups in the chain. The ring-opening polymerization of PLA under industrial conditions proceeds with a polymerization initiator, which is tin (II) octanoate (2-ethyl hexanoate) $Sn(Oct)_2$. The monomer used for this purpose must have high purity. It is purified and decomposed in distillation columns under reduced pressure. After the polymerization is complete, a small amount of unreacted monomer remains. It is turning back to the reactor with lactic acid after it has been distilled off under low pressure. This method allows obtaining a polymer with assumed end groups, the desired molecular weight in a wide range, and an appropriate macromolecular structure [7, 9, 13].

The third method is direct polycondensation in an azeotropic solution. Mitsui Toatsu Chemicals Inc. uses it to produce PLA with high molecular weight. No chain extenders or adjuvants are used in this process. Polylactide is formed by direct condensation, while condensation water is continuously removed by azeotropic distillation. The process involves lowering the lactic acid distillation pressure for 2–3 hours at 130 °C. During this time, most of the condensation water is removed. The catalyst is added along with the diphenyl ester using a 3Å molecular sieve tube attached to the reaction vessel. The solvent is added to the vessel through molecular sieves for 30–40 hours at 130 °C. Finally, the polymer is isolated or dissolved and precipitated for further purification [8, 14]. Figure 3 shows diagrams of all three methods of obtaining polylactide.

In industrial applications, a two-step method of obtaining polylactide with ring-opening polymerization is used. The most important advantage of this method is the possibility of obtaining polylactide with high molecular weight. Nature Works LLC begins PLA preparation by removing water under mild conditions (no solvent required) to produce a low molecular weight prepolymer. This prepolymer is then catalytically depolymerized to form a cyclic intermediate dimer (lactide). It is then purified by distillation, and the mesolactide is separated. The meso fraction is then combined with the L fraction to create a comprehensive range of Ingeo™ polylactide grades with very different physical and chemical properties. Polymers with a high level of L-lactide can be used to make crystalline polymers. Materials

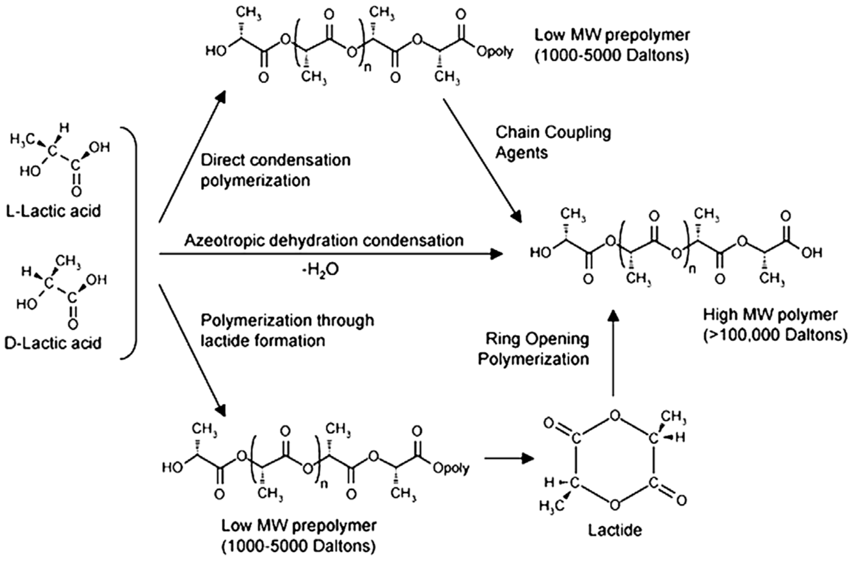

Fig. 3. Methods of obtaining polylactide PLA [100]

with a higher content of D-lactide are amorphous and have a lower degree of crystallinity. The purified lactide is polymerized in a solvent-free ring-opening polymerization and processed into polylactide granules. By controlling the purity of the lactide, a polymer with a wide range of molecular weights can be produced. After polymerization is complete, any residual lactide monomer is removed and turn back within the process. Examples of Ingeo grades: 2003D – can be used alone or as part of an extrusion blend; 3001D – for injection molding; 3100HP – has a medium viscosity for injection molding; 3260HP – designed to crystallize during processing leading to higher heat deflection temperatures under load, used in opaque applications; 4032D – for the production of films at high temperature; 4060D – for the production of a heat-sealable layer in multilayer systems with PLA [5, 6, 10, 11, 99].

Another large polylactide producer is Total Corbion. The polylactide they produce is obtained by polymerization of lactide, which is produced from purified lactic acid. After the polymerization is complete, any remaining lactide monomer is removed and turn back to the PLA manufacturing process. The polymer is further purified to produce PLA granules. The process is very similar to that used by Nature Works LLC. The trade name of the PLA produced by Total Corbion is Luminy®. Total Corbion's offer includes products in four categories:

- PLA with high processing temperature for demanding applications,
- Standard PLA for general use,
- PLA with a low processing temperature, usually used as a sealing layer,
- PDLA is used as a nucleating agent or for the formation of full stereocomplex compounds [12, 15].

Properties of the PLA

Polylactide is a thermoplastic polymer. The physical, mechanical, barrier properties and crystal structure of PLA depend on its molecular weight and stereochemical composition. This composition is very easily controlled by the polymerization of D-lactide, L-lactide, or meso-lactide to form random or block stereocopolymers. The molecular weight is directly controlled by the addition of hydroxyl compounds (i.e., lactic acid, water, alcohols). The ability to control the stereochemical structure allows for precise control of the crystallization rate and degree of crystallinity, mechanical properties, and material processing temperature. The optical purity also influences the structural, thermal, barrier, and mechanical properties of PLA. This value characterizes the composition of the mixture of two enantiomers. Optical purity is equal to the ratio of the optical rotation of the mixture to the optical rotation of the selected pure enantiomer [14, 16, 98].

L- and D, L-PLA can crystallize in three forms (α, β, and γ) depending on the composition of optically active enantiomers. The α structure is more stable than the β structure. The α structure has a melting point of 185 °C and β structure of 175 °C. Polylactide with an L-PLA enantiomer content greater than 90% is crystalline, and the polylactide with a lower content is more amorphous (has a lower degree of crystallinity). Polylactide with D-PLA isomer content greater than 8% is amorphous, even after 15 hours of isothermal treatment at 145 °C. L-PLA is translucent, but when 5% D-PLA is added, it becomes colorless and transparent. Products made of PLA with good thermal resistance can be injection molded. The composition of the PLA mixture may then contain a maximum of 1% of the D-PLA isomer. To achieve an acceleration of crystallization in relatively short moulding cycles, it is necessary to add nucleating agents to the PLA mixtures. PLA blends with higher D-PLA content, from 4% to 8%, are more suitable for thermoforming, extrusion, and blowing. These methods facilitate the processing of polymers with a low degree of crystallinity. The degree of crystallinity also affects the water absorption of the polylactide. With a decrease in the degree of crystallinity, water absorption increases because, in amorphous structures, it is easier to penetrate between molecules [7, 14]. The PLA L (–) and D (+) enantiomers are:

- homochiral,
- isotactic,
- have a relatively high degree of crystallinity - up to 60% (semicrystalline),
- their glass transition temperature (T_g) is 55–65 °C,
- their melting point (T_m) is 170–180 °C,
- the density of L-PLA is 1.25–1.29 g/cm^3,
- the density of D-PLA is 1.27 g/cm^3,
- their tensile strength amounts to approximately R_m = 60 MPa and it does not depend on the molecular weight,
- their bending strength depends on the molecular weight (for L-PLA: when its molar mass increases from 23,000 to 67,000, the flexural strength increases from 64 to 106 MPa) [7÷9, 13].

In turn, D, L - PLA is:

- amorphous,
- heterochiral,
- atactic,
- its glass transition temperature is 57 °C,
- has a higher melting point - 230 °C
- has worse mechanical properties and faster degradation than L (–) and D (+) PLA,
- its mechanical properties depend on the molecular weight, when its molar mass increases from 47,500 to 114,000, the tensile strength increases from 49 to 53 MPa, and the bending strength increases from 84 to 88 MPa,
- the addition of lactic acid fragments of different chirality reduces the ability to crystallize PLA, and the content of the crystalline phase depends on the number of individual isomers,
- can form stereocomplexes [7÷9, 13].

The mechanical properties of lactic acid polymers can be varied over a wide range, from soft and flexible plastics to stiff and high-strength materials. Table 1 shows some of the mechanical properties of annealed and unannealed L-PLA and D, L-PLA. It can be observed that the semi-crystalline PLA has better mechanical properties than the amorphous polymer [15].

Unmodified poly (D - lactide) or poly (L - lactide) has an equilibrium crystalline melting point of 207 °C. In practice, the melting points are in the range of 170–180 °C. The discrepancy in this temperature range is due to small and imperfect crystallites, slight racemization, and impurities. A 1:1 mixture of pure poly(L - lactide) with pure poly(D - lactide) will give an insoluble gel formed by the stereocomplex (racemic crystallite) of the two polymers during crystallization or polymerization. This pure stereocomplex has a melting point of 230 °C and mechanical properties better than that pure one. The glass transition and melting point of PLA depend on its molecular weight and optical purity. The relation of these temperatures with a change of optical purity is presented in Table 2. PLA above the glass transition temperature behaves like rubber, and below it behaves like glass, which is able to creep. It behaves this way until it is cooled below the transformation temperature β (approx. -45 °C). Below this temperature, it becomes a brittle polymer. PLA has a relatively high glass transition temperature and a low melting point in comparison to other thermoplastic polymers [14, 18].

The glass transition temperature decreases with the decrease in the L-PLA isomer cotent, from 63 °C to 56 °C. The maximum melting point for pure L-PLA is 178 °C, and the inherence of 20% meso-lactide in the PLA structure lowers the T_m by 53 °C.

