Review Article

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Recent advances in compatibility and toughness of poly(lactic acid)/poly(butylene succinate) blends

<https://doi.org/10.1515/epoly-2021-0072>
received May 25, 2021; accepted August 09, 2021

Abstract: Poly(butylene succinate) (PBS) has good impact strength and high elongation at break. It is used to toughen biodegradable poly(lactic acid) (PLA) materials because it can considerably improve the toughness of PLA without changing the biodegradability of the materials. Therefore, this approach has become a hotspot in the field of biodegradable materials. A review of the physical and chemical modification methods that are applied to improve the performance of PLA/PBS blends based on recent studies is presented in this article. The improvement effect of PLA/PBS blends and the addition of some common fillers on the physical properties and crystallization properties of blends in the physical modification method are summarized briefly. The compatibilizing effects of nanofillers and compatibilizing agents necessary to improve the compatibility and toughness of PLA/PBS blends are described in detail. The chemical modification method involving the addition of reactive polymers and low-molecular-weight compounds to form cross-linked/branched structures at the phase interface during *in situ* reactions was introduced clearly. The addition of reactive compatibilizing components is an effective strategy to improve the compatibility between PLA and PBS components and further improve the mechanical properties and processing properties of the materials. It has high research value and wide application prospects in the modification of PLA. In addition, the degradation performance of PLA/PBS blends and the methods to improve the degradation performance were briefly summarized,

and the development direction of PLA/PBS blends biodegradation performance research was prospected.

Keywords: PLA, PBS, physical blending, chemical modification, compatibilization

1 Introduction

In today's world, green development has become the mainstream trend that is followed to address the environmental problems caused by white pollution. Biodegradable materials are increasingly researched and developed, and have been gradually applied in packaging, clothing, medical care, and other fields (1). Poly(lactic acid) (PLA), a biodegradable material with excellent mechanical strength, machinability, and good biocompatibility, has the potential to replace traditional petroleum-based polymers (2–4). However, PLA exhibits inherent high brittleness, low elongation at break, and slow crystallization rate that limit the wide application (5). Blending with flexible polymers is one of the best ways to toughen PLA. Highly elastic polymers, such as natural rubber and nitrile butadiene rubber, can greatly improve the toughness of PLA, but can also destroy the biodegradability of the PLA materials. Biodegradable materials, such as poly(butylene succinate) (PBS) (6–8), poly(butylene adipate-co-terephthalate) (9–11), and polycaprolactone (12,13), are blended with PLA to toughen it and maintain the biodegradability of the PLA materials.

Among the above materials, PBS has good impact strength and high elongation at break (14,15). It is an ideal material for PLA modification because it toughens while maintaining PLA's own strength and improving PLA's crystallization performance (16). However, PLA and PBS have incompatible two-phase thermodynamics and small interface bonding force, and PBS, when used as a dispersed phase size, has an excessively large size; these characteristics result in the lack of considerable improvement in the overall performance of the resulting blends (17). Given this situation, improving blend

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compatibility and ensuring good PBS dispersion is particularly important in improving the performance of blends. According to a large number of studies and reports on PLA/PBS blend systems by domestic and foreign scholars, methods for the modification of PLA/PBS blend systems are mainly divided into physical and chemical modification techniques. Physical modification aims to realize the dispersion of the dispersed phase and filler with the help of shear force, to adjust the phase morphology of the dispersed phase, and to disperse the filler uniformly by changing the shear rate and process parameters. The addition of compatibilizers, nanoparticles, and other functional fillers in the modification process is a feasible scheme to achieve compatible blending (18). For example, the addition of a third component, such as montmorillonite (MMT) (19), nanocellulose (CNC) (20), talcum powder (talc) (21), and block or graft copolymers, can improve compatibility between PLA and PBS. In chemical blending, the mechanical properties, crystallization behavior of the materials, and the interfacial adhesion were improved by adding the substances which could react with the blends to produce the copolymer with clinched structure.

This article summarizes the main ways and methods for improving the compatibility of PLA/PBS blends and the physical and chemical modification methods for improving the mechanical properties, crystallization properties, and other properties of blends on the basis of recent research results. The preparation method of PLA/PBS two-phase blend systems was briefly introduced. The influence of non-reactive compatibilizers and nanoparticles on the compatibility and crystallization behavior of PLA/PBS blends was analyzed. The relationships among the phase morphology of the blend systems, the types of nanoparticles, and the physical properties of the blends were discussed in depth. The modification methods and mechanisms of PLA/PBS blends with three reactive functional groups, including epoxy chain and isocyanate chain extenders and free radical initiators, to improve the interfacial compatibilities of PLA/PBS blends and enhance the mechanical properties of materials were introduced in detail. Finally, the hydrolysis and degradation mechanism of PLA/PBS blends and the influencing factors of degradation performance during the degradation process were introduced.

