



Poly(lactic acid)-Based Blends: A Comprehensive Review

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Abstract: Aliphatic and aromatic polyesters of hydroxycarboxylic acids are characterized not only by biodegradability, but also by biocompatibility and inertness, which makes them suitable for use in different applications. Polyesters with high enzymatic hydrolysis capacity include poly(lactic acid), poly(ε -caprolactone), poly(butylene succinate) and poly(butylene adipate-co-terephthalate), poly(butylene succinate-co-adipate). At the same time, poly(lactic acid) is the most durable, widespread, and cheap polyester from this series. However, it has a number of drawbacks, such as high brittleness, narrow temperature-viscosity processing range, and limited biodegradability. Three main approaches are known for poly(lactic acid) modification: incorporation of dispersed particles or low molecular weight and oligomeric substances, copolymerization with other polymers, and blending with other polymers. The review includes an analysis of experimental works devoted to developing mixtures based on poly(lactic acid) and other polymers. Regularities in the formation of the structure of such systems and the possibility of controlling the properties of poly(lactic acid) are considered.

Keywords: poly(lactic acid); polymer composites; poly(ε-caprolactone); poly(glycolic acid); poly(butylene adipate-co-terephthalate); poly(3-hydroxybutyrate); poly(ethylene-co-vinyl acetate)

1. Introduction

Poly(lactic acid) or poly(lactide) (PLA) is an aliphatic semi-crystalline polyester obtained from renewable raw materials. As a rule, vegetable starch fermented under the action of microbiota from corn, cassava, sugar cane or sugar beet pulp serve as sources of lactic acid [1]. It is also possible to obtain lactic acid by chemical means from acetaldehyde and prussic acid. By condensation reaction, a lactide dimer is obtained from oligomerized lactic acid, followed by polymerization of the cyclic lactide dimer with ring opening to polylactic acid [2]. Due to the fact that lactic acid is able to exist in the form of two enantiomers (D and L), as a result of synthesis, it is possible to obtain poly(L-lactide) and poly(D-lactide), as well as their poly(D,L-lactide) stereocomplex (PDLLA). Most natural enzymes form L-lactide, however, at the stage of oligomerization and cyclization, while partial lactic acid racemization occurs when an isomer of the opposite configuration is formed from one isomer, for example, D-lactide or meso-lactide.

Depending on the ratio of the enantiomers used, various forms of PDLLA can be obtained. These different forms give materials with different degrees of crystallinity, thermal transitions, solubility and decomposition rate [3]. Due to the high degree of stereoregularity, poly(L-lactide) is a brittle transparent polymer with a melting point of about 170–180 °C and a glass transition temperature of about 63 °C [4]. Adding other stereoisomers into poly(L-lactide) reduces its melting point, degree of crystallinity, and rate



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of crystallization of the polymer [5]. At the same time, the poly(D,L-lactide) stereocomplex (PDLLA) is two interwoven polymer chains, between which additional intermolecular interactions along polar groups are formed and a new highly ordered crystal structure arises. As a result, the melting point increases to 220–230 °C, the thermal resistance and resistance to hydrolytic degradation increase, and the water permeability decreases [6]. The structure of the lactides and PLA is shown in Figure 1.



Figure 1. (a) The stereoisomers of lactic acid and the resulting polylactides [7]; (b) the chemical structure of poly(lactic acid).

The complex of PLA properties depends primarily on the composition of enantiomers and molecular weight. In general, the physical and mechanical characteristics of PLA are similar to poly(ethylene terephthalate) or poly(styrene) having a high modulus of elasticity (2.7–16 GPa), that is, an ability to heat welding and good technological properties [8]. However, because PLA has a high fragility, it is unsuitable for the manufacture of flexible polymeric products.

Considering in detail the strengths and drawbacks of PLA as a structural plastic, G. Li et al. [9] have noted that polylactic acid has a wide range of applications in both industry and medicine. The interest in its mass production is due to its good performance characteristics [10–13]. High-molecular-weight PLA is used to make filaments for surgical sutures, and low-molecular-weight PLA is used as a packaging agent for slow-release drugs [14].

Compared with other biopolymers, PLA has the following advantages: obtained from renewable resources (for example, corn, wheat, beet or rice); compostability and recycling ability; biocompatibility and bioresorbability (degradability safely within the body), which are especially important for biomedical materials; and improved processibility compared to other biopolymers such as polyhydroxyalkanoates (PHA), polyethylene oxide (PEO) and polycaprolactone (PCL) [15–17]. Thus, PLA can be processed in the same ways as traditional synthetic polymers (by casting, pressing, injection molding, blow molding, electrospinning) [17].

Despite the above-mentioned advantages, PLA has certain drawbacks: low impact strength (certain shortcomings in conditions of high mechanical strength); fragility (a relative elongation at break of PLA is 2.5–6% [15]); low degradation rate in natural soil; relative hydrophobicity (unsuitability for delivery of a range of drugs); and difficulty to

modify (because of a lack of reaction groups) [15]. In addition, PLA is characterized by a narrow temperature range of processing, which causes its modification by additives to regulate rheological properties [18].

A number of operational and technological properties of PLA strongly depend on molecular weight characteristics and a degree of crystallinity. This polymer belongs to a highly crystalline polymer, so this affects the mechanical characteristics, an ability to dissolve, and biodegradation. Amorphous PLAs are soluble in various organic solvents, including acetone, acetonitrile, and methylene chloride. Crystalline PLAs can be dissolved in dichloromethane or benzene only at high temperatures. Mechanical properties and behavior during crystallization are closely related to the molecular weight and stereochemical composition of the main chain [19]. Glass transition (T_g) directly affects the characteristics of the material both in terms of use and processing. Impact resistance increases with increasing crystallinity and molecular weight.

In line with other high-molecular compounds based on α -hydroxy acids and their derivatives, PLA has an ability for hydrolytic degradation due to the presence of ester groups. The process of its degradation depends on the degree of crystallinity, molecular weight, morphology and other factors [15]. Highly crystalline PLAs are stable for several years, while polymers with low crystallinity can decompose in a few weeks.

