Characteristics of composite materials based on polylactic acid (PLA)

ALEKSANDAR D. DRPIĆ, IMS Institute, a.d, Belgrade

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Polylactic acid (PLA) is aliphatic thermoplastic polyester. Composites based on PLA are biocompatible, biodegradable and non-toxic, which are the main advantages of using such composites. Based on the research results described in this paper, it was concluded that by adding natural fibers to the composite, certain characteristics can be significantly improved. This paper describes some of composite material characteristics based on PLA, modification of PLA, advantages and disadvantages of using PLA in composite materials, composition and methods of obtaining PLA-based composites, as well as the advantages of using wood plastic composites (WPC) based on PLA.

Key Words: *polylactic acid (PLA), PLA-based composite materials, natural fibers, WPC-based on PLA*

1. INTRODUCTION

Composite materials are those in which at least two different materials are combined in one material, whereby each of the components retains its properties, but a new composite material with improved properties is obtained [1]. The goal when processing composites is to improve the structural, thermal, chemical or some other material characteristics. The composite structure consists the matrix, which surrounds and holds together the groups of fibers or parts of the reinforcement, and the reinforcer, which gives the composite strength and hardness. Composite materials usually have low density, high strength, possibility of processing and shaping into various shapes, good stiffness, good impact resistance, stability at increased temperatures [1]. WPC composite materials are example of modern materials, which are obtained by combining the two most common recycling products - plastic and wood [2]. In wood plastic composites matrix represents a polymer material and wood material is the filler [2]. The composite can consist different materials, such as: non-metals, ceramics, metals or polymers. Biodegradable polymers represent a new type of polymers and along with polymer techniques are increasingly used. PLA has the widest application among biodegradable polymers and is an excellent alternative to traditional polymers [3].

Author's address: Aleksandar Drpić, IMS Institute, a.d, Belgrade, Bulevar vojvode Mišića 43
e-mail: aleksandar.drpic@institutims.rs
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2. POLYLACTIC ACID (PLA)

PLA is intensively researched in order to replace classic polymers obtained from fossil fuels with biodegradable polymers which have better chemical, mechanical and biological characteristics [3]. Biocompatibility, degradability and non-toxicity of the product are the characteristics that make PLA an excellent material for various purposes.

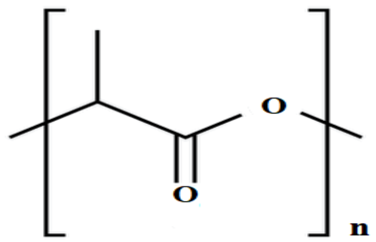

Figure 1 - Structural formula of PLA [4]

Polylactic acid (PLA) is a thermoplastic polyester with chemical formula $[–C(CH_3)HC(=O)O–]_n$ [4]. In Figure 1 is presented structural formula of PLA.

PLA, like any thermoplastic polymer, can be obtained by various methods such as extrusion,injection molding, vacuum molding, blowing [3].

2.1. Properties of polylactid ACID

The properties of PLA depend of the isomeric component, production temperature, heating and cooling time, molecular mass of polymer, etc. [5]. During polymerization, by opening the lactide ring of the polymer, three lactide isomers could be formed: poly (D-lactide acid) or PDLA, poly (L-lactide acid) or PLLA, and poly (DL-lactide acid) or PDLLA, which differ from each other by degradation rate, by mechanical properties, and by physical properties [6]. The composition of PLA affects the melting point and crystallization degree [7].

PLLA could have a crystalline structure, which makes it more difficult to hydrolyze than amorphous forms of the polymer. The time required for the degradation of PLLA is longer than the time required for the degradation of the PDLLA. The presence of the CH_3 group gives the polymer PLLA a hydrophobic property, due to which the speed of hydrolytic degradation of PLLA decreases compared to other isomers of polylactide [6]. Various mechanical, physical and thermal properties of some commercial PLA are represented in Table 1.

Table 1. Mechanical, physical and thermal properties of some commercial PLA [5]

	Biomer L900	*Nature Works PLA*
Physical properties		
Density (g/cm^3)	1.25	1.25
Mechanical properties		
Tensile strength (MPa)	70	53
Elongation degree (%)	2.4	10-100
Bending modulus (MPa)	3600	35-450
Thermal properties		
Shape stability during heating (°C)	135	40-45
Transition to the glass state (°C)	-	55-56
Melting point (°C)	-	120-170

At room temperature, polylactide isomers have similar mechanical properties [7].