The rheological properties of PLA are highly dependent on temperature, molecular weight, and shear rate. These parameters must be taken into account when designing and optimizing the processing. The viscosity of PLA with high molecular weight is 500–1000 Pa·s, at shear rates of 10–50 s^{-1}. Molten PLA with high molecular weight behaves like a pseudoplastic non-Newtonian fluid. In contrast, PLA with low molecular weight (~ 40,000) exhibits a behavior

Table 1. The influence of stereochemistry and crystallinity on the mechanical properties of PLA [17]

Properties	L-PLA	L-PLA (annealed)	D-, L- PLA
Tensile strength [MPa]	66	59	44
Elongation at break [%]	4	7	5,4
Elastic modulus [MPa]	4150	3750	3900
Yield strength [MPa]	70	70	53
Flexural strength [MPa]	119	106	88
Hardness [Rockwell]	88	88	76
Heat deflection temperature HDT [℃]	61	55	50

Table 2. Change of the glass transition and melting temperature depending on the optical purity of PLA [14]

Copolymer ratio PLA (L/D, L-PLA)	Glass transition temperature T_g [℃]	Melting temperature T_m [℃]
100/0	63	178
95/5	59	164
90/10	56	150
85/15	56	140
80/20	56	125

similar to that of Newtonian liquids in shear at rates typical for film extrusion. Semicrystalline PLA has a higher viscosity than amorphous under identical processing conditions. The rheological properties of PLA can be modified by introducing branches into the polymer chain. Branching in PLA occurs by adding multi-functional polymerization initiators, hydroxy cyclic esters, multicyclic esters, and crosslinking by adding free radicals [14, 17, 18].

PLA has good barrier properties. The addition of nanoclay or chitosan enables the improvement of this property. Slight changes in the stereochemical composition of PLA do not affect the barrier properties, but the crystallinity affects the permeation of oxygen, nitrogen, CO_2, and CH_4. PLA is highly polar and therefore has low adhesion to polyolefins. Amorphous PLA is soluble in most common organic solvents such as ketones, THF, benzene, acetonitrile, dioxane, and chlorinated solvents. The crystalline polymer is soluble only in chlorinated solvents or benzene at elevated temperatures [14, 17, 18].

The disadvantage of melt processing of PLA is its tendency to undergo thermal degradation. It is related to the process temperature and the residence time in the plasticizing system of the extruder. Thermal degradation of PLA takes place above 200 °C. The value of this temperature is inversely proportional to the molecular weight of PLA. During the preparation of polylactide, large amounts of residual lactide can occur, which causes problems such as viscosity changes, smoke during processing, or poor final mechanical properties. Residual unreacted lactide from the polymerization can be removed by degassing. As an effect of this procedure the residual initiator leaved in the polymer accelerates its thermal degradation. It has to be deactivated, for example, by using stabilizers based on boron compounds. Thermal degradation is also influenced by many hydroxyl groups (OH), which reduces the value of the depolymerization activation enthalpy. Blocking OH groups by esterification increases the enthalpy and, at the same time, increases the temperature of the thermal decomposition. PLA degradation also depends on low molecular weight impurities and catalyst concentration. Thermal degradation of PLA occurs as a result of:

- hydrolysis by trace amounts of water,
- depolymerization,
- oxidative, random cleavage of the main chain,
- intermolecular transesterification leading to the monomer formation and oligomeric esters,
- intramolecular transesterification resulting in the formation of monomers and low molecular weight lactide oligomers.

CO, CO_2, acetaldehyde, and methyl ketene are typical PLA degradation products as an effect of internal and intermolecular transesterification, radical, and coordinated non-radical reactions. The thermal degradation of PLA can also occur due to a non-radical ester exchange reaction involving the -OH chain's ends. Depending on the structure where the reaction occurs, its product may be a lactide molecule, an oligomeric ring, acetaldehyde, and carbon monoxide. Acetaldehyde is considered non-toxic and is naturally found in many foods. In contrast, the acetaldehyde generated during the processing of PLA must be minimized, especially if PLA products (e.g., containers, bottles, and films) are used for food packaging. The release of acetaldehyde into the food can cause an unpleasant aftertaste, affecting consumer acceptance of the product. The hydrolytic, oxidative, or depolymerization degradation of PLA may sometimes occur at the processing temperature of PLA, i.e., around 185-190 °C. The elimination of water and the limitation of oxygen access reduces the occurrence of degradation. The degree of polymer crystallinity also affects the hydrolytic degradation of PLA. Highly crystalline PLA takes months and sometimes years to fully hydrolyze to lactic acid, while amorphous one decomposes within weeks. At temperatures exceeding 270 °C, homolysis of the polymer may occur. One of the mechanisms of thermal degradation, i.e., intermolecular transesterification, can be minimized by adding benzoyl peroxide [19], 1,4-dianthraquinone [20], and other stabilizers [9, 14, 17, 18].

The temperature range in which PLA can be processed is narrow (about 12 °C). It makes its processing difficult. The most common method of improving the processability of PLA is to lower the melting point by randomly incorporating small amounts of lactide enantiomers of the opposite configuration into the polymer (i.e., adding a small amount of D-lactide to L-lactide). The addition of 10% of the D-PLA enantiomer extends the processing temperature range to 40 °C. The lowering of the melting point is unfortunately accompanied by a significant decrease in crystallinity and the rate of crystallization. Melt processing of PLA causes a decrease in molecular weight due to chain breakage. An increase in crystallization during cooling is also observed with an increase in the number of injection cycles, which can be explained by the greater mobility of shorter chains. The addition of stabilizers reduces the phenomenon of crystallization during cooling, but most of the mechanical properties of PLA deteriorate too much, which often excluded its use in production conditions. The intense degradation of PLA can explain this decrease during processing, which causes defragmentation of the main chain, as evidenced are the results of rheological studies and molecular weight measurements reported in the literature [17].

PLA has a low heat deflection temperature, i.e., 55-60 °C. The use of polylactide is excluded above this temperature. This is the main reason why pure PLA cannot be used as a biodegradable replacement for engineering polymers at elevated temperatures. The more significant amount of meso-lactide in the PLA monomer contributes to the deterioration of the thermal stability of PLA and the reduction of resistance to temperature deflection (HDT) [8, 21].

Polylactide waste management

PLA products can be disposed of by mechanical recycling, composting, incineration with energy recovery, and landfilling. The appropriate choice of a specific waste management method depends on various factors, such as the local availability of waste collection and treatment facilities, requirements set out in national legislation, and public perceptions of waste management. PLA is a biodegradable polymer. Its biodegradation degree depends on temperature and humidity because these two factors promote the hydrolysis of polymer chains and thus accelerate biodegradation [6, 8].

Recycling can be chemical or mechanical. During chemical recycling, PLA is hydrolyzed at high temperatures to form lactic acid monomer and oligomers. They can be easily converted into PLA, lactide, ethyl lactate, or other lactic acid derivatives. Chemical recycling can be carried out in the presence of water in a wide temperature range (100–250 °C). The reaction rate can be increased by adding a catalyst. A typical catalyst is a strong inorganic acid, e.g., nitric acid or sulfuric acid. The residence time of PLA in the reactor for its hydrolysis is measured in hours and depends on processing conditions, such as temperature and catalyst level. The reactor conditions are adjusted to the desired molecular weight and the level of the resulting product, i.e., lactic acid. Chemical recycling is more beneficial for PLA waste management, as it produces relatively little CO_2 compared to incineration or composting. Chemical recycling is complicated and expensive, which is a downside. Mechanical recycling of PLA can be considered the least complicated and cheapest way of post-consumer recycling. However, there are contraindications regarding whether PLA can be successfully recycled due to impurities in the material stream with polymers incompatible with polylactide. To recycle PLA, it must have properties similar to existing recycled polymers or be available in sufficient quantity to achieve the required critical mass. Mechanical recycling involves the recovery, sorting, shredding, and reprocessing (i.e., melt processing) of PLA waste [6, 8].

Biodegradation is considered a natural way of recycling. PLA is biodegradable under industrial composting conditions, from the hydrolysis process to the final degradation of PLA. The final degradation results from the action of naturally occurring microorganisms at high temperatures (58 °C) and 50% relative humidity. It is a typical large-scale composting process in which biodegradable materials are broken down to produce compost: CO_2, H_2O, and minerals. There are three factors necessary for polymer biodegradation: the substrate, the environment (temperature, oxygen, and moisture), and the microorganisms (metabolic pathways and enzymes). Polymer biodegradation usually takes place in two main steps. The first step is primary biodegradation, where the polymer chain fragmentation by hydrolysis or other oxidative reaction occurs. The second step is the final biodegradation, where microorganisms break down previously formed low molecular weight polymer chains. The result of this process is carbon dioxide, water, and residual humus. Composting is the optimal solution for decommissioning PLA waste. However, there are a limited number of composting plants on the market that accept biodegradable plastics. Therefore, biodegradable plastics cannot be easily distinguished from conventional non-biodegradable plastics, making it difficult to control the quality of the material before starting the process [6, 8].

The incineration of waste is not only a practice of reducing its volume but has also evolved in treatment plants to a mode of energy recovery, realized to generate heat or electricity. Burning waste with energy recovery allows becoming independent from the use of fossil resources and other fuel sources. Waste disposal PLA by incineration recovers the energy contained in PLA, which is a CO_2 – neutral method of energy production and contributes to the conservation of mine resources. Biopolymers, including PLA, are suitable for heat energy recovery because they have calorific values comparable to cellulose-based materials and do not produce additional toxicologically critical substances during combustion [6].

POLYLACTIDE MODIFICATION

Polylactide has several disadvantages that can be overcome by modifying it. It is high stiffness and brittleness at room temperature, caused by high glass transition temperature (55–65 °C). To eliminate this drawback, the impact strength, strength and thermo-mechanical resistance of PLA should be improved. Another disadvantage is the thermal degradation of PLA. The increase in the degree of crystallinity allows the use of PLA at a higher temperature, which unfortunately has a negative impact on this polymer's ability to plastic deformation. To fully adapt PLA to the requirements posed to it, it can be subjected to the modifications such as plasticization, incorporation of fillers, blending with different polymers, copolymerization, crosslinking, surface modification by chemical and physical methods, improving the molecular weight by the addition of chain extenders as well as heterogeneous nucleation [22, 23]. Those methods are discussed below with a detailed description of nucleating PLA methods and the possible direction of preparing PLA-based composites. These two polylactide modifications are the most promising methods to obtain better thermal properties. The nucleation process increases the crystallization temperature, providing PLA with a higher degree of crystallinity. These changes also improve the value of heat deflection temperature (HDT), which is very low for PLA (50–60 °C) [4, 59, 60]. The other way to enhance the thermal properties of polylactide is to incorporate powder and fiber fillers. The addition of fillers can also improve the HDT, thermal stability, and generally the thermomechanical properties.