2 Modification of PLA/PBS blends by physical blending

In the physical blending process, the microphase structure of the blend is adjusted by adjusting the components

of the PLA and PBS blends and changing the composition of the non-reactive compatibilizer and filler. In the blending process, shear force and diffusion help blend and disperse the blend components to improve PLA material properties. The addition of PBS improves toughness by maintaining the excellent performance of PLA itself. The addition of functional fillers in the blending process can improve compatibility and enhance the system.

2.1 PLA/PBS binary blend systems

PLA and PBS are thermodynamically incompatible systems. In melt blending, the size of the dispersed PBS phase is regulated by the shear force of the internal mixer and extruder. This effect reduces the aggregation of the PBS dispersed phase, refines the size of the PBS phase, and regulates the phase structure and mechanical properties of the PLA/PBS blend.

Lertwongpipat *et al.* (22) and Natphichon *et al.* (23) discussed the toughening of PLA by adjusting the proportion of PLA and PBS in the blending process. In these two studies, the impact strength of the blend increased to $48.7 \text{ J}\cdot\text{m}^{-1}$ with the addition of PBS, and processing fluidity was also improved. Deng and Thomas (24) controlled the phase morphology and dispersion behavior of blends by changing the blending ratio of PLA and PBS. As shown in Figure 1, the phase morphology of the blends showed different dispersion morphologies at varied ratios. The tensile toughness of the PLA/PBS blends greatly improved, and the elongation at break increased from 20% to 520%.

In contrast to traditional processing technologies, advanced processing technologies can maintain the PLA/PBS blends' physical properties and improve other properties by different degrees. These advanced technologies include 3D printing, electrospinning, and coextrusion, which was developed in the 1960s. Abudula *et al.* (25) used PLA and PBS to conduct electrospinning. They analyzed the size distribution and orientation of PLA/PBS hybrid fibers by using digital image processing and determined the optimal conditions, such as polymer concentration, voltage, and feeding speed, for preparing PLA/PBS hybrid fibers with uniform sizes. The fabrication of scaffolds by using 3D technology could provide high-precision internal structure control and enable printing complex structures. The porosity, average pore size, and Young's modulus of the scaffolds fabricated on the PLA matrix were 77%, $160 \mu\text{m}$, and 1.35 MPa , respectively, and the composite scaffolds exhibited good biocompatibility, activity, and osteogenic induction performance (26). Messin *et al.* (27) applied the nanometer

Figure 1: Schematic diagrams of the morphological evolution of PBS/PLA blends (24). Copyright 2015. Reproduced with permission from Elsevier.

multilayer co-extrusion process (Figure 2) to improve the barrier effect of semi-crystalline polymers by controlling the number of layers and the thickness of each layer of the PLA/PBS polyester multilayer film. The obtained limited PBS structure improved the barrier performance of the PLA/PBS film against oxygen, water, and carbon dioxide by 30%, 39%, and 70%, respectively.

The phase structure and dispersed phase size of PLA/PBS blends were adjusted by changing the proportion of blend components and processing parameters. The toughness of the blends was improved. The nanolayered structures obtained by using new processing technologies, such as coextrusion technology, show significant gas barrier performance and enhanced mechanical properties. 3D printing technology provides a new material feeding method that greatly shortens the development cycle of the products. Electrospinning technology, a widely used processing technology, can produce ultrathin fibers with

thicknesses ranging from 100 nm to 10 μm . Advanced processing technology provides a new way for the modification of PLA by PBS. However, PLA and PBS are thermodynamically incompatible systems, and compatibilization strategies should be adopted to improve the interfacial compatibility of PLA and PBS components and further improve the toughness and strength of the blends.

2.2 PLA/PBS and third-component blending systems

The size of the dispersed PBS phase in the PLA/PBS binary blend system is large. The occurrence of macroscopic phase separation at the phase interface shows that PLA and PBS are thermodynamically incompatible, and early cracks develop under the action of tensile stress.

Figure 2: Schematic of the PLA/PBS polyester multilayer film co-extrusion process (27). Copyright 2020. Reproduced with permission from Elsevier.

Blending PLA and PBS with a third component achieves a good modification effect by improving interfacial interaction. This approach can effectively decrease the interfacial tension between two phases, promote the dispersion of the dispersed phase, and improve the effectiveness of adhesion. The types of the third blending component can be divided into special compatibilizers, nanofillers, and other kinds of packing.

2.2.1 Compatibilizers

The addition of a compatibilizer can enhance adhesion between PLA and PBS, reduce the agglomeration of dispersed phase particles, and improve the compatibility of the system. Block copolymers or graft copolymers can be used as parts that are compatible with the PLA and PBS phases. Their diffusion into the PLA phase and the PBS equivalent induces entanglement such that the interface has sufficient bonding strength, thus improving the physical properties of the blends.