Hydrolytic degradation occurs when PLA is exposed to moisture: the ester groups of the polymer main chain are cleaved, which leads to a decrease in molecular weight and the yield of soluble oligomers and monomers [20]. Thus, the hydrolysis begins with the diffusion of water molecules into amorphous regions, which in turn initiate the cleavage of ester bonds. After that, the destruction continues in the boundary layers of the crystal domains [21]. However, a high rate of PLA hydrolysis is possible only in the case of a transition through the glass transition temperature with an increase in the macro chains mobility. Thus, PLA realizes its biodegradability only under the conditions of industrial composting with heating above 60 °C [22]. At the same time, PLA is subjected to hydrolytic cleavage with a decrease in molecular weight during processing in the melt, which complicates its technological processing [23].

There are several ways to regulate the disadvantages of PLA, one of which is mixing with other polymers [24]. Studying the relationship between the properties of PLA and different polymers allows us to develop polymeric materials with improved properties compared to individual polymers, and achieve synergy in the interaction of components that expands the scope of materials application. This review analyzes research papers on blends of PLA with polymers such as $poly(\epsilon$ -caprolactone), poly(glycolic acid), poly(butylene-adipate-co-terephthalate), poly(ethylene-co-vinyl acetate) and poly(3-hydroxybutyrate).

2. Composites of Poly(lactic acid) with Poly(ε-caprolactone)

Poly(ε -caprolactone) (PCL) (Figure 2) is a semi-crystalline aliphatic polyester, which is usually synthesized by ring-opening polymerization from caprolactone monomer, where divalent alcohols and tin (II) or tin salts serve as initiators [1]. PCL has a high mobility of chain segments with low intermolecular interactions, which leads to a very low melting point (+60 °C) and glass transition point (-60 °C) [25]. Due to its high flexibility, PCL demonstrates mechanical properties similar to those of other conventional non-biodegradable synthetic polymers (for example, poly(ethylene)). PCL is used to create long-term implants, drug delivery systems, and microcellular foams. Lower molecular weighted PCLs are used as plasticizers or compatibilizers for other biopolymers, as well as adhesives for the medical-pharmaceutical industry [26].

Since PCL refers to biodegradable, biocompatible, and non-toxic polymers, the direction of creating materials based on blends of PLA and PCL is actively developing. The main drawbacks of PCL include its low barrier properties and modulus of elasticity. Mixing with PLA partially allows us to improve these drawbacks of PCL. PLA gives PCL an increased strength and rigidity, while PCL provides high-impact strength due to its rubber-like characteristics [27,28]. Further, a decrease in water vapor permeability has been proven when adding PLA to PCL [29].



Figure 2. The chemical structure of $poly(\varepsilon$ -caprolactone).

The blends of PLA and PCL have been studied by many researchers around the world. A number of works are devoted to the study of the phase structure of PLA and PCL blends. Considering the structure of such blends, separate researchers have pointed out the presence of interphase layers. N. Noroozi et al. [30] studied the blends of PLA/PCL of various compositions. It was found that when the content of PCL is up to 30 wt.%, uniformly dispersed droplets of almost spherical PCL as a dispersed phase are formed in the blends (Figure 3). However, with an increase in the PCL content, the droplet size increases due to coalescence [31]. A clear interface between the two phases indicates a high immiscibility of this system. With an increase in the PCL content above 50 wt.%, the morphology begins to change into a continuous structure. The morphology change is caused by a significant increase in the coalescence of PCL droplets [32]. The images demonstrate a good level of dispersed phase distribution (PCL) in the PLA matrix. It is also noted that even when using different grades of PLA, with high and low molecular weight, the morphology of PCL droplets is similar. This morphology is also noted in other scientific studies [33,34].

Broz et al. [35] have found a significant increase in an elongation at break for the blend with PCL content more than 60 wt.% with a simultaneous decrease in a modulus of elasticity and tensile strength. Nevertheless, most researchers have defined the blend with a lower PCL content as the most optimal from the point of view of synergetic improvement of mechanical characteristics. M. Todo and T. Takayama [36] have obtained PLA/PCL blends by a film-casting method using methylene chloride as a solvent. They observed an improvement in the elongation at break for the blend with 15 wt.% of PCL. Ostafinska et al. [37] have found that the blend with a content of 20 wt.% of PCL in the PLA matrix is characterized by a minimum size of PCL domains (~0.6 μ m). In the subsequent work [38], the authors have revealed that the blends of PCL with the most viscous PLA are characterized by the maximum synergistic improvement in the impact strength (>16× compared to pure PLA, surpassing even pure PCL). A decrease in the viscosity of the PLA matrix has led to an increase in the average particle size of PCL and a sharp decrease in the overall impact strength (Figure 4).

H. Bai and Ch. Huang et al. [39] have found that the size of the domains of the smaller phase (PCL) is affected by the crystallinity of the matrix (PLA), which in turn affects the mechanical properties of materials. With a significant increase in the crystallinity of the matrix, a clear decrease in the mechanical properties of composites has been revealed. It has been defined that the highly crystalline matrix of PLA can work effectively during hardening, provided that the PCL domains size should be $0.3-0.5 \,\mu$ m. At the same time, PCL works as a plasticizer in the blend with PLA that increases the crystallinity of PLA [40]. Some researchers have found that the compatibility of PLA and PCL can be improved by using certain compounding technologies. The samples of PLA/PCL blends with a PCL content of 10 and 20 wt.% contains much smaller PCL domains when obtaining by injection moulding as opposed to hot pressing, regardless of the mixing method used [40]. Reducing the size of PCL domains increased the elasticity of materials under tension.



Figure 3. SEM images of the blends of PLA/PCL: 90/10 (a), 70/30 (b), 30/70 (c), 10/70 (d) [33].



Figure 4. Change in impact strength from the composition of the blends of PLA/PCL [37].