Plasticization

This modification method allows lowering the glass transition temperature of polymers in the amorphous and partially crystalline state. Effective PLA plasticizers are citrate esters, triacetin, and polyoxyethylene (PEG). The use of triethyl, tributyl, acetyltriethyl, and acetyl tributyl citrate in the amount of 10–30 wt% reduces the T_g to a minimum of 14 °C and increases the elongation at break-even up to 600% [24]. PEG use in the amount of 5 and 10 wt% reduces the glass transition temperature and the cold crystallization temperature. Plasticization is much more efficient for amorphous PLA, but the partially crystalline material's plasticity can also be significantly improved. With the increase in the number of plasticizers, a decrease in the stress value at the yield point is observed [23, 25].

Blending of PLA with thermoplastic polymers

Blending polymers is an effective, simple, and versatile method of developing new materials with tailored properties without synthesizing new compounds. By mixing different polymers (biodegradable and non-biodegradable) with PLA, you can achieve the desired combination of properties and even new properties that arise due to the interaction between the components of the polymers. Biodegradable polymers that bind to PLA are: poly(ethylene oxide) PEG [26], poly(β-hydroxybutyrate) PHB [27], poly(ε-caprolactone) PCL [28], poly(1,4-butylene adipate 1,4-butylene-co-terephthalate) PBAT [29], chitosan [30] and starch [31]. Rheological tests have shown that PLA/PCL mixtures have good thermal stability, which is an important property of polymers in the context of the extrusion process [28]. The non-biodegradable polymers blended with PLA are: LDPE low-density polyethylene [32], PVA poly(vinyl acetate) [32] and PP polypropylene [34]. PLA/PP mixtures have much better resistance to biodegradation and hydrolysis and a better ability to dye with dispersed dyes [22].

Copolymerization

The carboxyl and hydroxyl groups of lactic acid allows the formation of copolymers with other monomers. This phenomenon is possible through polycondensation with monomers such as ε-caprolactone [35], which leads to the formation of low molecular weight copolymers. It is also possible through the ring-opening copolymerization of lactide with cyclic monomers such as glycolide [36], δ-valerolactone [37], and carbonate trimethylene [38] as well as with monomers such as ethylene oxide (EO) [39] to produce high molecular weight copolymers. Due to biodegradability and good biocompatibility, PEG-PLA block copolymers can be produced in the form of nanoparticles used for drug transport. By adjusting the molecular weight of PLA and PEG and the PEG/PLA ratio, block copolymers may have increased drug delivery efficiency and reduced transport particle sizes [39]. PLA-PCL-PLA block copolymer has a higher ability to degrade than PCL homopolymer. The degradation of PLA segments leaves behind PCL-rich crystalline polymer residues that require a much longer time to resorb [35].

Crosslinking

Crosslinked PLA structures can be achieved by irradiation or chemical reactions. Electron beam and γ radiation are widely used to crosslink PLA in the presence of small amounts of crosslinking agents such as triallyl isocyanurate (TAIC). Due to crosslinking, the thermal stability of PLA can be significantly increased. Crosslinking mixtures of L-PLA and D-PLA may result in obtaining stereocomplexes with low molecular weight. Radiation crosslinked stereocomplexes are resistant to alkaline hydrolysis and enzymatic degradation because the alkaline solution does not attack the crosslinked polymer structure. Unfortunately, irradiation instrumentation is expensive, and PLA samples must be thin to absorb enough energy from the radiation to initiate the crosslinking reaction. This causes a significant limitation in applying this method in industrial practice [22, 40, 41].

Surface modification

The surface properties of materials play a crucial role in determining their application. The presence of specific chemical surface properties such as hydrophilicity, roughness, surface energy, and topography are critical to the biomedical applications of PLA and its interaction with biomacromolecules. One of the simplest methods of surface modification of polymers is the application of coatings. PEG coatings on PLA delay the phagocytosis of PLA nanoparticles and extend the circulation time of nanoparticles inside the living organism during drug transport [22, 42]. Plasma treatment is widely used to improve the hydrophilicity and affinity of cells to the PLA surface. The apparent advantages of plasma treatment over other surface modification methods include its ability to control surface structure, energy, and charge. Another advantage is to uniformly modify the surface without affecting the bulk properties [43]. Functional groups such as -NH_2, -COOH, and -OH, which tend to form covalent bonds with other materials for further modification, are most often introduced by plasma treatment [44]. The surface of polymeric materials can also be modified by chemical modification. The first step of chemical modification is usually surface hydrolysis (with base) or aminolysis. Hydrophilic –COOH and –OH groups or reactive –NH_2 groups are formed on the surface by cleavage of ester bonds [22].

Incorporation of chain extenders

In order to obtain a wider range of PLA processing and thus extend the scope of its application, the strength of polylactide should be improved. Modification by achieving a branched structure with high molecular weight is an effective method to increase polylactide strength. There are several ways to branch PLA. One of them is solution polymerization using a free radical initiator and functional group reaction. Functional group reactions tend to form long-chain branched structures more efficiently than the branching results from free radical reactions. Chain extension reactions are used to increase the strength of linear polymers and to increase the molecular weight. An advantage of using functional group chain extenders is that the degraded chains are reattached to each other. In polyesters such as PET and PLA, chain lengthening causes an increase in molecular weight. It is caused by the bridging of reactive hydroxyl or carboxyl groups with di- or multi-functional molecules. The most commonly used chain extenders with different functional groups are di- and multi-functional epoxides [45], diisocyanates [46], and dihydrochlorides [47]. Rheological studies have shown that Joncryl 4368-C (polyfunctional epoxide) and pyromellitic dianhydride (PMDA) improve the storage modulus, complex viscosity, molecular weight, and tensile properties of PLA. It is due to the formation of long-chain branched structures [45, 48].

Heterogeneous nucleation

The polymer nucleation process increases the crystallization temperature, which shortens the processing time of the material. This modification also causes the polymer to crystallize in a specific state of macromolecule orientation. The appropriate selection of a heterogeneous nucleating agent is responsible for this. Thanks to its addition and effect on the polymer, the polymer crystallization effect is obtained in a specific crystallographic system. It usually also causes an additional change in material properties. The nucleation of crystallizing polymers shortens the processing time in injection molding and reduces spherulite's average size. It means that the addition of a nucleating agent improves the mechanical properties and reduces the haze of the compacts [49÷51].

Although PLA is a crystalline polymer, no crystallization is observed at the higher cooling rates. As a result, the products' heat resistance and heat deflection temperature (HDT) is very low, around 50-60 °C. Pure PLA is limited to single-use devices that do not require resistance to elevated temperature [4, 59, 60].

The introduction of a nucleating agent to PLA increases the primary nucleation in this polymer. Layered silicates such as talc [52], montmorillonite [53], and fluorine mica [54] are used as nucleating agents. The use of talc gives the highest efficiency of nucleation compared to other inorganic fillers. Talc can nucleate crystallization on the surface of its grains and disperse well in the polymer. Talc nucleates the crystallization of polymers through an epitaxial mechanism. The content of a minimum of 0.5 wt% talc causes the intensification of crystallization while cooling the sample. Nanometric inorganic salts [55] or carbon materials [56] can also be used as nucleating agents. Another group of materials used as nucleating agents is synthetic inorganic compounds, for example, WS_2 nanotubes [67] zinc phenylphosphonate [58], cadmium phenylmalonate [59], and MgO whiskers [60]. These inorganic nucleating agents have a substantial crystallization-promoting effect of PLA. They are not suitable for industrial applications as surface modification is often required to increase the compatibility between the inorganic nucleating agents and the polylactide. This phenomenon makes the process longer, more complex, and expensive. Other synthetically obtained compounds are organic compounds such as bis-urea derivatives [61], benzoyl hydrazine derivatives [62], polyhedral oligomeric silsesquioxane derivatives [63], 1H-benzotriazole derivatives [64]. Compared to their inorganic counterparts, they show excellent compatibility with PLA, making organic nucleating agents more advantageous to use. Due to the synthesis of more organic nucleating agents, the relationship between the organic groups and the nucleation efficiency is being explored in more detail. High molecular weight poly (D-lactic acid) can also be used as the nucleating agent. As the content of D-PLA increases, stereocomplexes are formed more efficiently, which act as nucleation sites. This modification effectively increases the number of L-PLA spherulites and the overall rate of crystallization [23, 65÷67]. Table 3 shows the influence of some of the above mentioned nucleating agents on the PLA crystallization process.

The first mentioned nucleating agent analyzed is talc, which has excellent nucleating properties. As a result, after its addition, the degree of crystallinity of PLA increases. In both publications listed in Table 3, the same percentage of talc causes a different increase in the degree of crystallinity X_c. In one case, the addition of 20 wt% talc causes an increase in the degree of crystallinity by 23% [52], and in the second - by 10.8% [70] compared to pure PLA. Finally, in both cases, the value of the degree of crystallinity is similar. It is 25% for the first example [52] and 20.8% for the second [70]. The difference in this increase may be due to the different ways of producing the samples. In the first case, the samples were pressed under a load of 10-12 tons at the temperature of 180 °C. In the second case, they were injected at the die temperature of 190-196 °C. The difference in this result is also caused by the way the DSC test was carried out. In the second case, the crystallinity was determined while heating the samples. In both analyzed cases, the common denominator is lowering the cold crystallization temperature [52, 70].