Supthanyakul *et al.* (28) prepared random poly(-butylene succinate-co-lactic acid) (rPBSL) as the compatible agent of the PLA/PBS blend (Figure 3). The glass transition temperature (T_g) of the blend system decreased from 52°C to 43°C. Moreover, the crystallization temperature (T_c) of the system decreased from 103°C to 85°C, and the elongation at break increased by four times. The increase in crystallinity and spherulite growth rate also proved that rPBSL could effectively induce the rapid nucleation of the blend system. In another study, Supthanyakul *et al.* (29) used a hydroxyl-terminated PBS macroinitiator to prepare the triblock copolymer PLLA-*b*-PBS-*b*-PLLA as a compatibilizer for PLA/PBS blends. Dispersion promoted by rapid cocrystallization effectively adjusted the crystalline and amorphous phases of the PLA/PBS blends. After modification, the T_g of the blend was reduced by approximately 30°C. Relative to those of the pure PLA/PBS film, the elongation at break

and transparency of the blend had increased by 2 and 5 times, respectively. The PLLA chain length and content in PLLA-*b*-PBS-*b*-PLLA played a major role in controlling the performance of the blend. Given that the synthesis of a specific block copolymer as the compatibilizer of PLA/PBS blend improves the compatibility of the blend, the motion of the block copolymer chain segment can induce the motion of the PLA and PBS chain segment during the heat treatment of the blends. This motion plays a crucial role in plasticizing and toughening, and is beneficial to the processing of blends films.

Ding *et al.* (30) synthesized monomethoxy polyethylene glycol-poly lactone diblock copolymer (MPEG-PLA) as a compatibilizer of PLA/PBS mixture. With the addition of MPEG-PLA, the size of the dispersed phase decreased from 2 to 0.3 μm , the elongation at break of the PLA/PBS blends reached 234%, and tensile strength increased to 43 MPa. At the same time, the diblock copolymer with low melting point and low molecular weight, accelerated the chain movement, decreased the T_g of PLA, and exerted a plasticizing effect by acting as the plasticizer. Valerio *et al.* (31) synthesized polyglyceryl succinate maleic acid copolymer (PGSMA) by using glycerin, succinic acid, and maleic anhydride, and used it as a compatibilizer for PLA/PBS blends. The tensile strength, tensile modulus, and impact strength of the PLA/PBS/PGSMA blends reached 33.8 MPa, 1.47 GPa, and 159 $\text{J}\cdot\text{m}^{-1}$, respectively, and the properties of the blends were similar to those of some polypropylene products. Somsunan *et al.* (32) mixed PLA/PBS and polyadipate (G40), and found that with the gradual increase in G40 content, the polymer chain was reoriented. The phase morphology of the blend tended to be uniform and exhibited a cocontinuous phase morphology that improved the barrier property of the material. And the elongation at break reached 72.3% under the condition that the tensile strength and Young's modulus were maintained.

The compatibilization efficiency of PLA/PBS blend systems can be effectively improved by synthesizing

Figure 3: Preparation of rPBSL (28). Copyright 2016. Reproduced with permission from Elsevier.

specific compatibilizers, such that the PLA/PBS blend can maintain their original form in long-term mixing and subsequent processing (33). However, such compatibilizers are applicable only in the current blend systems, and problems, such as complicated processes and low synthesis efficiency, are encountered in the synthesis process. In contrast to the specific compatibilizers used in PLA/PBS blends, nanoparticles are suitable for most blends and can produce blends with excellent mechanical properties.

2.2.2 Nanoparticle compatibilization of PLA/PBS blend systems

Nanoparticles with large specific surface areas and strong stability can increase the number of interfaces in PLA/PBS blends, strengthen the adhesion between PLA and PBS, and prevent the aggregation of the PBS phase, to achieve different degrees of improvement in the mechanical properties, crystallization properties, flame retardancy, and other aspects. Currently, CNC, MMT, graphene, and talc are commonly added into PLA/PBS blend systems.

CNC has been used as a “green” nucleating agent to enhance PLA/PBS blends due to its high strength and unique optical properties. In PLA/PBS composites reinforced with cellulose nanofibers (CNFs), the minimum fiber size of the blends was only 410 ± 50 nm. The strong molecular interaction between the PLA/PBS matrix and CNFs and the reduction in fiber size caused the maximum tensile strength of the composites to reach 3.46 MPa, the elastic modulus to reach 119.6 ± 3.2 MPa, and the elongation at break to reach 115.6%, which is the highest value in human natural tissue. However, the maximum tensile strength and elastic moduli of natural human tissue were only 2.5 and 9.6 MPa, respectively (34). The composite fibers obtained by introducing CNFs into PLA/PBS scaffolds had ideal sizes, good biocompatibility, sustainable biodegradation behavior, and sustainable mechanical properties. Zhang et al. (35) compared PLA/CNC, PBS/CNC, and PLA/PBS/CNC composite films to discuss the crystallization of PLA binary and ternary composite systems. Although CNC and PBS promoted the crystallization and spheroidal growth rate of PLA by providing nucleation centers, the strong interaction between PBS and CNC in the ternary blend system weakened the promotion of nucleation. Luzi et al. (36) added unmodified CNC and surfactant-modified CNC (s-CNC) into the PLA matrix and PLA/PBS blend, respectively, to address the interference between CNC and PBS, and thus solve the problem of nuclear capability. The presence of surfactants on s-CNC was advantageous to the dispersion of nano-crystals in the

polymer matrix. After blending, Young’s modulus increased, barrier performance improved, and water vapor permeability decreased by 44%.