Like other mixtures of high-molecular compounds, the blends of PLA and PCL are incompatible; therefore, a number of works are devoted to the study of the effect of compatibilizers on the compatibility of PLA and PCL. Semba et al. [41] investigated the process of reactive mixing of PLA/PCL using dicumyl peroxide as a crosslinking agent. They have observed an improvement in an elongation at break for the optimal ratio of PLA/PCL = 70/30. M. Przybysz-Romatowska et al. [42] also have proven the effectiveness of peroxide crosslinking agents in the improvement of the compatibility of PLA and PCL phase; however, it has also been found to decrease in the melt flow rate. In the papers [27,28], tributyl citrate (3% by weight of PCL) was studied as a compatibilizer. H. Jeong et al. have shown that the PCL additive has a positive effect on the strength and plasticity of the composites with a low content of it. In the range of compositions of PLA/PCL = 99/1–95/5 wt.%, the mechanical properties of films with a compatibilizer exceeded the properties of films without it (an increase in the strength and elongation by 20–30%). W. Chee and N. Ibrahim et al. [43] have found an improved interfacial adhesion between PLA and PCL in the presence of a reactive glycidyl methacrylate compatibilizer (up to 3 wt.%), which improved the impact strength. H. Tsuji and T. Yamada [44] have used a copolymer (L-lactide- ε -caprolactone) as a compatibilizer for the blend of PLA/PCL = 50/50. The effectiveness of this compatibilizer in improving polymer compatibility has been demonstrated. However, L-lactide- ε -caprolactone causes a decrease in the hydrolysable interfacial surface in the blends of PLA and PCL that decreases the biodegradability.

3. Composites of Poly(lactic acid) with Poly(glycolic acid)

Poly(glycolic acid) (PGA) (Figure 5) has a glass transition temperature of 35–40 °C, a melting point of 220–230 °C, and a density of 1.53 g/mL [45]. PGA also has an increased degree of crystallinity, about 45–55%, which leads to insolubility in water. The solubility of this polyester varies from the molecular weight and the degree of crystallinity. Its high-molecular form is insoluble in almost all common organic solvents (acetone, dichloromethane, chloroform, ethyl acetate, tetrahydrofuran) with the exception of highly fluorinated organic compounds such as hexafluoroisopropanol [46], while low-molecular oligomers are quite different in their physical properties and are more soluble. The mechanical properties of PGA are much higher than those of other biodegradable plastics and the most traditional plastics. It has a tensile strength of about 115 MPa and a Young's modulus of about 7 GPa. The flexural strength and elastic modulus of PGA are about 222 MPa and 7.8 GPa, correspondingly. The molecular structure of PGA has a flat zigzag conformation, which may be the reason for high mechanical properties compared to other biopolymers [47]. Poly(glycolic acid) is widely used in medicine, as well as in the fields of packaging and the oil and gas industry [48].



Figure 5. The chemical structure of poly(glycolic acid).

The presence of hydrolysable ester bonds in the structure of macromolecules makes the polymer capable of enzymatic hydrolysis during composting. According to the studies, the duration of biodegradation for PGA is 1.5–3 months [49]. Therefore, PGA has better mechanical properties and faster degradation than PLA that provides appealing to develop materials based on PLA/PGA blends.

Due to the widespread use of PGA for medical purposes, special attention is paid to nonwovens based on PLA/PGA blends. Y. You et al. [50] have obtained the matrices from ultrafine PLA/PGA fibers by an electrospinning method. Figure 6 shows SEM images of the developed nonwoven materials of different compositions. All ultrathin fibers of the matrices were characterized by a round shape and an average diameter from 200 to 500 nm.

By varying the ratio of PLA/PGA in the blend, it is possible to control the rate of biodegradation [51], as well as the mechanical properties of the materials obtained by an electrospinning method [52]. An acceptable level of physical and mechanical characteristics of PLA/PGA nonwovens allows us to create natural soft tissues, in particular the stretching of blood vessels on their basis. PLA/PGA scaffolds have shown effectiveness in the proliferation and stability of epithelial cells in the intestinal epithelium, and in the treatment



of short bowel syndrome [53]. In addition, such materials have shown an increase in the ability to pass the blood-brain barrier [54].

Figure 6. SEM images of blends of PLA/PGA: 100/0 (a), 70/30 (b), 30/70 (c), 0/100 (d) [50].

R.P. Pawar et al. [55] have studied PLA/PGA blends in orthopaedic applications such as tissue growth implants and fracture fixation devices. Bioabsorbable fixing devices and ultrahigh-strength implants consist of PLA and/or PGA are widely used in orthopaedic and craniofacial surgery. The main areas of application of such materials are stabilizing frames for fractures, bone grafting, reattaching ligaments and tendons, etc. It has been shown that the application of PLA/PGA blends reduces the risks during preimplantation osteoporosis and the risks arising from infections, as well as showing promise for the slow release of bioactive agents in the field of orthopaedics. I. Cantón et al. [56] have created a wound-healing dressing based on PLA/PGA composites, which provides a temporary basis for cell migration in the wound, while simultaneously delivering ibuprofen as an antiinflammatory and analgesic agent. This material collapses in 6 days, which avoids the need to remove this bandage. The flexibility of the electrospinning method allows combining fibre production to support cell attachment and migration with simultaneous drug release. Such dressings based on PLA/PGA blends can be applied in the treatment of superficial burns and for simultaneously reducing the pain and accelerating reepithelization [56].

4. Composites of Poly(lactic acid) with Poly(butylene adipate-co-terephthalate)

Poly(butylene adipate-co-terephthalate) (PBAT) is a biodegradable statistical copolymer from the class of polyesters, in particular the copolymer of adipic acid, 1,4-butanediol, and terephthalic acid (from dimethyl terephthalate). The structural formula of the PBAT monomer units is shown in Figure 7.



Figure 7. The chemical structure of poly(butylene adipate-co-terephthalate).