Nanonucleating agents used as an additive to PLA are WS_2 nanotubes. The addition of 1 wt% causes an increase in the crystallinity of 30.8% compared to pure PLA. The addition of 1 wt% also causes a decrease in the temperature of cold crystallization [57]. Another highly effective nano-nucleating agent is polyhedral oligomeric silsesquioxane derivatives. In the analyzed publication [63], aminopropyl-isobutyl POSS was used. As the content of this nucleating agent increases, the degree of crystallinity of PLA increases too. The addition of 10 wt% POSS derivative

Table 3. The influence of the addition of nucleating agents on the PLA crystallization process

PLA matrix/ grade	Nucleating agents type and concentration	Change in the degree of crystallinity (X_c) compared to pure PLA	Cold crystallization changes (T_{cc})	Cooling conditions	References
PLA HM1011	10 wt% talc	+ 23 percentage point (p.p.)	Lowering the cold crystallization temperature from 127 ℃ for PLA to 96 ℃ PLA + 10 wt% talc	DSC 10 ℃/min	[52]
	20 wt% talc	+ 23 p.p.			
	30 wt% talc	+ 25 p.p.			
PLA 3001D	2 wt% talc	+ 7.9 p.p.	Lowering the cold crystallization temperature from 115.9 ℃ for PLA to 92.9 ℃ for PLA + 20 wt% talc	X_c and T_{cc} were determined during the heating of the samples	[68]
	5 wt% talc	+ 5.4 p.p.			
	10 wt% talc	+ 2.3 p.p.			
	20 wt% talc	+ 10.8 p.p.			
PLLA 24	0.5 wt% nanotubes WS_2	+ 30.8 p.p.	Lowering the cold crystallization temperature	DSC 10 ℃/min	[67]
PLA 2022D	1 wt% POSS	+ 1 p.p.	Lowering the cold crystallization temperature	DSC 10 ℃/min	[63]
	3 wt% POSS	+ 9.3 p.p.			
	10 wt% POSS	+ 11.2 p.p.			
PLA 2500HP	1 wt% LAK	+ 17.3 p.p.	The disappearance of cold crystallization	DSC 10 ℃/min	[69]
PLA 3001D with 1.5% D-lactide	0.25 wt% LAK	+ 34.2 p.p.	The disappearance of cold crystallization	DSC 5 ℃/min	[70]
	0.5 wt% LAK	+ 34.5 p.p.			
	0.75 wt% LAK	+ 37.7 p.p.			
	1 wt% LAK	+ 40.2 p.p.			

causes an increase of X_c by 11.2% over pure PLA. A decrease in the cold crystallization temperature is also observed [63].

The last analyzed nucleating agent is LAK-301, i.e., the potassium salt of 3,5-bis(methoxycarbonyl) benzenesulfonate. In the first publication, an addition of 1 wt% caused an increase of X_c by 17.3% [69]. The same amount of LAK-301 caused increases by 40.2% [70] against pure PLA in the second publication. However, this finally gives very similar values of crystallinity of PLA. The first example is 47.9% [69] and in the second 50.8% [70]. The difference in the amount of growth is due to the dissimilarity in the crystallinity of pure PLA. This difference is caused by various sample injection temperatures and different cooling rates during the DSC test. In both cases, the use of 1 wt%. LAK-301 causes the disappearance of the cold crystallization peak on the DSC curve [69, 70].

Polylactide composites

Polylactide has many desirable characteristics such as high tensile strength and high stiffness, but on the other hand, it also has many disadvantages:

- low flexibility, ductility, and toughness,
- low heat deflection temperature (HDT),
- low crystallization rate,
- high sensitivity to moisture,
- reduced resistance to hydrolysis.

Many modification techniques can be used to improve the properties of PLA. One of them is the addition of reinforcements and various phases dispersed in the polymer matrix. This technique includes reinforcement with powder or fibrous fillers. Depending on the filler used, it is possible to obtain different final properties of the composites [71].

PLA composites reinforced with particle shaped fillers

The main purpose of adding particle-shaped fillers to polymers is to lower the material's cost and modify the physical, rheological, and optical properties. If the fillers do not make worse the molecular, thermal, and mechanical properties of PLA, their use can effectively reduce costs. It also can improve mechanical properties, e.g., increasing the stiffness at room temperature or elevated temperature. It is evident in the case of PLA grades that provide a high degree of crystallinity. PLA can form composites filled with both micro- and nanofillers [71]. In industrial practice and in the literature, the use of inorganic fillers such as calcium metaphosphate [72], calcium carbonate [73], montmorillonite [74] and carbon nanotubes [75] has also been reported. The presence of montmorillonite (nanoclays) stiffens PLA and improves barrier properties [22, 23]. The addition of fillers may also affect the flammability of the polylactide. A PLA flame retardant study showed that the addition of two commercial organically modified phyllosilicates, Bentone 104 and Cloisite 30B, reduced the flammability of these highly filled composites. The use of these organically modified layered silicates leads to a ceramic protective surface layer formation during combustion. The thermally stable ceramic surface layer can act as a heat shield and barrier against the transfer of heat and oxygen from the flame to the material and the degradation products from the material to the flame [77]. The examples which have better thermal properties include the use of the following materials. Mechanical properties of the composites reinforced with particle shaped fillers are also discussed.

Hexagonal Boron Nitrile

Polylactide composites reinforced with h-BN are a combination of an organic matrix and inorganic filler. Added hexagonal boron nitrile has an averaged particle size of 1.5 μm. PLA composites containing 5% of h-BN were prepared by mixing in a molten state and compression molding. The addition of h-BN increased the crystallization rate of these composite. The percentage crystallinity of PLA containing h-BN is higher than for neat PLA. The percentage crystallinity of PLA/h-BN composite is 8.1% in the first DSC scan and 2.1% in the second. For neat PLA, the degree of crystallinity is 3.2% in the first DSC scan, and in the second one, the melting peak of PLA disappeared. The modulus of elasticity increased after the addition of h-BN in the PLA matrix, but tensile strength decreased. The addition of these particles also improves the heat deflection temperature (HDT) but only by 4.3 °C. This filler can be considered as one which improves the thermal properties of PLA [78].

Carbon fillers

Polylactide is used as a matrix in carbon micro- and nanocomposites containing carbon fillers of various geometries. Such composites exhibit increased crystallinity, favorable mechanical and thermal properties, increased flame resistance, and adapted electrical and thermal conductivity. Graphite or graphene fillers are suitable for applications where high stiffness, thermal stability, increased thermal conductivity, antistatic properties, and resistance to abrasive wear are required. Expanded graphite (EG) are micrometric fillers that also can be blended with PLA. Depending on the amount of filler, PLA-EG composites have better properties than unmodified PLA. These composites have higher stiffness, as evidenced by Young's modulus values assessed in tensile tests, modified crystallization kinetics, a moderate increase in thermal stability, and antistatic properties for electric current conduction [71].

Halloysite nanotubes

Halloysite nanotubes (HNT) are a natural aluminosilicate ($Al_2Si_2O_5(OH)_4 \cdot nH_2O$) that has a tubular structure in the submicrometer range and a high aspect ratio. Halloysite nanotubes are commonly used as bioreactors, polymer degradation catalysts, matrices, and ceramics referred to as "high-tech". In recent years, HNT has been appreciated as one-dimensional nanofillers for polymers. They are cheap, widely available, environmentally friendly, mechanically robust, and biocompatible. Polymer nanocomposites with HNT show a significant increase in mechanical and thermal properties. The addition of HNT improves tensile strength and flexural strength. The improvement of these properties is directly proportional to the amount of nanofiller in composites. For example, the tensile strength, flexural strength, and flexural modulus of nanocomposites with 30 pph HNT of PLA were respectively 74.1 MPa, 108.2 MPa, and 6.56 GPa. It means that they were 34%, 25%, and 116% higher than in the case of pure PLA. Most powder fillers degrade tensile strength, but this is different in this case. The addition of HNT also increases the Vicat softening point by approx. 8 °C for the composite with 40 wt% HNT up to 100 wt% PLA compared to pure PLA. This result may be the basis for considering halloysite nanotubes as a filler improving thermal resistance of polylactide [79].

Basalt powder

Basalt is an inorganic mineral whose deposits are located in Europe, including Poland. This mineral can be formed into fibers and finely ground powder. Basalt has excellent abrasion, chemical, and wear resistance. Therefore, it offers the possibility of finding new ways of using basalt, e.g., as a filler for polymer composites. The addition of basalt powder (BP) to the iPP matrix composite increases Young's modulus from 1.51 GPa for pure iPP to 2.41 GPa with the addition of 40 wt% BP. The tensile strength of these composites has deteriorated. However, the heat deflection temperature increased. Basalt powder as a filler in polymer composites improves mechanical and thermomechanical properties. So, its use in the PLA composites seems to be justified. Basalt powder is a natural material and a waste product of basalt mining. After the biodegradation of the polymer matrix, the remaining basalt has a neutral effect on the environment. It can be used as a soil fertilizer. The addition of basalt powder to PLA reduces the tensile strength of the composite but increases its stiffness, which is typical behavior for thermoplastic composites reinforced with micrometric inorganic particulate filler. As the amount of basalt powder increases, the heat deflection temperature (HDT) and the degree of crystallinity increase [69, 90].