After the enhancement effect of CNCs on PLA was verified, Pal et al. (37) and Lin et al. (38) evaluated the compatibilization effect of thermally reduced graphene oxide (RGO). They found that abundant oxygen-containing groups on the surfaces of RGO could act as coupling agents in PLA/PBS blends and increase the adhesion of the two phases. The addition of 3.0 wt% of RGO could increase the notched impact strength of the PLA/PBS/RGO composite to $6.33 \text{ kJ}\cdot\text{m}^{-2}$ (39).

Nano-MMT, when used as an additive to improve the performance of PLA blends, has a good effect in toughening, strengthening, and improving the dimensional stability of the blends. In PLA/PBS/MMT composites, MMT is embedded in the PLA/PBS matrix to form an “intercalation” structure that participates in capacitation enhancement and heterogeneous nucleation. In foaming, the synergistic effect of PBS and MMT can effectively improve the density and size uniformity of the PLA blends and the shape distribution of bubbles (40). With the addition of MMT, the size of the PBS phase decreases, and the mechanical properties and thermal stability of the blends are improved. Ojijo et al. (41,42) revealed the relationship between the phase morphology and properties of MMT blends in surface modification. They found that the layer spacing enthalpy interaction between the components of the blends and surfactants determined the microstructure and properties of the PLA/PBS blends and that the addition of MMT reduced the size of the PBSA phase and improved the mechanical properties and thermal stability of the blends. Zhou et al. (43), in consideration of the lack of problems between the melt viscosities of PLA and PBS, used cetyl trimethyl ammonium chloride to prepare organic MMT to improve the foaming performance of PLA/PBS blends. They found that MMT was likely to be modified in the PLA/PBS material layer and that the foaming effect improved. The compressive, bending, and impact strengths of the composites increased to 9.2 MPa, 14.0 MPa, and $31.2 \text{ kJ}\cdot\text{m}^{-2}$, respectively, and the average bubble hole size decreased from 475.6 to 261.4 μm . Tan et al. (44) described the intercalation and stripping effects of modified MMT nanocomposites (OMMT) in PLA/PBS (Figure 4). Eccentric rotor elongational flow produced by an extrusion machine enabled the efficient insertion of layers and the stripping of OMMT. Given that the interaction between PBS and clay was better than that between PLA and clay, clay was mainly scattered in PBS phases and localized at the interface of PLA/PBS. The addition of clay inhibited the accumulation of PBS and the role of

Figure 4: Evolution of the dispersion, intercalation, and exfoliation of OMMT in a blend (44). Copyright 2019. Reproduced with permission from Elsevier.

elongational flow and provided a composite material that was characterized by continuous structures. With the addition of OMMT, the tensile strength and impact strength of the blends reached 50.8 MPa and $5.0 \text{ kJ}\cdot\text{m}^{-2}$, respectively, and the Young's modulus of the blends increased from 2,638 to 3,454 MPa.

Talc is a kind of magnesium silicate mineral with a layered crystal structure, special lubricity, water resistance, and chemical inertness. It can be used as a filling material for the nucleation of PLA through an epitaxial mechanism. A study on the isothermal and nonisothermal crystallization kinetics of PLA/PBS/talc blends revealed that the heterogeneous nucleation induced by the talc promoted the 3D growth of the PLA crystals and that the crystallization rate of the blends was significantly improved (45). Li and Huneault (46) used talc, sodium stearate, and calcium lactate as potential nucleating agent to increase the crystallization content of PLA/PBS blends. They applied a combination of acetyl citric acid ethyl ester and polyethylene glycol to evaluate the heterogeneous nucleation effect of the three nucleating agents. Their results showed that over the 80–120°C temperature range, talc could effectively cause PLA nucleation to match plasticizer nucleation, whereas calcium lactate and sodium stearate had almost no nuclear capability. Weraporn and Sommai (47) studied the effects of different addition amounts of talc on the physical and mechanical properties of PLA/PBS blends. Their results illustrated that the tensile strength, Young's modulus, and impact strength of the PLA/PBS/talc composites increase by up to 30% with the talc content. Mhlabeni *et al.* (48) prepared nanocomposites by using layered double hydroxide (SaLDH) with surface stearic acid functional groups, PLA, and PBSA. They reported that SaLDH particles

tended to be distributed in the PBSA phase and lacked good affinity with PBSA. Clay particles were pushed into the interface between PLA and PBSA, thereby reducing the interfacial tension among SaLDH, PLA, and PBSA, the interfacial tension between PLA and PBSA, the size of the PBSA phase, and the compatibility between PLA and PBS. Liu *et al.* (49) modified PLA/PBS blends with halloysite nanotubes (HNT). HNTs were dispersed at the interface of the two polymers and interacted with each other. This phenomenon not only improved the energy storage modulus of the PLA/PBS composites, but also increased the tensile strength of the blends to 31.48 MPa and the elongation at break by 2-fold. At the same time, by acting as the nucleating agent of PLA, HNT decreased the cold crystallization temperature of PLA and increased the crystallinity of PLA.