Biodegradation rate of PLA and mechanical properties are depending of the molecular mass, crystal structure and morphology. Polylactid is dissolved in chloroform, methylene dichloride, dioxane, benzene and acetone, while is insoluble in alcohols such as methanol and ethanol [8].

The most important property of PLA is its biodegradability (Figure 2). In most cases, PLA can be degraded in nature by non-enzymatic hydrolysis, but there is also the possibility of biodegradation[9].

Figure 2 - Biodegradable polylactic acid (PLA)

Thermal treatments of PLA are much easier compared to other biopolymers. When fossil raw materials are used in the production of PLA, energy use is up to 50% less than with commercial polymers, and that causes a decrease in CO_2 emissions [6]. PLA is a chemically inert and hydrophobic material and its modification is complex.

2.2. PLA modification

PLA, like any polymer material, has certain disadvantages that can be improved by modification. PLA can be modified by mixing with one or more different polymers, and also by adding different fillers, reinforcers, softeners, etc. [10]. The goal is to obtain a polymer material with better properties, without polluting the environment and with acceptable price on the market. Using recycled wood fibers in combination with PLA can improve mechanical and thermal characteristics [10]. If PLA is mixed with cellulose powder, better elastic properties are obtained compared to when PLA is mixed with starch. Reinforcements are used to modify the mechanical characteristics. Organic reinforcers or fillers have low density, better toughness, with less use of non-renewable resources during the production, compared to inorganic ones [11]. PLA is a brittle material that needs to be softened. Different types of softeners are used depending on the purpose of PLA: poly (ethylene glycol), poly (propylene glycol), esters of unsaturated fatty acids, glycerol triacetate, citrates, lactide monomers, etc. [11]. Softeners are used when lowering the melting and glass transition temperature, and they affect on polymer biodegradation rate [11]. The mixture of PLA and poly (ethylene oxide) - PEO has good mechanical properties [12]. If PLA/starch composites are softened with poly (ethylene glycol), starch does not affect the thermal or mechanical characteristics of PLA, but lowers its cost [13].

3. WOOD PLASTIC COMPOSITE MATERIALS (WPC) BASED ON PLA

WPC have better properties such as resistance to moisture and acid, good deformation resistance, high resistance to rots, no formaldehyde release, easy maintenance (cleaning) etc., compared to other wooden materials [14]. WPC based on PLA are biodegradable because PLA is a thermoplastic material. Sawdust, wood flour and wood fibers are basic components of WPC [15]. Wood fibers are obtained by chemical or thermomechanical wood processing [16]. The advantage of fibers is stiffness, while the disadvantages are decreased impact resistance and more difficult bonding with the polymer. In order to obtain better WPC properties, wood fibers and fillers with a higher length/thickness ratio, are used [16]. In order to obtain good performance of wood-plastic composites based on PLA fibers, it is necessary to treat the fibers with one of the aforementioned processes, with the addition of additives.

Wood fibres dimensions affect on WPC properties. Madyan et al. [17] concluded that most wood fibres (WF) after processing have dimensions greater than before processing. The natural fibers exposed to fungal and mold can affect on WPC aestetic and mechanical properies. Borysiuk et al. [18] found that antimicrobial properties of composites decrease when smaller particles are applied. Metallic antimicrobial agents could be used to increase antimicrobial properties. Yang et al. [19] found that copper-zinc particles improve the antimicrobial characteristics, mechanical characteristics, thermal stability and also give nice colours and shine of the composites.

WPC based on PLA are used in flooring, household and construction, because they have good impact resistance, without appearance of cracking during use. In order to obtain better mechanical charachteristics, to minimize production costs and to make the lighter composites, Wang et al. [20] used azodicarbonamide (AC) in wood flour/PLA composite.

3.1. Properties of natural fibre composite materials based on PLA

In recent years, there is an increasing need to reinforce PLA composites with natural fibers. *Table 2* represents various physical and chemical characteristics of PLA isomers.