Fiber-reinforced PLA composites

Natural fibers are the most commonly used reinforcement for PLA. This is due to the lower cost compared to synthetic fibers, low density, high specific strength, and stiffness. The addition of natural fibers allows the production of biocomposites. The mechanical properties of the fiber-reinforced composite depend on the type of polymer matrix, the type of fiber (including type, extraction method, aspect ratio, and additional surface treatment), fiber content, the composite manufacturing process, dispersion and orientation of the fibers in the matrix, and their compatibility with the selected polymer. Fibrous fillers are used to increase the thermal stability, hydrolytic resistance, or mechanical properties of PLA shaped by injection or pressing processes. Examples of used organic fillers: jute [81], flax fiber [82], bamboo fibers [83], or microcrystalline cellulose [84]. Improving the mechanical properties of PLA composites reinforced with natural fibers is critical to minimizing their cost, adjusting biodegradability, and extending the scope of application. One of the most significant disadvantages of using natural fibers for polymer composites' production is their hydrophilic nature. Polylactide is very sensitive to hydrolysis. It is necessary to thoroughly dry the PLA and the fibers before shaping them in a molten state. Pre-treatment of the surface of natural fibers is required to increase the hydrophobicity and reduce water absorption (due to many hydroxyl groups on their surface). The most commonly used chemical surface treatment is modifying the fibers with alkali, acetyl, silane, acryl, permanganate, peroxide, isocyanate, titanate, or zirconate [71]. Examples of composites reinforced with fiber fillers showed below discussed the ways of enhancing thermal properties of PLA and nucleating properties with those fibers. The mechanical properties of these comopsites are also presented below.

Flax fibers

Flax-filled polylactide composites can successfully replace polypropylene (PP) based composites reinforced with flax fibers, which are often used in the automotive industry. The tensile strength and Young's modulus of PLA-flax composites have a higher value than PP-flax composites. Pure PLA has higher mechanical properties than PP. Pure PLA's tensile strength and modulus of elasticity are 50 MPa and 3.4 GPa, respectively, compared to 28 MPa and 1.3 GPa for PP. The addition of flax fibers causes a significant increase in the modulus of elasticity. After the addition of 30% of flax fibers the value of the modulus of elasticity is higher for PLA composites than PP composites. The tensile strength does not change significantly for PLA composites due to poor adhesion between the flax fibers and the polymer matrix. As a result, stresses are not transferred efficiently from the matrix to fibers with high stiffness and mechanical strength. The use of flax fibers as PLA fillers also improves the thermal properties of the composite. The glass transition temperature for pure PLA is approx. 50 °C, and after adding flax fibers, and it increases even to 60 °C [71, 85].

Hemp fibers

The use of hemp fibers in polylactide composites increases the tensile strength and Young's modulus, which increases the number of fibers into the composite structure. It is caused by the good adhesion and efficiency of stress transfer between the hemp fibers and the PLA matrix. The tensile strength of single hemp fiber is approx. 443 MPa and Young's modulus is approx. 23 GPa. Tensile strength and Young's modulus of PLA composite with 30 wt% natural fiber are respectively 65.92 MPa and 7.0 GPa. Combining the PLA matrix with hemp fiber causes a decrease in elongation at break with an increase in the amount of filler. It is due to their high brittleness. The addition of hemp fibers also increases the composite's degree of crystallinity due to hemp's effect as a nucleating agent. Hemp fibers can be modified to increase adhesion to the matrix. The modification is carried out with 5% sodium hydroxide solution and 0.5 wt% 3 - (2 - aminoethyl amino)propyltrimethoxy silane coupling agent in acetone. The use of both agents and their combination increases the tensile strength and Young's modulus of composites compared to composites with unmodified fibers. This shows that the matrix is correctly connected with the fiber. PLA composites exhibit the highest tensile strength and Young's modulus with hemp fibers modified with 5% sodium hydroxide solution. Fiber modification also increases the degree of crystallinity of the composite. In composites with modified fibers, a decrease in elongation at break is observed to increase with rising filler content [86, 87].

Glass and carbon fibers

Glass fiber (GF) reinforced PLA composites can partially overcome the disadvantages of unmodified PLA. Their mechanical and thermal properties allow them to be used as an eco-friendly alternative to petroleum-based reinforced plastics such as polypropylene and polyamide. The higher glass fiber content in polylactide, the more distinct tensile and flexural strength of the composite. The addition of glass fibers also significantly improves the heat deflection temperature (HDT) and impact strength. It was proved that the modulus of elasticity with the addition of 30 wt% GF is 6.7 GPa, which is an increase of this property by 145% compared to pure PLA. On the other hand, the addition of glass fibers has an unfavorable effect on the crystallization process. The addition of 30 wt% GF decreases the degree of crystallinity and the crystallization temperature. Another inorganic fiber added as reinforcement to PLA composites is carbon fiber (CF). It has excellent tensile strength, low density, high thermal and chemical stability, and good thermal and electrical conductivity. The addition of 25 wt% of glass fibers increases the modulus of elasticity by more than 20 GPa compared to pure PLA. PLA - CF composites are used in biomedical and special engineering applications [71, 88, 89].

Cellulose

Cellulose is the most common biomass material in nature. Cellulose fibers can be obtained from the recycling of regenerated wood fibers. Cellulose reinforced polymer composites are gaining ground due to their lightness, biodegradability, non-toxicity, low cost, and structural reinforcement. From the point of view of cellulose-reinforced polymers in industrial use, one of the greatest disadvantages is the hydrophilicity of these fibers. It leads to a weak bond between the matrix and the reinforcement. This results in a reduction of mechanical properties. In the case of PLA, this high tendency to absorb water by cellulose fibers is much more dangerous. It can lead to the degradation of the polymer at high temperatures. PLA - cellulose fibers composites can be successfully used in the automotive industry. After adding 2.5 wt% cellulose to polylactide, a decrease in the storage modulus value in the glassy state can be observed. In the thermomechanical curves showing changes in the damping factor (tanδ), it can be observed that the addition of cellulose in the PLA matrix significantly modifies the relaxation phenomenon and PLA crystallinity. These results suggest that fibers' addition may lead to mechanical strengthening, but not as well as expected. Probably due to insufficient adhesion at the fiber-matrix interface and/or the absence of appropriate chemical bonds. On the other hand, these fibers strongly modify the molecular mobility of PLA macromolecules, which leads to changes in the crystallization of the polymeric matrix. Tests carried out on composites with CreaMix TC 1004 cellulose fiber show that the tensile strength decreases with simultaneous enhancement of the modulus of elasticity with an increase in the filler content. With the increase in the number of fibers, the impact strength of the composite also decreases. This may be due to insufficient adhesion of the fibers to the matrix. An increase in the degree of crystallinity of PLA is observed in composites containing up to 20 wt% celluloses [71, 90, 91].

Basalt fibers

The addition of basalt fibers (BF) to polylactide composites strengthens them. It is much greater than in the case of composites filled with plant fibers. Modulus of elasticity and tensile strength increase with an increasing amount of basalt fibers. Composites with the addition of 30 wt% basalt fibers have the highest tensile strength and modulus of elasticity. Further increasing the amount of filler does not significantly change these properties. The tensile strength of polylactide composites with 30 wt% of basalt fibers is 119.7 MPa, and the elastic modulus is 7.62 GPa. The low impact strength of pure PLA has improved thanks to the addition of basalt fibers. Charpy impact strength without and with a notch increases from 23 to 38.4 kJ/m^2 and 2.7 to 9.5 kJ/m^2 for samples after the addition of 40 wt% fibers. Moreover, basalt fibers show a defined interaction efficiency as a PLA nucleating agent, both at high and low cooling rates. During faster cooling, the highest crystallinity degree is obtained for samples containing 20 wt% of the fibers. Further increase in their amount does not increase the degree of crystallinity. During slow cooling, a much higher degree of crystallinity is obtained, and for samples with a content of more than 20 wt% BF is obtained the highest possible crystallinity for PLA. Due to the ability to nucleate PLA with basalt fibers, it is possible to obtain significant crystallinity during continuous injection production. This will allow the production of PLA with a high heat deflection temperature. The increasing quantity of natural basalt fibers increases the PLA storage modulus. This increase is linear in the range from 0 to 40 wt% of BF. An increasing amount of fibers increases the storage modulus in the temperature range above Tg, thus the value of the heat deflection temperature increases.

In summary, the heat deflection temperature is strongly delayed by the use of basalt fibers. It can be explained by increasing the storage modulus and crystallinity due to the nucleating effect induced by inorganic filler. The addition of basalt fibers improves the properties of the samples obtained at different temperatures of compression molding. When a higher processing temperature is applied, the glass transition temperature value of the PLA-based composite increases significantly. The high crystallinity observed for the samples produced at the processing temperature of 170 °C was a consequence of the incomplete melting of the matrix. The high crystallinity of the samples is only due to the lack of complete fusion of the crystalline domains formed during the cold crystallization of the polymer. This phenomenon is confirmed by the low glass transition temperature observed during thermomechanical tests (DMA). The highest degree of crystallinity was observed for samples prepared at 200 °C [92, 93].

Hybrid composites

The word “hybrid” has a Greek-Latin origin and can be found in many areas of science. In polymer composites, hybrid composites are those in which one type of reinforcing material is incorporated into a mixture of different polymers. Another definition is that either two or more reinforcing materials are present in a single matrix, or both options are combined [94].

Filled with basalt and carbon fibers

Hybrid PLA composites filled with basalt and carbon fibers with a density of 7.5 and 12.5 wt% were injected into a cold mold to prevent crystallization and, at the same time, significantly reduce cycle times. A part of the samples obtained in this way was heat-treated. This operation requires keeping PLA-based parts in the oven at the temperature of 100 °C for 45 minutes. The annealed samples do not show cold crystallization after the first heating cycle during the DSC test. Therefore, heat treatment is fully justified. Composite samples have a lower cold crystallization temperature than untreated PLA. Fibers play the role of nucleating agents, accelerating the crystallization process’s initiation, but they do not significantly affect the degree of crystallinity of composites compared to unreinforced materials. The presence of the crystalline phase provides physical blocking of deformations and the synergistic effect with reinforcement fibers. The addition of fibers reduces the possibility of movement of the amorphous phase macromolecules and contributes to a significant increase in heat resistance. Comparing the mechanical properties of hybrid composites with the literature data for PLA composites with basalt [92] and glass [88] fibers, it can be concluded that hybrid composites are characterized by more favorable mechanical properties, such as higher modulus of elasticity [95].