In terms of technological and operational properties, PBAT is similar to polyethylene; however, its properties can vary in a wide range depending on the composition and molecular weight of the copolymer (a number of adipic acid and terephthalic acid units) [57]. A modulus of elasticity increases, and an elongation at break decreases with an increase in the content of terephthalic units [58]. It has been defined that a tensile strength of PBAT increases while the elongation at break decreases with an increase in molecular weight [59,60]. On average, PBAT is characterized by the following parameters: a tensile strength of 20–22 MPa, an elongation at break of 600–700%, a bending strength of 7–8 MPa, and a modulus of elasticity at a bending of 120–130 MPa.

The monomeric composition of PBAT has a significant effect on the rate of biological degradation (mineralization) of the material. It has been shown that the decomposition rate of PBAT under industrial compost at 60 °C depends on the content of terephthalic acid units and aromatic sequences [61]. With an increase in the proportion of terephthalic acid units, a rate of biological decomposition decreases. Longer aromatic oligomers can be biodegradable in the compost conditions only at elevated temperatures.

The statistical structure of PBAT causes an absence of structural ordering, which affects a low degree of crystallinity up to its absence. A flexible-chain nature of the polymer and a low degree of crystallinity, in turn, causes a low modulus of elasticity and stiffness, but high flexibility. Precisely, the flexibility of this polymer makes it promising for mixing with other rigid polymers, for example, with PLA, to give flexibility while maintaining a complete biodegradability of the blends [62].

In addition, PBAT is used for the lamination of cardboard and paper products used as a part of the flexible films for developing highly filled composites with nano- and micro-sized particles, including biobased fillers. The most well-known commercial trademarks of the materials based on PLA/PBAT blends are Ecoflex and Ecovio, both produced by BASF Corporation.

A number of works consider the problems of combining PLA and PBAT [63], as well as a mutual influence of the polymers on the structure and properties of the blends on their basis. Y.Y. Liu et al. [64] have reported that the solubility parameters (δ) of poly(L-lactide) (PLLA) and PBAT are 19.70 and 19.83 J^{0.5}/cm^{1.5}, respectively. The proximity of these values suggests that these two polymers are potentially miscible. According to the results of the study, the highest miscibility has been demonstrated for the blend with 25 wt.% of PBAT. However, in subsequent studies, the researchers have pointed out a limited solubility of PBAT in the PLA matrix when added up to 2.5 wt.% [63,65]. Above this amount, it is possible to distinguish droplets (domains) separated by phases, the so-called "sea island" morphology [66].

J. Jian et al. [57] have concluded that PLA/PBAT blends exhibit multi-phase behavior due to the incompatibility of the characteristics of each component. It has been shown that a high difference in solubility parameters between PLA and PBAT indicates the immiscibility of this pair of polymers [67,68]. F. Signori et al. [69] have reported that an average diameter of dispersed PBAT domains increased with increasing PBAT content in the blend. In addition, a fracture pattern under tension for specimens changed from brittle to ductile fracture with increasing PBAT content. The signs of interfacial separation in the blends observed by SEM have indicated poor interfacial adhesion between PLA and PBAT in the blends (Figure 8) [70,71].



Figure 8. SEM image of the blend of PLA/PBAT 90/10 wt.% [71].

Despite the limited compatibility of these polymers, numerous researchers have shown synergistic effects when mixing PLA and PBAT. Studying the patterns of changes in the phase structure of the PLA/PBAT blends depending on the composition allows us to control the formation of two continuous phases and create an interpenetrating structure with an appropriate unique combination of properties. As a rule, the methods of capillary rheometry, scanning electron microscopy, atomic force microscopy, dynamic mechanical and thermomechanical analysis are used for the structure investigation. To improve the compatibility of PLA and PBAT, special mixing conditions and compatibilizers can be applied. It has been shown that temperature or pre-treatment conditions (removal of moisture and oxygen during the mixing process) influence developing PLA oligomers with high diffusion and reactivity, which easily migrate to the PLA/PBAT interface region, with the formation of mixed chains (copolymers) that, in turn, determine the materials' degradability [72].

Y. Deng et al. [73] have calculated the threshold value for the formation of a cocontinuous phase structure for the blend of φ PBAT/ φ PLA, equal to 0.235, which corresponds to a PBAT concentration of 19 wt.%. This result has been confirmed by the mechanical properties study: an elongation at break sharply increases from about 10% to 300% in the composition range from 10 to 20 wt.% PBAT in the blend. E. Sritham et al. [74] have stated that a modulus of elasticity of the blends of PLA/PBAT can be improved if the PLA content is at least 40 vol.%. When the content of PLA in the blend is from 10 to 40 vol.%, there is no significant effect on the tensile strength of the materials. L. Jiang et al. [70] have shown that with an increase in the PBAT content (5–20 wt.%) a decrease in tensile strength and modulus of elasticity occurs; however, elongation and toughness increase suddenly. With the addition of PBAT, a type of deformation under tension changes from brittle fracture for pure PLA to plastic flow for the blend with PBAT content more 20 wt.%. H.Z. He et al. [72] have shown that the introduction of PBAT significantly contributes to the cold crystallization of PLA using the method of differential scanning calorimetry. The degree of PLA crystallinity has increased from 2 to 19% and the PLA crystallization temperature has increased from 121.9 °C to 99.1 °C in the blend PLA/PBAT = 70/30 wt.% compared to pure PLA.

An ability to degrade the PLA/PBAT blends has been studied under the influence of various media [75,76]. The degradability of such blends was influenced by a composition of the mixture, hydrophilicity, and the mechanisms of biodegradation of the components. It

has been shown that a presence of butylene adipate units in the PBAT copolymer causes an increased ability to hydrolyse under the action of microbiological enzymes [57,77]. According to these studies, in the process of biodegradation, the molecular weight of polymers decreases; however, the crystallinity increases, which is due to the greater availability of amorphous regions for microorganisms. Hydrolysis during biodegradation also affects the thermal stability and thermal decomposition of PLA/PBAT composites. The TGA curves of composite films before and after 24 months of biodegradation are shown in Figure 9. The degradation temperature of PBAT after degradation migrates to a lower temperature, though not as significantly as PLA, which can be attributed to the faster molecular chain fracture of PLA [76].