As a compatibilization method, the addition of nanoparticles not only increases the compatibility of the blends and improves crystallization properties, but also ensures the strength of the PLA/PBS blends and increases the tensile modulus of the materials. However, nanofillers easily agglomerate, and their dispersion in the polymer matrix requires further improvement. Therefore, additional research on the theoretical mechanism underlying the compatibility-enhancing effect of nanofillers and the surface modification of nanoparticles will provide nanomaterials with improved dispersion, nucleation, and mechanical properties.

2.2.3 Other fillers

The addition of some common fillers not only improves the mechanical properties of PLA/PBS blends, but also

enables the full utilization of resources. Totaro et al. (50) and Chuayjuljit et al. (51) used silver skin and wood powder, the by-products of coffee bean roasting, as fillers. Under the condition of constant crystallinity, the mechanical strength and thermal stability of the blends were improved to a certain extent. The uniform dispersion of hydroxyapatite (HAP) particles in the PLA matrix improved the mechanical properties of the material. The addition of a high concentration of calcium carbonate (CaCO_3) helped form polymer structures in the bioplastics that could increase the polymer crystal fraction and decelerate the water absorption rate of the material (52). After HAP was blended with PLA/PBSL, HAP was evenly distributed in the blend, smoothening the surface of the blend matrix, and significantly decreasing the size of the PBSL domain (53). Gigante et al. (54) used acrylic acid copolymer (PS) as a melt enhancer and CaCO_3 as an inorganic filler in a PLA and PBS blend. PS and CaCO_3 enhanced melting by promoting interaction between macromolecules, thus increasing the melt viscosity and yield stress of the hybrid system, the elongation at break and tensile performance of the PLA/PBS blend membrane improved. The blend membrane also showed increased biocompatibility and good antibacterial effect relative to those of the low density polyethylene.

Carboxylate, when used as a nucleating agent to increase the crystallization rate of the PLA component in the PLA/PBS blend, induced the rapid nucleation and growth of the α' -type crystals of PLA, thus improving the mechanical properties of the blend and increasing the crystallinity to 52.2% (55). By using one-step extrusion technology, Meng et al. (56) uniformly distributed starch particles modified with stearic acid in a PLA/PBSA matrix. This modification improved the compatibility between the starch and the PLA/PBSA matrix and minimized the decomposition of the polyester. The tensile properties and impact strength of the PLA/PBS blend improved by 15–20% and approximately 30%, respectively. Furthermore, energy consumption by the one-step extrusion method was 35% lower than that by the two-step extrusion method.

The compatibilization effect of the block/graft polymer that is used as a compatibilizer and the properties of the blends are improved obviously through the addition of a third component to PLA/PBS blends. Controlling the additive amount in the blending process of nanoparticles and PLA/PBS is crucial, because when the additive amount is excessively high, the stress concentration caused by agglomeration leads to a sharp decline in material toughness. Nanoparticles are widely used because they are suitable for PLA/PBS and many other blend systems and easily enter blend systems during blending. Other fillers

may not show outstanding efficiency and effectiveness in increasing compatibility, but may exert a heterogeneous nucleation effect that improves the crystallization property of PLA to a certain extent when used as nucleating agents. This property along with low prices and a wide range of sources are the major advantages.

3 Reactive blending compatibilization of PLA/PBS blend systems

Reactive compatibilization is an effective way to inhibit the phase separation of blends and improve the compatibility of blends. Table 1 summarizes and compares the improvement effects of physical and chemical methods on the mechanical properties, and proves the significance of the effect of reactive blending and compatibilization. This is mainly because in the blending process, the coupling or branching reaction that occurs at the interface between the reactive compatibilizer and the two blends results in the formation of a block or graft copolymer that enhances the interfacial interaction of the blends. In PLA/PBS chemical blending, chain extenders containing different types of groups, such as isocyanate ($\text{R}-\text{N}=\text{C}=\text{O}$), epoxy group ($-\text{CH}[\text{O}]\text{CH}-$), and carboxyl group ($-\text{COOH}$), react with functional groups in the molecular structure of the first phase of the blend. The compatibility of one component with the other improves compatibility.

3.1 Compatibilization of PLA/PBS blends with epoxy chain extenders

Epoxy chain extenders realize chain extension and increase viscosity via coupling or branching reactions between several epoxy functional groups in their molecular structures and the carboxyl and hydroxyl groups on polyester. In PLA/PBS blend systems, the epoxy group in the macromolecular epoxy chain extender is opened, and this reaction generates ether and ester bonds that link the two components together. This phenomenon accounts for the improvement in the compatibility and toughness of the whole blend system.