Filled with hemp and sisal fibers

Another example of a hybrid composite is the composition of polylactide with hemp and sisal fibers. The content of fibers in this composite is 15 wt% each. The tensile strength of these composites is 46.25 MPa, while the modulus of elasticity increases by 43% compared to pure PLA, which gives 6.1 GPa. This fully biodegradable composite’s mechanical properties allow it to replace other polymers previously used in the automotive industry, such as glass fiber reinforced polypropylene. The combination of these two fibers to reinforce PLA composites also increases their impact strength. Its value varies between 9.21–11.08 kJ/m^2 when for pure PLA, it is 6.4 kJ/m^2. The thermomechanical properties of these composites, such as changes in the storage modulus (E'), loss modulus (E") and damping factor (tanδ), show that there are significant differences in the degree of molecular mobility. The ratio of E' to E" turned out to be higher for hybrid composites than for PLA in the entire spectrum of the tested temperature. The glass transition temperature (Tg) increased from 50 °C for PLA to 80 °C for composites [96].

Filled with jute fiber based on a mixture of polylactide (PLA) and polycaprolactone (PCL)

This example of a hybrid composite is based on the definition that hybrid composites are materials reinforced by one type of filler in a matrix of a mixture of different polymers. In this case, the matrix is a mixture of two biodegradable polymers PLA and PCL. Composite samples contain 50 wt%. jute fiber and different PCL content (0, 5, 10 and 15%). They were made by hot pressing prepregs prepared by solvent impregnation. In one of the samples based only on PLA, a jute fiber modified with a silane coupling agent was added. The composite containing modified fibers has higher tensile strength and modulus of elasticity than the unmodified fiber-reinforced series. The addition of PCL biodegradable polymer to PLA reduced the tensile strength and modulus of the composites' elasticity. The modulus of elasticity of the samples with 5%, 10, and 15 % of PCL was 6.9, 6.5 GPa, and 5.5 GPa, respectively. It decreases by approximately 5%, 11%, and 24%, respectively. The tensile strength value also declines with increases in PCL content. It drops by 4%, 9%, and 19%, respectively. This phenomenon is due to PCL's low stiffness and incompatibility between composites' components. The addition of PCL to the matrix has some advantages. It increases the impact strength of the composite. The impact strength for samples with 5% PCL is 46 kJ/m^2, with 10% it is 58 kJ/m^2, and for samples with 15%, it is 62 kJ/m^2. It increases by 24%, 57%, and 67%, respectively compared to only PLA-based composite. The modification of jute fibers also positively affects the degree of crystallinity of the composite, increasing it by 9%. On the other hand, the increasing content of PCL in the matrix reduces the glass transition temperature, crystallization enthalpy, melting enthalpy, and hybrid composites' crystallinity. This is due to the higher molecular mobility of the PCL phase in the PLA/PCL mix. It is also confirmed by studies of dynamic mechanical properties [97].

CONCLUSIONS

A significant number of research studies on the synthesis, production, and modification of polylactide (PLA) are presented and discussed herein. Referring to the presented studies, it can be stated that the most significant disadvantages of polylactide, resulting from its structure and chemical structure, can be adequately eliminated through the use of comprehensive modification methods. The discussed numerous possibilities of improving selected properties, including mechanical and thermomechanical ones, can be obtained by various methods; therefore, the application scope can be increased not only on a laboratory scale but also during technological works in industrial production conditions.

Acknowledgment

The results presented in this paper were partially funded with grants for education allocated by the Ministry of Science and Higher Education in Poland executed under the subject of No 0513/SBAD/4720.

REFERENCES

1. Penczek S, Pretula J, Lewinski P. Polimery z odnawialnych surowców, polimery biodegradowalne. Polimery/Polymers. 2013; 58(11–12): 835–46.
2. Directive (EU) 2018/852 of the European Parliament and of the Council of 30 May 2018 amending Directive 94/62/EC on packaging and packaging waste.
3. Łopot D., M. Siołek, S. Maślanka, and Ł. Hamryszak, Zastosowanie odpadów z przemysłu mleczarskiego do produkcji polimerów biodegradowalnych. Chemik, 2014, 68(8), 703–709.
4. Gruber P. and M. O'Brien, Polylactides' NatureWorks® PLA. Biopolym. Online, 2002, 235–239, doi: 10.1002/3527600035.bpol4008.
5. Vink E.T.H. and S. Davies, Life Cycle Inventory and Impact Assessment Data for 2014 Ingeo® Polylactide Production. Ind. Biotechnol., 2015, 11(3), 167–180, doi: 10.1089/ind.2015.0003.

6. Vink E.T.H. et al., The sustainability of nature works™ polylactide polymers and ingeo™ polylactide fibers: An update of the future. Initiated by the 1st International Conference on Bio-based Polymers (ICBP 2003), November 12-14 2003, Saitama, Japan. Macromol. Biosci., 4(6), 551–564, 2004, doi: 10.1002/mabi.200400023.
7. Żenkiewicz M. and Richert Józef, Synteza, właściwości i zastosowanie polilaktydu, Przetwórstwo Tworzyw, 8, 192–199, 2009.
8. Castro-Aguirre E., F. Iñiguez-Franco, H. Samsudin, X. Fang, and R. Auras, Poly(lactic acid)—Mass production, processing, industrial applications, and end of life. Adv. Drug Deliv. Rev., 107, 333–366, 2016, doi: 10.1016/j.addr.2016.03.010.
9. Gołębiewski J., E. Gibas, and R. Malinowski, Wybrane polimery biodegradowalne - otrzymywanie, właściwości, zastosowanie. Polimery, 3(11), 799–807, 2008.
10. Vink E.T.H., D.A. Glassner, J.J. Kolstad, R.J. Wooley, and R.P. O'Connor, The eco-profiles for current and near-future NatureWorks® polylactide (PLA) production. Ind. Biotechnol., 3(1), 58–81, 2007, doi: 10.1089/ind.2007.3.058.
11. Vink E.T.H., K.R. Rábago, D.A. Glassner, and P.R. Gruber, Applications of life cycle assessment to NatureWorks™ polylactide (PLA) production. Polym. Degrad. Stab., 80(3), 403–419, 2003, doi: 10.1016/S0141-3910(02)00372-5.
12. Morão A. and F. de Bie, Life Cycle Impact Assessment of Polylactic Acid (PLA) Produced from Sugarcane in Thailand. J. Polym. Environ., 27(11), 2523–2539, 2019, doi: 10.1007/s10924-019-01525-9.
13. Foltynowicz Z. and P. Jakubiak, Poli(kwas mlekowy) – biodegradowalny polimer otrzymywany z surowców roślinnych. Polimery, 47(11–12), 769–774, 2002.
14. Lim L.T., R. Auras, and M. Rubino, Processing technologies for poly(lactic acid). Prog. Polym. Sci., 33(8), 820–852, 2008, doi: 10.1016/j.progpolymsci.2008.05.004.
15. Luminy ® PLA neat resins Luminy ® PLA neat resins PLA bioplastics for a brighter future, 2011.
16. Garlotta D., A Literature Review of Poly (Lactic Acid) A Literature Review of Poly (Lactic Acid). J. Polym. Environ., 9(2), 63–84, 2019.
17. Farah S., D.G. Anderson, and R. Langer, Physical and mechanical properties of PLA , and their functions in widespread applications – A comprehensive review. pp. 26, 2016.
18. Hartmann M.H., High Molecular Weight Polylactic Acid Polymers. Biopolym. from Renew. Resour., 367–411, 1998, doi: 10.1007/978-3-662-03680-8_15.
19. Siiderg A. and J.H. Niisman, Stabilization of poly(L-lactide) in the melt. Polym. Degrad. Stab., 46, 25–30, 1994.
20. McNeill I.C. and H.A. Leiper, Degradation studies of some polyesters and polycarbonates-2. Polylactide: Degradation under isothermal conditions, thermal degradation mechanism and photolysis of the polymer. Polym. Degrad. Stab., 11(4), 309–326, 1985, doi: 10.1016/0141-3910(85)90035-7.
21. S. Spinella et al., Polylactide/cellulose nanocrystal nanocomposites: Efficient routes for nanofiber modification and effects of nanofiber chemistry on PLA reinforcement. Polymer (Guildf), 65, 9–17, 2015, doi: 10.1016/j.polymer.2015.02.048.
22. L. Xiao, B. Wang, G. Yang, and M. Gauthier, Poly (Lactic Acid)-Based Biomaterials: Synthesis, Modification and Applications. 2012.
23. Gałęski A., E. Piórkowska, M. Pluta, Z. Kuliński, and R. Masirek, Modyfikacia fizycznych właściwości polilaktydu. Polimery, 50, 7–8, 2005.
24. Labrecque L.V., R.A. Kumar, V. Davé, R.A. Gross, and S.P. Mccarthy, Citrate esters as plasticizers for poly(lactic acid). J. Appl. Polym. Sci., 66(8), 1507–1513, 1997, doi: 10.1002/(SICI)1097-4628(19971121)66:8<1507::AID-APP11>3.0.CO;2-0.
25. Gadzinowska K., Z. Kuliński, and E. Piórkowska, Plastyfikacja polilaktydu. Polimery, 54(2), 83–90, 2009.
26. Younes H. and D. Cohn, Phase separation in poly(ethylene glycol)/poly(lactic acid) blends. Eur. Polym. J., 24(8), 765–773, 1988.
27. Abdelwahab M.A., A. Flynn, B. Sen Chiou, S. Imam, W. Orts, and E. Chiellini, Thermal, mechanical and morphological characterization of plasticized PLA-PHB blends. Polym. Degrad. Stab., 97(9), 1822–1828, 2012, doi: 10.1016/j.polymdegradstab.2012.05.036.
28. Patrício T. and P. Bártolo, Thermal stability of PCL/PLA blends produced by physical blending process. Procedia Eng., 59, 292–297, 2013, doi: 10.1016/j.proeng.2013.05.124.
29. Weng Y.X., Y.J. Jin, Q.Y. Meng, L. Wang, M. Zhang, and Y.Z. Wang, Biodegradation behavior of poly(butylene adipate-co-terephthalate) (PBAT), poly(lactic acid) (PLA), and their blend under soil conditions. Polym. Test., 32(5), 918–926, 2013, doi: 10.1016/j.polymertesting.2013.05.001.
30. Xu J., J. Zhang, W. Gao, H. Liang, H. Wang, and J. Li, Preparation of chitosan/PLA blend micro/nanofibers by electrospinning. Mater. Lett., 63(8), 658–660, 2009, doi: 10.1016/j.matlet.2008.12.014.
31. N. Wang, J. Yu, and X. Ma, Preparation and characterization of thermoplastic starch/PLA blends by one-step reactive extrusion. Polym Int, 56(11), 1440–1447, 2007.
32. Vrsaljko D., D. Macut, and V. Kovačevic, Potential role of nanofillers as compatibilizers in immiscible

PLA/LDPE Blends. J. Appl. Polym. Sci., 132(6), 1–14, 2015, doi: 10.1002/app.41414.