Figure 9. TG curves of PLA/PBAT composite films (a) before and (b) after 24 months of degradation [76].

5. Composites of Poly(lactic acid) with Poly(ethylene-co-vinyl acetate)

The copolymer of poly(ethylene-co-vinyl acetate) (EVA) belongs to the class of poly(olefins) and is obtained as a result of copolymerization of poly(ethylene-co-vinyl acetate) monomer (Figure 10). The properties of EVA vary in a wide range depending on the number of vinyl acetate groups in the chain.



Figure 10. The chemical structure of poly(ethylene-co-vinyl acetate).

The vinyl acetate content has two fundamental effects affecting the properties of EVA copolymers. The first effect is the destruction of crystalline regions formed by poly(ethylene) segments of the copolymer. Low- and medium-density poly(ethylenes) obtained by volumetric method under high pressure usually have a degree of crystallinity in the range of

40–65%. The degree of crystallinity of poly(ethylene-co-vinyl acetate) gradually decreases as the content of VA units increases, the copolymer with 40–50 wt.% of VA units becomes completely amorphous. The second most important effect of the vinyl acetate content is related with their polar nature. Thus, with an increase in the vinyl acetate content, a polarity of the copolymer changes. Although an increase in polarity is not as important as a decrease in crystallinity, it also leads to certain patterns of behaviour of the material [78]. The molecular structure of EVA determines a wide variety of applications of this copolymer.

F. Singla et al. [79] have studied the blends based on PLA and EVA with a scanning electron microscopy (SEM). It has been shown that the blend of PLA/EVA is characterized by a two-phase morphology with EVA domains dispersed in the PLA matrix (Figure 11) [80,81]. Droplet-matrix morphology of the blends were typical for all the blends with lower content of EVA with signs of phase adhesion [82] and the blends with a higher content of EVA (more 30 wt.%) are characterized by the structure of interpenetrating phases of polymers [83–86].



Figure 11. TEM images of the blends of PLA/EVA: 90/10 (a), 70/30 (b) [81].

By compounding PLA and EVA, the possibility of improving the mechanical properties is realised [87]. It has been found that the compatibility of PLA and EVA increases with an increase in EVA content in the blend [81]. Due to a high elasticity and low crystallinity of EVA, it is possible to fill PLA/EVA blends with dispersed particles. P. Sinha et al. have used crushed pine needles as a reinforcing filler for the PLA/EVA blends. The applied treatment with sodium hydroxide of pine needles increases thermal stability and reduces water absorption, compared to the initial materials [88]. R.K. Singla et al. have found that adding EVA reduces the crystallinity and glass transition temperature of PLA. Lower crystallinity leads to an increase in the rate of water absorption and accelerates biodegradation in the amorphous phase. An increase in the EVA content during the continuous PLA phase increases a number of EVA droplets in the material, which, in turn, enhances biodegradation due to facilitated water diffusion [79]. Some scientists have investigated PLA/EVA mixtures as a coating of the stents for drug elution. It became known that a rate and an amount of drug release can be adjusted by varying PLA/EVA ratio.

The study by thermogravimetric analysis has showed a two-stage degradation of the blends PLA/EVA. The intensity of the second degradation peak increases symbiotically to increase in the EVA content, and, consequently, the thermal stability of the materials drops. A dynamic modulus of elasticity of the PLA/EVA blends gradually decreases with the addition of EVA component. The rheology data results have shown a monotonous increase in the dynamic modulus of elasticity, loss modulus, and complex viscosity with an increase in EVA content in the blend. This increase has been explained by an enhanced phase interaction between polymers [79].

T.A. Makhetha et al. [89] developed the composites of PLA/EVA filled by sugarcane bagasse for obtaining the materials to purify water. The best indicators have been achieved for the blend of PLA/EVA/bagasse = 50/50/15 that has been explained by a continuous morphology ensuring constant penetration of the solution into the composite. D.V. Cong et al. have investigated the biodegradation of PLA and the PLA/EVA blends in the local soil (for 15 months, with intervals of 3 months). According to the results, the PLA/EVA blends have been subjected to a high degree of decomposition [90].

P. Lohrasbi et al. [91] have created the super strong materials based on PLA/EVA blends. It has been achieved by crosslinking with the initiator dicumyl peroxide (DCP), adding silicate nanoparticles, and simultaneous dynamic vulcanization. Such treatment has induced better compatibility and interfacial adhesion of the polymers, as well as improved elongation at break and impact strength. D.-H. Han et al. [92] have studied the foams based on the PLA/EVA blends. The results of the study have shown that the materials with 10–20 wt.% of PLA have similar cells and a foaming coefficient as neat EVA. With an increase in PLA content of more than 40 wt.%, a significant decrease in the number of cells occurs. It is also claimed that the properties of foams can be controlled by varying the ratio of PLA/EVA (Figure 12).



Figure 12. Physical properties of the EVA and EVA/PLA blends Young's modulus [92].

T. Zhang et al. [93] have studied the behaviour of the blends of 85PLA/15EVA with the addition of hydrophilic SiO₂ with different amounts of silanol. SiO₂ with a low silanol number is mainly distributed in the EVA phase, SiO₂ with an average silanol number is dispersed uniformly in EVA droplets and at the interface of the PLA and EVA phases, while almost all SiO₂ with a high silanol number accumulate at the phase interface in the form of large agglomerates. The localization of SiO₂ in the interface region significantly increases an impact strength and preserves the strength and modulus of elasticity.

6. Composites of Poly(lactic acid) with Poly(3-hydroxybutyrate)

Poly(3-hydroxybutyrate) (PHB) was the first isolated and characterized among poly(hydroxyalkanoates) [94]. It is formed as a carbon reserve in a wide range of producing bacterial strains and is produced industrially by bacterial fermentation [95]. Figure 13 shows the typical chemical structure of poly(3-hydroxybutyrate). PHB is characterized by the presence of a methyl functional group (-CH₃) and a group of ester bonds (-COOR); these functional groups are responsible for the thermoplasticity of materials, hydrophobicity, high crystallinity, and brittleness.