ADR is a multifunctional epoxy chain extender produced by BASF in Germany. Its monomers include glycidyl methacrylate (GMA), styrene, and methyl methacrylate. It is often used in PLA blend systems to expand chains,

Table 1: Mechanical properties of PLA/PBS composite materials

System	Proportion	YS (MPa)	TS (MPa)	EB (%)	IS	Remarks	Reference
PLA/PBS	80/20	1,300	45.5	310		$T_g = 53.3^\circ\text{C}$ $X_c = 16\%$	(23)
PLA/PBS/rPBLS (film)	80/20/5		40	32		$T_g = 52^\circ\text{C}$, $T_c = 85^\circ\text{C}$	(28)
PLA/PBS/PLLA- <i>b</i> -PBS- <i>b</i> -PLLA (film)	80/20/3	900		5.5		$T_g = 20^\circ\text{C}$	(29)
PLA/PBSA/MPEG-PLA	70/30/3		43	195			(30)
PLA/PBS/G40	70/30/5	600	20	72.3		$T_g = 52^\circ\text{C}$	(32)
PLA/PBS/CNFs	50/48/2		3.46	115.6			(34)
PLA/PBS/RGO	70/30/3		81.8	9	6.33 ^a		(39)
PLA/PBS/OMMT	90/10/3	3,100	50.8	102.7	18.62 ^a		(44)
PLA/PBS/HNT	70/30/6		31.48	17.86			(49)
PLA/PBS/ADR	60/40/0.6			179	38.4 ^a		(57)
PLAPBS/ADR	70/30/1	2,440	47.5	225.9			(58)
PLA/PBS/MCC/ADR	70/30/10/0.5	2,578	38.8	5.3	7.6 ^a		(59)
PLA/PBS/MDI	60/40/5	1,340	280	38			(65)
PLA/PBS/PLA- <i>g</i> -MA (film)	70/30/1	741.5	24.77	4.91		$T_g = 57.2^\circ\text{C}$	(66)
PLA/PBS/TDI (film)	70/30/9	688.5	34.32	28.17		$T_g = 54.3^\circ\text{C}$	(66)
PLA/PBS/PAPI	70/30/0.3		49	220	10.4 ^a		(68)
PLA/PBS/DCP/PLA- <i>g</i> -CNC	70/30/0.2/2.0	27.9	43.3	298	726 ^b		(70)
PLA/PBS/EGMA	78/10/12		38	460	98 ^a		(77)
PLA/PBS/EGMA	78/10/12	6,618			160.3 ^a	$T_g = 64.3^\circ\text{C}$, $T_{cc} = 108^\circ\text{C}$	(78)

YS – Young's modulus; TS – Tensile strength; EB – Elongation at break; IS – Impact strength; units: a – $\text{kJ}\cdot\text{m}^{-2}$, b – $\text{J}\cdot\text{m}^{-1}$.

increase viscosity and the average molecular weights of polymers, and improve the compatibility between PLA and other polyesters. Ojijo and Ray (57) used ADR and PLA/PBS blends to address the high brittleness shown by PLA. The reaction mechanism is shown in Figure 5. In the interface reaction during the blending of nonlinear copolymer structures, ADR reduced interfacial tension, and the blending components formed linear to long-chain branched structures that reduced the size of the dispersed phase after blending. The morphology of the dispersed phase changed from spherical to fibrous. The elongation at break of the blend reached 179%, and crystallization, melt strength, strain hardening, and thermal stability were improved with almost no loss of tensile strength.

Chaiwutthinan et al. (58,59) studied the use of an ADR epoxy chain extender in PLA/PBS and PLA/PBS/microcrystalline cellulose (MCC) blends. They found that toughness improved with the addition of the chain extender, which promoted molecular chain segment motion, increased molecular weight and long branched chain structures, hindered the close packing of polymer chains, and increased the free volume of the composite materials. Compared with pure PLA, the elongation at break and impact strength of the modified PLA/PBS blends had increased by approximately 225.9% and 2-fold, respectively. Cao et al. (60) increased the capacity of PLA/PBS blends by using MCC as the reinforcement material of the polymer matrix and ADR as the chain extender. With the increase in ADR content, the melting

enthalpy of the blends decreased, and the melt viscosity increased significantly. At the same shear frequency, the storage and loss moduli of the blends exhibited an upward trend. Palai et al. (61) used epoxy-functionalized styrene-acrylate (ESA) as the raw material to prepare a PLA/PBSA blend film. The epoxy group in ESA reacted with the carboxyl and hydroxyl groups of PLA and PBSA in a ring-opening reaction to extract hydrogen from the carboxyl group and formed secondary hydroxyl and ester bonds at

Figure 5: Generalized reaction mechanism of Joncryl-PLA and/or PBSA carboxyl end groups (57). Copyright 2015. Reproduced with permission from Elsevier.