33. Li H.Z., S.C. Chen, and Y.Z. Wang, Thermoplastic PVA/PLA blends with improved processability and hydrophobicity. Ind. Eng. Chem. Res., 53(44), 17355–17361, 2014, doi: 10.1021/ie502531w.
34. Yoo T.W., H.G. Yoon, S.J. Choi, M.S. Kim, Y.H. Kim, and W.N. Kim, Effects of compatibilizers on the mechanical properties and interfacial tension of polypropylene and poly(lactic acid) blends. Macromol. Res., 18(6), 583–588, 2010, doi: 10.1007/s13233-010-0613-y.
35. Huang M.H., S. Li, and M. Vert, Synthesis and degradation of PLA-PCL-PLA triblock copolymer prepared by successive polymerization of ε-caprolactone and DL-lactide. Polymer (Guildf)., 45(26), 8675–8681, 2004, doi: 10.1016/j.polymer.2004.10.054.
36. Agrawal C.M., D. Huang, J.P. Schmitz, and K.A. Athanasiou, Elevated temperature degradation of a 50:50 copolymer of PLA-PGA. Tissue Eng., 3(4), 345–352, 1997, doi: 10.1089/ten.1997.3.345.
37. Kasyapi N. and A.K. Bhowmick, Nanolamellar triblock of poly D, L-lactide- δ-valerolactone- D, L- lactide with tuneable glass transition and crystallinity for drug delivery vesicle Nibedita. R. Soc. Chem., 2014, [Online]. Available: http://xlink.rsc.org/?DOI=C5TC02043C.
38. Matsumura S., K. Tsukada, and K. Toshima, Novel lipase-catalyzed ring-opening copolymerization of lactide and trimethylene carbonate forming poly(ester carbonate)s. Int. J. Biol. Macromol., 25(1–3), 161–167, 1999, doi: 10.1016/S0141-8130(99)00030-6.
39. Xiao R.Z., Z.W. Zeng, G.L. Zhou, J.J. Wang, F.Z. Li, and A.M. Wang, Recent advances in PEG-PLA block copolymer nanoparticles. Int. J. Nanomedicine, 5(1), 1057–1065, 2010, doi: 10.2147/IJN.S14912.
40. Quynh T.M., H. Mitomo, N. Nagasawa, Y. Wada, F. Yoshii, and M. Tamada, Properties of crosslinked polylactides (PLLA & PDLA) by radiation and its biodegradability. Eur. Polym. J., 43(5), 1779–1785, 2007, doi: 10.1016/j.eurpolymj.2007.03.007.
41. Quynh T.M., H. Mitomo, M. Yoneyama, and N.Q. Hien, Properties of Radiation-Induced Crosslinking Stereocomplexes Derived From Poly(L-Lactide) and Different Poly(D-Lactide) Tran. Polym. Eng. Sci., 49(5), 970–976, 2009.
42. Gref R., Y. Minamitake, M.T. Peracchia, V. Trubetskoy, V. Torchilin, and R. Langerl, Biodegradable Long-Circulating Polymeric Nanospheres. Science (80-). 263, March, p. 1600, 1994, [Online]. Available: www.sciencemag.org.
43. P.K. Chu, J.Y. Chen, L.P. Wang, and N. Huang, Plasma-surface modification of biomaterials. Mater. Sci. Eng. R Reports, 36(5–6), 143–206, 2002, doi: 10.1016/S0927-796X(02)00004-9.
44. Favia P. and R. D'Agostino, Plasma treatments and plasma deposition of polymers for biomedical applications. Surf. Coatings Technol., 98(1–3), 1102–1106, 1998, doi: 10.1016/S0257-8972(97)00285-5.
45. Al-Itry R., K. Lamnawar, and A. Maazouz, Reactive extrusion of PLA, PBAT with a multi-functional epoxide: Physico-chemical and rheological properties. Eur. Polym. J., 58, 90–102, 2014, doi: 10.1016/j.eurpolymj.2014.06.013.
46. Zhong W.E.I. et al., Study on Biodegradable Polymer Materials Based on Poly-. 2546–2551, 1999.
47. Dawin T.P., Z. Ahmadi, and F.A. Taromi, Bio-based solution-cast blend films based on polylactic acid and polyhydroxybutyrate: Influence of pyromellitic dianhydride as chain extender on the morphology, dispersibility, and crystallinity. Prog. Org. Coatings, 119, 23–30, 2018, doi: 10.1016/j.porgcoat.2018.02.003.
48. Yahyaee N., A. Javadi, H. Garmabi, and A. Khaki, Effect of Two-Step Chain Extension using Joncryl and PMDA on the Rheological Properties of Poly (lactic acid). Macromol. Mater. Eng., 305(2), 1–13, 2020, doi: 10.1002/mame.201900423.
49. Barczewski M., D. Czarnecka-Komorowska, J. Andrzejewski, T. Sterzyński, M. Dutkiewicz, and B. Dudziec, Właściwości przetwórcze termoplastycznych tworzyw polimerowych modyfikowanych silseskwioksanami (POSS). Polimery/Polymers, 58(10), 805–815, 2013, doi: 10.14314/polimery.2013.805.
50. Thierry A., B. Fillon, C. Straupé, B. Lotz, and J. C. Wittmann, Polymer nucleating agents: Efficiency scale and impact of physical gelation. Solidif. Process. Polym., 31, 28–31, 2007, doi: 10.1007/bfb0115569.
51. Kawamoto N., A. Sakai, T. Horikoshi, T. Urushihara, and E. Tobita, Nucleating agent for poly(L-lactic acid) - An optimization of chemical structure of hydrazide compound for advanced nucleation ability. J. Appl. Polym. Sci., 103(1), 198–203, 2007, doi: 10.1002/app.25109.
52. Shakoor A. and N. L. Thomas, Talc as a nucleating agent and reinforcing filler in poly(lactic acid) composites. Polym. Eng. Sci., 54(1), 64–70, Jan. 2014, doi: 10.1002/pen.23543.
53. Nam P. H., N. Ninomiya, A. Fujimori, and T. Masuko, Crystallization characteristics of intercalated poly(L-lactide)/organo-modified montmorillonite hybrids. Polym. Eng. Sci., 46(1), 39–46, Jan. 2006, doi: 10.1002/pen.20436.
54. Ray S.S., K. Yamada, A. Ogami, M. Okamoto, and K. Ueda, New polylactide/layered silicate nanocomposite: Nanoscale control over multiple properties. Macromol. Rapid Commun., 23(16), 943–947, 2002, doi:10.1002/1521-3927(200211)23:16<943::AID-MARC943>3.0.CO;2-F.