PHB is semi-crystalline polymer due to its linear-chain structure containing both amorphous and crystalline phases. Typical values of the degree of crystallinity range from 50 to 80% [96]. A higher the degree of crystallinity induces more rigidity and durability. The degree of crystallinity can also influence hardness, the modulus of elasticity, density, transparency and a pattern of cold drawing or ductile flows. One of the problems associated with PHB is its narrow temperature range of processing, particularly a small difference

13 of 24

between malting and decomposition temperatures, as a result of which this material is subjected to thermal decomposition at temperatures around the melting point. The addition of PLA to PHB provides an increase in the thermal stability of the latter.



Figure 13. The chemical structure of poly(3-hydroxybutyrate).

PHB has better barrier properties compared to both polyethylene terephthalate (PET) and polyvinyl chloride (PVC); however, it is more rigid and less flexible than traditional synthetic polymers. PHB is characterised by a high ability to biodegrade when the material is in contact with decomposing microorganisms in biologically active media, such as soils, fresh water, and industrial composting conditions, which make it an environmentally friendly alternative to synthetic polymers.

The creation of blends based on PLA and PHB makes it possible to level the disadvantages of each of the polymers. M.K. Patel et al. [97] have described the effect of PHB on barrier properties of PLA in the blends. The materials were obtained from PLA/PHB blends with glycerin triacetate (GTA) as a plasticizer and chitin nanocrystals (CNA) as a structural modifier (increasing the crystallinity). The blend of 75PLA/25PHB showed the formation of many small spherulites of PHB with the highest crystallinity of PHB among the studied composites and was chosen as a matrix for nanocomposites with CAN (Figure 14).



Figure 14. Polarized optical micrographs of melted films on the hot stage showing the crystallization of (**a**) pure PLA, (**b**) 90:10 with no visible crystallization, (**c**) 75:25 small crystallites well-dispersed in the PLA matrix, (**d**) 50:50 with large spherulites and (**e**) pure PHB showing very large spherulite size compared to the blends [97].

GTA has a negative effect on thermal properties. CNA acts as a nucleating agent for the PHB phase and lead to the formation of well-dispersed PHB spherulites in the PLA phase and a significant increase in the crystallization rate and degree of crystallinity. The nanocomposite with the highest crystallinity is characterized by significantly reduced permeability to oxygen and carbon dioxide and increased mechanical properties compared to the non-filled blend. A significant improvement in crystallinity and the formation of homogeneous spherulites was reflected in the excellent barrier characteristics of nanocomposites.

M. Abdelwahab et al. [98] have studied a surface morphology of the PLA/PHB blends by SEM (Figure 15). Neat PLA is cauterized by a smooth and uniform surface containing several holes, while neat PHB is characterized by an uneven surface due to its crystalline structure. Roughness has been observed on the surface of the 75PLA/25PHB, and cracks mainly develops in one direction, indicating that the resistance to crack propagation is rather low.



Figure 15. SEM images of the blends of PLA/PHB: 100/0 (a), 0/100 (b), 75/25 (c) [98].

M.P. Arrieta et al. [99] have investigated the compatibility of PLA and PHB by block copolymer of ethylene oxide/propylene oxide in the form of flakes and a mixture of two liquid natural surfactants with variable lipophilic-hydrophilic composition. A morphological analysis of the compatibilized blends has shown that liquid surfactants are more effective than solid copolymers in improving homogeneity, as also evidenced by the results of rheological measurements. In addition, thermal analyses have shown that the presence

(c)

of both types of compatibilizers causes an increase in the degree of crystallinity of the polymers. A noticeable increase in an elastic modulus value for the compatibilized blends has been identified in comparison with pure analogues. It has been shown that both selected surfactants improve the compatibility of PLA and PHB and give them improved mechanical properties. In the further study [100], the ability of PHB acting as a nucleating agent for PLA has been investigated. It has shown a positive influence of PHB on the mechanical resistance and barrier properties of PLA.

D. Aydemir et al. [101] have developed the materials on PLA, PHB, and cellulose nanofibrils (CNF). It has been proven that the mechanical properties of neat PHB improved markedly due to the good intermolecular interaction between PLA and PHB. The thermal stability of PHB has increased by the addition of PLA. The dynamic mechanical and rheological properties of PHB generally improved with adding both PLA and CNF.

M.J. Garcia-Campo et al. [102] have reported the development of the composites with improved impact strength due to the preparation of triple mixtures with PHB and two flexible-chain polyesters obtained from succinic acid, namely, poly(butylene succinate) (PBS) and poly copolymer (butylene succinate-co-adipate) (PBSA), by reactive extrusion. The results obtained have shown that the introduction of flexible-chain polymers improves the toughness and elasticity of PLA/PHB blends. The addition of epoxidized vegetable oils (soy and olive) slightly improves the compatibility of all three polyesters in the blends, which gives additional improvement in plastic properties compared to the original triple mixtures. In addition, the operating temperature range of these materials is expanding.

Z. Vanovčanová et al. [103] have studied the triple blends of biodegradable polymers PLA/thermoplastic starch (TPS)/PHB with a constant content of TPS (50 wt.%). The PHB content in the mixtures varies from 0 to 20 wt.%. The results showed that differences in morphology strongly affect the mechanical properties of the studied materials with the same composition.

M. Zhang et al. [104] have studied the blends of PLA, PHB, polyethylene glycol (PEG) and corn starch (CS) with PEG in three different concentrations (2, 5, and 10 wt.%). The glass transition temperature and crystallization temperature have decreased with increasing PEG content, while the thermal stability of the materials did not change. The physical properties have turned out to be optimal at a ratio of 70PHB/30CS. Starch granules act as nucleating agents for PHB. Intermolecular hydrogen bonds have been observed in the blends, and the bonds are stronger between PHB and starch with a high amylose content. It has been determined that PLA and PHB are not compatible; however, they demonstrate some molecular interaction. PHB enhances the recrystallization of PLA. The addition of PLA improves the mechanical properties of PHB. The blend of 75PLA/25PHB demonstrates significantly high tensile properties compared to pure PLA. The biodegradability of the mixtures improved with an increase in the PHB content.