the interface between the polymer and ESA. A nonlinear long-chain branched structure was formed between PLA and PBSA. After chain extension, the tensile strength and elongation at break of the blends increased by 50.8% and 172.2%, respectively. Meanwhile, the oxygen permeability and water vapor permeability of the blends decreased by 60% and 14%, respectively. Ludwiczak et al. (62) modified the mixed system with Joncryl 4368 (BASF) as the chain extender, while enhancing PLA/PBS with wood powder. With the addition of chain extender, macromolecular chain extension was observed, as well as an improvement in tensile strength, whereas elasticity remained at the same level as that for the wood flour filled composite. Zhang et al. (63) melted and mixed the PLA-based compatibilizer (PBS-PLLA) and the block copolymer PLLA-*b*-PGMA with PLA/PBS. As shown in Figure 6, the epoxy group of (PLLA-*b*-PGMA)₃ reacted with the end groups of PLLA, PBS-PLLA, and PBS for branching and chain extension. Synergies generated by the *in situ* reaction through the tangling of the branched structure increased the molecular weight of the polymer, limited the movement of the molecular chain, and improved the viscosity of the composite materials. The tensile strength of the PLA/PBS blends continued to exceed 40 MPa after the improvement in polymer compatibility. However, the elongation at break of the blends reached 379.2%.

3.2 Compatibilization of PLA/PBS blends with isocyanate chain extenders

The highly unsaturated –NCO group in the molecular structure of isocyanate chain extenders has high chemical

activity and can react with the carboxyl and hydroxyl groups of PLA and PBS to form polyurethane keys. PLA and PBS that have formed via interface bonding can improve the interfacial compatibility of blends such that the mechanical properties, crystallization properties, and thermal stability of the blends increase by different degrees. Ding et al. (64) prepared a long-chain branched PLA/PBS via PLA/PBS melt blending by adding pyromellitic dianhydride and triglycidyl isocyanurate. A PLA/PBS foam with overall uniform pore structure was obtained. The average pore diameters reached 60 μm . Li et al. (65) used methylene-diphenyl diisocyanate (MDI) to cross-link PLA/PBS composites. The isocyanate group in MDI coupled PLA and PBS to the long-chain polymer, resulting in the formation of a macromolecular network between PLA and the PBS matrix. The elongation at break of the PLA/PBS blend increased from approximately 24.7% to 280%. Phetwarotai et al. (66) used toluene diisocyanate (TDI) and maleic anhydride-grafted poly(lactic acid) (PLA-*g*-MA) as compatibilizers and triethyl citrate (TEC) and tricresyl phosphate (TCP) as plasticizer to modify PLA/PBS blended membranes and studied the effects of the type and content of compatibilizers and plasticizers on the mechanical properties, crystallization behavior, and phase morphology of the PLA/PBS blended films. TEC and TCP changed the crystallization behavior, affected the formation of α' and α crystals, and improved the thermal stability of the PLA/PBS blend films. After reaction with TDI, the PLA/PBS blends exhibited an impact strength of 424 $\text{kJ}\cdot\text{m}^{-2}$ and an elongation at break of 28.17%. This effect was better than that demonstrated by PLA-*g*-MA, proving that TDI was a more effective compatibilizer than PLA-*g*-MA.

Figure 6: Schematic of the *in situ* reactive blending of PBS-PLLA, PLLA, and PBS in the melt in the presence of (PLLA-*b*-PGMA)₃ (63). Copyright 2017. Reproduced with permission from American Chemical Society.

Harada et al. (67) reacted lysine triisocyanate (LTI) with a polymer, the reaction is shown in Figure 7. The sea-island structure formed by blending PLA and PBS was unstable and irregularly shaped. LTI produced components with high molecular weights and insoluble cross-linked components after reacting with PLA and PBS. These phenomena had a certain stabilizing effect on the morphologies and structures of the PLA/PBS blended composites. The PBS-rich domain formed spherical particles through phase separation, thereby adsorbing impact, and increasing the impact strength of the PLA/PBS blend to $50\text{--}70\text{ kJ}\cdot\text{m}^{-2}$.

Hao et al. (68) added polyphenyl polymethylene polyisocyanate (PAPI) to improve the mechanical properties and heat resistance of a PLA/PBS blend. After the addition of PAPI, the gel fraction of the blend increased to 52.2%, the size of the PBS dispersed phase was reduced, and the compatibility of the two phases improved. The elongation at break of the PLA/PBS blend increased from 137% to approximately 220%. Moreover, impact strength increased from 2.7 to $10.4\text{ kJ}\cdot\text{m}^{-2}$, which was approximately 3.9 times the impact strength of pure PLA.

Figure 7: Predicted reaction pathways of PLA-LTI-PBS, PLA, and PBS (67). Copyright 2007. Reproduced with permission from John Wiley and Sons.

3.3 PLA/PBS blends compatibilized by free radical initiator

The addition of a free radical initiator during the blending of PLA and PBS can initiate an *in situ* reaction. For example, dibenzoyl peroxide (BPO) and dicumyl peroxide (DCP) can generate the primary free radicals $\text{BO}\cdot$ and $\text{DO}\cdot$ during thermal decomposition. PLA and PBS form the large free radicals $\text{PLA}\cdot$ and $\text{PBS}\cdot$ through hydrogen abstraction in the presence of the free radicals $\text{BO}\cdot$ and $\text{DO}\cdot$. Through the combination of $\text{PLA}\cdot$ and $\text{PBS}\cdot$, a large number of cross-linked/branched structures form in the phase interface layer of the PLA/PBS blend. These structures can enhance the bonding force of the phase interface, the compatibility of the system, and the blend strength of PLA/PBS.