55. Han L. et al., Preparation and characteristics of a novel nano-sized calcium carbonate (nano-CaCo3)-supported nucleating agent of poly(L-lactide). Polym. Eng. Sci., 52(7), 1474–1484, Jul. 2012, doi: 10.1002/pen.23095.
56. Devaux E., C. Aubry, C. Campagne, and M. Rochery, PLA/carbon nanotubes multifilament yarns for relative humidity Textile sensor. J. Eng. Fiber. Fabr., 6(3), 13–24, 2011, doi: 10.1177/155892501100600302.
57. Shalom H. et al., Nanocomposite of poly(L-lactic acid) with inorganic nanotubes of WS 2. Lubricants, 7(3), 2019, doi: 10.3390/lubricants7030028.
58. Han L., P. Pan, G. Shan, and Y. Bao, Stereocomplex crystallization of high-molecular-weight poly(l-lactic acid)/poly(d-lactic acid) racemic blends promoted by a selective nucleator. Polymer (Guildf)., 63, 144–153, 2015, doi: 10.1016/j.polymer.2015.02.053.
59. Li C., Q. Dou, Z. Bai, and Q. Lu, Non-isothermal crystallization behaviors and spherulitic morphology of poly(lactic acid) nucleated by a novel nucleating agent. J. Therm. Anal. Calorim., 122(1), 407–417, 2015, doi: 10.1007/s10973-015-4677-y.
60. Zhao Y., B. Liu, C. You, and M. Chen, Effects of MgO whiskers on mechanical properties and crystallization behavior of PLLA/MgO composites. Mater. Des., 89, 573–581, 2016, doi: 10.1016/j.matdes.2015.09.157.
61. Xu Y. and L. Wu, Synthesis of organic bisurea compounds and their roles as crystallization nucleating agents of poly(l-lactic acid). Eur. Polym. J., 49(4), 865–872, 2013, doi: 10.1016/j.eurpolymj.2012.12.015.
62. Bai H., C. Huang, H. Xiu, Q. Zhang, and Q. Fu, Enhancing mechanical performance of polylactide by tailoring crystal morphology and lamellae orientation with the aid of nucleating agent. Polymer (Guildf)., 55(26), 6924–6934, 2014, doi: 10.1016/j.polymer.2014.10.059.
63. Turan D., H. Sirin, and G. Ozkoc, Effects of POSS particles on the mechanical, thermal, and morphological properties of PLA and Plasticised PLA. J. Appl. Polym. Sci., 121(2), 1067–1075, Jul. 2011, doi: 10.1002/app.33802.
64. Cai Y.H., Y. Tang, and L.S. Zhao, Poly(l -lactic acid) with the organic nucleating agent N,N,N′-tris(1H-benzotriazole) trimesinic acid acethydrazide: Crystallization and melting behavior. J. Appl. Polym. Sci., 132(32), 1–7, 2015, doi: 10.1002/app.42402.
65. He D., Y. Wang, C. Shao, G. Zheng, Q. Li, and C. Shen, Effect of phthalimide as an efficient nucleating agent on the crystallization kinetics of poly(lactic acid). Polym. Test., 32(6), 1088–1093, 2013, doi: 10.1016/j.polymertesting.2013.06.005.
66. Cai Y.H., L.L. Tian, and Y. Tang, Crystallization and melting behavior of poly(L-lactic acid) modifed with salicyloyl hydrazide derivative. Polimery/Polymers, 62(10), 734–742, 2017, doi: 10.14314/polimery.2017.734.
67. Li H. and M.A. Huneault, Effect of nucleation and plasticization on the crystallization of poly(lactic acid). Polymer (Guildf)., 48(23), 6855–6866, 2007, doi: 10.1016/j.polymer.2007.09.020.
68. Harris A.M. and E.C. Lee, Improving mechanical performance of injection molded PLA by controlling crystallinity. J. Appl. Polym. Sci., 107(4), 2246–2255, Feb. 2008, doi: 10.1002/app.27261.
69. Barczewski M. et al., Development of polylactide composites with improved thermomechanical properties by simultaneous use of basalt powder and a nucleating agent. Polym. Compos., 41(7), 2947–2957, 2020, doi: 10.1002/pc.25589.
70. Nagarajan V., A.K. Mohanty, and M. Misra, Crystallization behavior and morphology of polylactic acid (PLA) with aromatic sulfonate derivative. J. Appl. Polym. Sci., 133(28), 1–11, 2016, doi: 10.1002/app.43673.
71. Murariu M. and P. Dubois, PLA composites: From production to properties. Adv. Drug Deliv. Rev., 107, 17–46, 2016, doi: 10.1016/j.addr.2016.04.003.
72. Jung Y. et al., A poly(lactic acid)/calcium metaphosphate composite for bone tissue engineering. Biomaterials, 26(32), 6314–6322, 2005, doi: 10.1016/j.biomaterials.2005.04.007.
73. Kasuga T., H. Maeda, K. Kato, M. Nogami, K. I. Hata, and M. Ueda, Preparation of poly(lactic acid) composites containing calcium carbonate (vaterite). Biomaterials, 24(19), 3247–3253, 2003, doi: 10.1016/S0142-9612(03)00190-X.
74. Zhou J., Z. Yao, C. Zhou, D. Wei, and S. Li, Mechanical properties of PLA/PBS foamed composites reinforced by organophilic montmorillonite. J. Appl. Polym. Sci., 131(18), 9319–9326, 2014, doi: 10.1002/app.40773.
75. Kuan C.F., H.C. Kuan, C.C.M. Ma, and C.H. Chen, Mechanical and electrical properties of multi-wall carbon nanotube/poly(lactic acid) composites. J. Phys. Chem. Solids, 69(5–6), 1395–1398, 2008, doi: 10.1016/j.jpcs.2007.10.060.
76. Zhang Y., B. Deng, Q. Liu, and G. Chang, “Non-isothermal crystallization kinetics of poly(lactic acid)/nanosilica composites. J. Macromol. Sci. Part B Phys., 52(2), 334–343, 2013, doi: 10.1080/00222348.2012.701551.
77. M. Murariu, L. Bonnaud, P. Yoann, G. Fontaine, S. Bourbigot, and P. Dubois, New trends in polylactide (PLA)-based materials: ‘Green’ PLA-Calcium sulfate (nano)composites tailored with flame retardant properties. Polym. Degrad. Stab., 95(3), 374–381, 2010, doi: 10.1016/j.polymdegradstab.2009.11.032.

78. Wootthikanokkhan J, Cheachun T, Sombatsompop N, Thumsorn S, Kaabbuathong N, Wongta N, et al. Crystallization and thermomechanical properties of PLA composites: Effects of additive types and heat treatment. J Appl Polym Sci. 2013; 129(1): 215–23.
79. Liu M., Y. Zhang, and C. Zhou, Nanocomposites of halloysite and polylactide. Appl. Clay Sci., 75–76, 52–59, 2013, doi: 10.1016/j.clay.2013.02.019.
80. Barczewski M., K. Sałasińska, A. Kloziński, K. Skórczewska, J. Szulc, and A. Piasecki, Application of the Basalt Powder as a Filler for Polypropylene Composites With Improved Thermo-Mechanical Stability and Reduced Flammability. Polym. Eng. Sci., 59(2), E71–E79, 2019, doi: 10.1002/pen.24962.
81. Plackett D., T.L. Andersen, W.B. Pedersen, and L. Nielsen, Biodegradable composites based on L-polylactide and jute fibres. Compos. Sci. Technol., 63(9), 1287–1296, 2003, doi: 10.1016/S0266-3538(03)00100-3.
82. Wong S., R.A. Shanks, and A. Hodzic, Poly(L-lactic acid) Composites With Flax Fibers Modified by Plasticizer Absorption. Polym. Eng. Sci., 43(9), 1566–1575, 2003, doi: 10.1002/pen.10132.
83. Tokoro R., D.M. Vu, K. Okubo, T. Tanaka, T. Fujii, and T. Fujiura, How to improve mechanical properties of polylactic acid with bamboo fibers. J. Mater. Sci., 43(2), 775–787, 2008, doi: 10.1007/s10853-007-1994-y.
84. Mathew A.P., K. Oksman, and M. Sain, Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC). J. Appl. Polym. Sci., 97(5), 2014–2025, 2005, doi: 10.1002/app.21779.
85. Oksman K., M. Skrifvars, and J.F. Selin, Natural fibres as reinforcement in polylactic acid (PLA) composites. Compos. Sci. Technol., 63(9), 1317–1324, 2003, doi: 10.1016/S0266-3538(03)00103-9.
86. Sawpan M.A., K.L. Pickering, A. Fernyhough, N. Zealand, B. Engineering, and N. Zealand, Hemp Fibre Reinforced Poly(lactic acid) Composites Moyeenuddin A. Sawpan 1. Adv. Mater. Res., 29–30, 1–4, 2007, [Online]. Available: http://www.scientific.net/AMR.29-30.337.
87. Sawpan M.A., K.L. Pickering, and A. Fernyhough, Improvement of mechanical performance of industrial hemp fibre reinforced polylactide biocomposites. Compos. Part A Appl. Sci. Manuf., 42(3), 310–319, 2011, doi: 10.1016/j.compositesa.2010.12.004.
88. Huda M.S., L.T. Drzal, A.K. Mohanty, and M. Misra, Chopped glass and recycled newspaper as reinforcement fibers in injection molded poly(lactic acid) (PLA) composites: A comparative study. Compos. Sci. Technol., 66(11–12), 1813–1824, 2006, doi: 10.1016/j.compscitech.2005.10.015.
89. Wan Y.Z., Y.L. Wang, X.H. Xu, and Q.Y. Li, In vitro degradation behavior of carbon fiber-reinforced PLA composites and influence of interfacial adhesion strength. J. Appl. Polym. Sci., 82(1), 150–158, 2001, doi: 10.1002/app.1834.
90. Frone A.N., S. Berlioz, J.-F. Chailan, D.M. Panaitescu, and D. Donescu, Cellulose fiber-reinforced polylactic acid. Polym. Compos., 32(6), 976–985, Jun. 2011, doi: 10.1002/pc.21116.
91. Huda M.S., A.K. Mohanty, L.T. Drzal, E. Schut, and M. Misra, 'Green' composites from recycled cellulose and poly(lactic acid): Physico-mechanical and morphological properties evaluation. J. Mater. Sci., 40(16), 4221–4229, 2005, doi: 10.1007/s10853-005-1998-4.
92. Czigány T., J.G. Kovács, and T. Tábi, Basalt Fiber Reinforced Poly(Lactic Acid) Composites for Engineering Applications. 19th Int. Conf. Compos. Mater., 4377–4384, [Online]. Available: http://real.mtak.hu/8877/1/Czigany_ICCM19_megjelent.pdf.
93. Matykiewicz D., M. Barczewski, and S. Michałowski, Basalt powder as an eco-friendly filler for epoxy composites: Thermal and thermo-mechanical properties assessment. Compos. Part B Eng., 164, 272–279, 2019, doi: 10.1016/j.compositesb.2018.11.073.
94. Jawaid M. and H.P.S. Abdul Khalil, Cellulosic/synthetic fibre reinforced polymer hybrid composites: A review. Carbohydr. Polym., 86(1), 1–18, 2011, doi: 10.1016/j.carbpol.2011.04.043.
95. Kuciel S. and P. Romańska, Hybrid composites of polylactide with basalt and carbon fibers and their thermal treatment. Materials (Basel), 12(1), 2018, doi: 10.3390/ma12010095.
96. Pappu A., K.L. Pickering, and V.K. Thakur, Manufacturing and characterization of sustainable hybrid composites using sisal and hemp fibres as reinforcement of poly (lactic acid) via injection moulding. Ind. Crops Prod., 137, May, 260–269, 2019, doi: 10.1016/j.indcrop.2019.05.040.
97. Goriparthi B.K., K.N.S. Suman, and M.R. Nalluri, Processing and characterization of jute fiber reinforced hybrid biocomposites based on polylactide/polycaprolactone blends. Polym. Compos., 33(2), 237–244, Feb. 2012, doi: 10.1002/pc.22145.
98. McNaught A.D. and A. Wilkinson, Compendium of Chemical Terminology (Gold Book). Int. Union Pure Appl. Chem., Oxford: Bl, 135–151, 1997, doi: 10.1002/9783527626854.ch7.
99. NatureWorks Products. https://www.natureworkslic.com/Products (accessed Jan. 05, 2021).
100. Auras R., B. Harte, and S. Selke, An Overview of Polylactides as Packaging Materials. Macromol. Biosci., 4(9), 835–864, 2004, doi: 10.1002/mabi.200400043.