I. Armentano et al. [105] have obtained the blends of PLA/PHB plasticized with lactic acid oligomer (LAO) at three different concentrations (15, 20, and 30 wt.%) to improve processability and mechanical properties. It has proven to be a good plasticizing effect of LAO (glass transition temperature has significantly decreased and plasticity has increased). At the same time, the barrier properties have improved. The blend of PLA/PHB with 30 wt.% OLA has been chosen as an optimal composition for food packaging, since it provides an optimum between plasticity and barrier properties for oxygen and water vapor with almost no migration of OLA.

G. Cárdenas-Triviño et al. [106] has studied the thermal degradation of PLA/PHB mixtures with the addition of Ag and Cu nanoparticles. The blended materials demonstrate a fairly high rate of degradation with an exception of the composition of PLA/PHB = 70/30. According to the authors, it is evidence of the best compatibility of polymers in this mixture. The PLA/PHB/nanoparticle blends have showed a higher value of Young's modulus. TGA shows two different decomposition temperatures for all mixtures and a mass loss proportional to the percentage of the initial components of the mixture; however, for the blend of



70PLA/30PHB, decomposition intervals have not been observed, which may indicate some compatibility (Figure 16).

Figure 16. Typical of TGA (a) and DTA (b) of PLA/PHB blends [107,108].

M. Kervran et al. [107] have attempted to explain the kinetics and mechanism of thermal decomposition of PHB and PLA in the blends. They concluded that the thermal stability of PLA in a mixture with PHB is lower than that of pure PLA, in contrast to PHB with higher thermal stability in a mixture with PLA. Consequently, the mechanism of thermal decomposition of PLA/PHB mixtures should be considered as a complex physicochemical phenomenon (Figure 16). Moreover, the choice of additive strongly affects the thermal stability of the mixtures. The method of processing and localization of the additive in different phases or at the interface of phases are factors determining the ultimate heat resistance of the mixture.

D. Kong et al. [109] have shown that PLA and PHB are not compatible, but there is a molecular interaction between these two polymers in the entire range of compositions. It has been noted that the crystallization of PLA increased in mixtures of PLA/PHB with an increase in the content of PHB to 25 wt.%. It has been established that, according to rheological and thermal properties, the blends with a content of 20–25 wt.% of PHB are the most promising.

J. Surisaeng et al. [110] have developed 3D printing filaments from mixtures of PLA/PHB with PEG for use in 3D printing technology as an alternative material for making a model of a bone frame. The fibres were manufactured with a ratio of PHB/PLA: 100/0, 90/10, 70/30, 50/50, 30/70, 10/90 and 0/100 wt.%. The results of the DMA showed that the optimal 3D printing temperature for all mixed rods is 190 °C. Changes in thermal properties indicate partial compatibility of PHB and PLA in the mixtures. PLA plays a key role in improving the mechanical properties of PHB (Figure 17).



Figure 17. DSC thermogram of neat PHB, neat PLA, PHB/PPG, PLA/PPG and PHB/PLA blends [110].

M. Culenova et al. [111] have conducted a comprehensive in vitro study of the characteristics of a mixed material based on PLA, PHB, and thermoplastic starch (TPS) in order to assess its potential for use in the field of tissue engineering. The authors focused on the biological behaviour of the material, mechanical, and morphological properties, as well as the possibility of manufacturing a frame from a mixture using a 3D printer. It has been found that the materials have no toxic effect on cell culture and, therefore, can be considered biocompatible. In addition, the mixture is applicable for 3D printing. The printed frames had a highly porous morphology and were also capable of absorbing water. The work demonstrates that cells can attach and multiply/reproduce on the surface of the frame. The material can be successfully used in tissue engineering.

7. Discussion

As mentioned above, PLA is an aliphatic thermoplastic polyester, which is one of the most widely studied and promising among biodegradable polymers. PLA has a high modulus of elasticity and strength, good transparency, and barrier properties. These properties make PLA a suitable candidate for use in goods and machinery to replace some traditional synthetic polymers. However, there are disadvantages that limit its production and use in some applications. PLA is hydrophobic, and it is characterized by fragility, low degradation temperature, and a slow crystallization rate, which reduce its manufacturability, formability, and foaming [17,112–114].

Therefore, many researchers have set a course to improve the properties of PLA, mainly by mixing with other polymers, including, for example, $poly(\epsilon$ -caprolactone); poly(glycolic acid); poly(butylene adipate-co-terephthalate); poly(3-hydroxybutyrate); poly(ethylene-co-vinyl acetate). As a result of mixing, a synergistic effect is obtained. For example, its fragility decreases and the elasticity of the PLA increases. Of course, mixing two polymers brings its properties to the polymer–polymer system.

According to equilibrium thermodynamics, two polymers undergo complete mixing when the Gibbs free energy during mixing is negative, and a homogeneous composition is obtained as a result. Unfortunately, most of the polymers are practically immiscible and the presence of interfacial interactions between polymer components plays an important role in the structure and properties of the mixture [115]. Consequently, if two polymers are incompatible, their interfacial tension is very high and each polymer contributes to T_g . However, when two non-miscible polymers are more or less compatible, the interfacial layer will not be so pronounced, and thus the interfacial adhesion between the two phases will improve. Despite these difficulties, the phase interface creates prerequisites for increasing and expanding the range of diffusion-transport properties (water vapor, gases) and accelerating biodegradation. At the same time, even a small intermolecular interaction (by the type of adhesion) along the phase interface does not allow for a significant decrease in strength and elongation.