Table 2. Physical and chemical characteristics of PLA isomers [21, 22, 23]

Characteristics	PDLLA poly (DL-lactid acid)	PDLA poly (D- lactid acid)	PLLA poly (L- lactid acid)
Density (g/cm^3)	1.25	1.248	1.290
Transition to glass state T_g (°C)	43-53	40-60	55-80
Melting point T_m (°C)	120-170	120-150	173-178
Solubility	Ethyl lactate, tetrahydrofuran, ethyl acetate, dimethyl sulfoxide and dimethyl formamide		Chloroform and furan

Parameters affecting the mechanical characteristics of PLA composites are: type of fibers, the dimensions/diameter of the fibers, and the fiber processing method [23]. Shih et al. [24] studied composites with recycled disposable chopsticks, which are integrated in PLA matrix. They applied melt-mixing process and they found that tensile strength was improved when fiber content is increased. PLA/spruce wood flour composites (40 wt. %) are studied by Gregorova et al. [25]. The treatment with silane is used to improve the integration of spruce wood flour into PLA matrix. The conclusions were that applied surface treatment of wood flour leads to decreasing of tensile strength and increasing of Young modulus. In order to improve the flame-retardant properties and thermal stability of PLA composites, Ren at al. [26] used 3-aminopropyltriethoxysilane (KH550) for microcrystalline cellulose modification. Compared to untreated samples, Yussuf et al. [27] found that addition of kenaf and fibers of rice husk leads to thermal stability decrease. When WPC is produced from PLA and bamboo fibers with high cellulose and high lignin content, at low ash content, obtained WPC have better mechanical characteristics [28]. If the hot pressing process is used to prepare bamboo fiber/PLA composites, it was concluded that pressure had the most important affect on tensile strength [29]. If the pressing method is used to prepare PLA composites reinforced with bamboo fibers, Lee et al. [30] concluded that Young modulus increased with increasing fiber content, but tensile strength decreased.

Pérez-Fonseca et al. [31] used compression and rotational molding techniques to prepare PLA composites with white ash and tzalam. They found that annealing improved crystallinity, as well as thermal and dimensional stability of composites.

Reinforcement effects of fillers was studied by Farrokhpayam et al. [32]. Reinforced effects of wood flour was better than with the pulp fiber and mechanical characteristics of the composites could be improved when filler content is increased.

Carbon nanotubes (CNT) mixed with polymers can be used to improve the most of polymer-characteristics (mechanical, thermal, electromagnetic) [33]. In order to decrease the thermal conductivity and to improve the thermal stability, Zhang et al. [34] used melt-mixing process with sodium dodecylbenzene sulfonate for surface modification of CNT, and then fused PLLA with modified CNT.

Flame-retardants (FR) added to the polymer in the melting process, improved the fire resistance of PLA composites based on natural fibers [35]. Fiber-reinforced PLA composites after exposure to sunlight, especially in moisture conditions, can be damaged by change of chemical bonds in polymers. That can cause color fading and deterioration of some mechanical and physical characteristics [27, 36, 37]. Weather conditions and the region in which the material is used affect the process of deterioration and aging of PLA composites. Many researchers have examined the durability of PLA composites reinforced with different types of the aforementioned fibers under the influence of exposure to different weather conditions and have come to the conclusion that durability of composite is better when there is larger amount of natural fibers presence.

4. CONCLUSIONS

PLA composites are biodegradable and biocompatible. In recent years there is more research in strengthening PLA with natural fibers. Many researchers concluded that PLA composites reinforced with natural fibers are suitable for processing, have high specific strength, compostability, high toughness and renewability. PLA is a polymer material whose characteristics can be improved by mixing with one or more different polymers, and also by adding different fillers, reinforcers, softeners, etc. Mechanical characteristics of composites can be mostly improved by adding fillers to the polymer matrix. PLA-based WPC fulfill many requirements, but the higher price compared to other polymers still limits its use, but optimal solutions are expected in the future. The advantage of PLA production is that less fossil raw materials are used compared to production of some other polymers and therefore it has no negative impact on the environment. PLA composites can have improved performance such as good strength and stiffness, better processability (due to crystallization), and low flammability.

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REZIME

KARAKTERISTIKE KOMPOZITNIH MATERIJALA NA BAZI POLILAKTIDNE KISELINE (PLA)

Polilaktidna kiselina (PLA) je alifatični termoplastični poliester. Kompoziti na bazi PLA su biokompatibilni, biorazgradivi i netoksični, što čini glavne prednosti upotrebe ovakvih kompozita. Na osnovu rezultata istraživanja opisanih u ovom radu, došlo se do zaključka da se dodavanjem prirodnih vlakana kompozitu mogu znatno poboljšati pojedine karakteristike kompozita. U radu su opisana neke karakteristike kompozitnih materijala na bazi PLA, modifikacija PLA, prednosti i nedostaci upotrebe PLA u kompozitnim materijalima, sastav i metode dobijanja kompozita na bazi PLA, kao i prednosti upotrebe WPC kompozita na bazi PLA.

Ključne reči*: polilaktidna kiselina (PLA), kompozitni materijali na bazi PLA, prirodna vlakna, WPC na bazi PLA*