Attention should be paid to the possibility of regulating the architecture of polydimensional mixtures using the entropy factor. In [116], the theoretical foundations of the influence of the entropy factor on the morphology of bicomponent crystallizing polymer mixtures are considered on the example of polyolefins, using the Flory–Huggins theory. Using the example of PS and PMMA mixtures in [117], the possibility of changing the morphology of mixtures using special BBPS-m-PMMA copolymers was demonstrated. The authors show thermodynamic and technological effects that control segregation near surfaces of different chemical nature. The use of the addition of architecturally complex copolymers provides a universal approach to the separation of surface and bulk chemistry, and the possibility of introducing new surface properties or functional capabilities [117].

These studies demonstrate that the process of surface segregation is controlled by a combination of weak enthalpy and strong entropy factors. In particular, coordinated experimental and modeling efforts can guide the design of materials and reduce the number of experimental iterations, which is important for the development of coatings, films, and adhesives based on architecturally complex polymer mixtures [118].

In the work [69] demonstrated the effect of the enthalpy component in improving the architecture of mixtures of biodegradable polymers. Using the example of mixtures of biodegradable aliphatic poly(lactic acid) (PLA) and poly(butylene adipate-co-terephthalate) (PBAT), the possibility of compatibilization using thermal degradation products has been demonstrated. The authors found the ability of these polymers to copolymerize under conditions of intensive processing in the melt state. Process parameters, such as temperature or working conditions (removal of moisture and oxygen) determine the degree of decomposition of PLA with the formation of PLA oligomers with high diffusion capacity and reactivity, which easily migrate to polymer phases where copolymerization (twisted polymerization) takes place. The formation of transition copolymers leads to improved compatibility between the PLA and PBAT phases, which is illustrated by the example of thermomechanical properties and morphological features.

Enthalpy and entropy factors can significantly influence the equilibrium structural organization in heterogeneous polymer systems. However, this innovative technology is based on the use of special polymers or copolymers, the synthesis of which may not be economically viable. Another problem is the instability of the equilibrium state in multicomponent mixtures, which varies depending on the type and intensity of external influence.

Speaking about complex interactions in the structure of polymer blends, including those based on PLA, it is worth noting that depending on the second component, the structure and properties of the entire blends change. The main task, which is largely aimed at by many studies, is that the mixture should demonstrate good characteristics in those aspects where PLA shows weakness in order to compensate for them. The properties are determined not only by the components of the mixture, but also largely depend on the morphology of the mixture. The typical morphology of polymer–polymer mixtures include drop-shaped and double emulsion, laminar, fibrillar, continuous or ordered structures. As a result of such interactions, morphological changes can be: increased toughness, improved barrier properties, increased strength and thermal stability (Table 1).

Polymer Blend Systems	Morphology (SEM)	Tensile Strength, MPa	Elongation at Break, %	Elastic Modulus, MPa	Impact Strength, kJ/m ²	Degree of Crystallinity, %	Degradation Temperature, °C	Researchers
80PLA/ 20PCL	to m	68 ± 2	20 ± 2	2600 ± 100	37 ± 1	62.39/28.63	361.93 ± 2.65	[33]
80PLA/ 20PGA	<u>io,im</u>	130	22.6	3.9	-	39/35	354	[50,119,120]
80PLA/ 20PBAT	<u>to pm</u>	38.95 ± 1.21	387.85 ± 26.88	2250	4.85 ± 0.27	39	422.9/378.7	[121,122]
80PLA/ 20EVA	<u>10µт</u>	45	340	64	8.28 ± 0.11	3.8	331	[87,90]
75PLA/ 25PHB	ος <u>Ιψμη</u>	16 ± 3	7.1 ± 1	1270 ± 110	2.5 ± 0.5	36	356/283	[98,104]

Table 1. The main characteristics of blends bas	ed on PLA.
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Thus, the development of mixtures based on PLA with better operational characteristics and lower cost is growing every year. Among binary systems, mixing PLA with biopolymers is of great interest to researchers due to the good properties of the final products. The main purpose of the research on binary compositions based on PLA was to improve the plasticity and impact properties of PLA products with minimal losses in strength and modulus of elasticity.

8. Conclusions

In this review, the positive aspects of using poly(lactic acid) blends with other fossiland biobased polymers to improve a complex of physical-mechanical, diffusion-transport properties and biodegradation were studied. As a rule, most of polymer-polymer blends are considered thermodynamically incompatible. In case of polyesters such as poly(lactic acid), due to the presence of polar groups, blended polymers have a fairly strong intermolecular interaction by the mechanism of hydrogen bond formation. In turn, a high intermolecular interaction in PLA-other polymers blends induces an increase in miscibility of polymers and homogeneity of the materials structure, as well as an improvement of mechanical properties. In the numerous studies conducted, an effectiveness of the modification of PLA with various polymers to increase its elasticity, impact strength, heat resistance, rheological properties and biodegradation have been shown. The most promising modifiers for PLA are flexible-chain polymers, including $poly(\varepsilon$ -caprolactone), poly(glycolic acid), poly(butylene adipate-co-terephthalate) and poly(ethylene-vinyl acetate). The blends PLA with poly(3-hydroxybutyrate) are also considered as the most promising for the creation of biocompatible and bioresorbable materials. The use of various oils, oligomers, and other liquid surfactants for PLA plasticization has a short-term effect associated with the intensive migration of these substances from the polymer matrix. According to a number of studies, PCL, PBAT, and EVA, when processed in the melt, can improve the processability

and have a plasticizing effect on PLA. In addition to that, it has been proven that flexible chain polymers have a significant effect on the structural and dynamic properties of PLA, which are expressed in a change of crystallinity and crystallites size. Polyesters that are more susceptible to hydrolysis, such as PCL, PBAT, and PHA, can accelerate the biodegradation of PLA under nature and living conditions. PHA, first of all, PHB, are the most effective; however, these polymers cannot improve the physical and mechanical properties of PLA. In the near future, it is possible to predict the development of environmentally friendly multicomponent polymer blends based on PLA for a combination of high relative elongation, strength, and impact strength, on the one hand, and manufacturability during processing, on the other hand.

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