Campuzano and Lopez (69) blended DCP with PLA/PBS blends and used azodicarbonamide as the foaming agent. They then investigated the foaming properties of the PLA/PBS blends. They found that high melt viscosity at a low shear rate was a material feature that was necessary to prevent cell collapse and obtain a good foam structure during the foaming of PLA/PBS blends. After the addition of DCP, the crystallization temperature of the PBS phase increased by 9.02°C . This effect increased the compatibility, melt viscosity, and crystallinity of the blends and improved cell stability during cooling, thus preventing collapse and resulting in unit cell structures with increased stability. Zhang (70) blended DCP, PBS-g-CNC, and a PLA/PBS blend. The effects of the biological fillers on the morphology and mechanical properties of the blends were studied. The cross-linking structure that resulted from the addition of DCP and PBS-g-CNC greatly weakened the molecular chain mobility of the PLA/PBS matrix and increased the energy storage modulus and T_g of the PLA/PBS blends. Moreover, crystallinity increased from 12% to 30%, and the impact strength of the blends increased from 105 to $726\text{ J}\cdot\text{m}^{-1}$, which was considerably higher than that of the PLA/PBS composites reported in other studies.

Ji et al. (71) blended DCP and PLA/PBS to improve the crystallization performance of the blend system. DCP acted as an initiator to generate cross-linked/branched structures that could induce heterogeneous nucleation, which improved the crystallization capability of PLA. In accordance with the gel fraction and crystallization behavior of the blend, some cross-linked/branched structures were confirmed to act as the nucleation sites of the blend, and their formation enhanced the isothermal crystallization of PLA. Monika et al. (72) used DCP to modify PLA/PBS/functionalized chitosan (FCH)-based nanocomposites. Under the joint action of FCH and DCP, the cross-

linked/branched chain structure that had formed in the blend system participated in nucleation, which increased the crystallization rate and nucleation density of PLA/PBS/FCH and increased the elongation at break, molecular weight, and hydrophobicity of the blend material by approximately 45%, 22%, and 27%, respectively.

Srimalanon et al. (73) used DCP as a free radical initiator to prepare a reactive PLA/PBS blend with *in situ* compatibility (Figure 8). The presence of DCP reduced the size of the PBS domain, and transformed the articular and co-continuous PBS domains into well-distributed PBS domains in the PLA matrix. *In situ* compatibility enhancement resulted in the presence of branched-chain and cross-linked networks at the interface between PLA and PBS. These networks prevented the aggregation of polymer domains and improved the tensile properties of the blends.

Zhao et al. (74) prepared a PLA/PBS/PBS-*g*-GMA blend by grafting GMA with BPO and PBS. The elongation at break of the composite increased from 8.60% to 63.92% with the improvement in compatibility. Hu et al. (75) modified PLA/PBS blends with BPO as a cross-linking agent, and the elongation at break of the blends increased to approximately 400%. Moreover, the rate of degradation by protease K reached 67% after 96 h.

GMA molecules polymerized via the ionic reactions of the active functional vinyl and epoxy groups are commonly used in the modification of ethylene polymers and the polycondensation of polymers. GMA-grafted PLA was used as a compatibilizer in a PLA/PBS/potato pulp (CP) blend, and the mechanical properties of the composites improved obviously (76). Xue et al. (77,78) used PLA, PBS, and ethylene-methyl acrylate, the methyl glycidyl ester of acrylic (EGMA), in the preparation of a new super-toughening ternary blend. The *in situ* reaction of EGMA with the carboxyl and hydroxyl groups of PLA and the hydroxyl group of PBS formed an elastic graft copolymer at the phase interface (Figure 9). The elongation at break and impact strength of the ternary blend containing EGMA reached 549.4% and $46.5 \text{ kJ}\cdot\text{m}^{-2}$, respectively, relative to those of the original PLA. In addition, the *in situ* reaction caused the morphology of the sample to change into a new 3D structure formed by PBS-EGMA-PLA units via EGMA bridging (Figure 10). As a result, the microscopic structures of the PLA/PBS blend from typical matrix dispersion evolved laminar morphologies. The blend showed a high temperature storage modulus of 210 MPa, which was higher than the storage modulus of pure PLA samples. Moreover, the blend demonstrated excellent toughness and stiffness due to the *in situ* reaction and phase interface among PLA, PBS, and EGMA during the formation of the elastic graft copolymer.

Ojijo et al. (79) used triphenyl phosphite (TPP) for melt blending with PLA and PBS. As shown in Figure 11, the heterogeneous coupling of PLA and PBS chains led to the formation of *in situ* block copolymers and acted as a compatibilizer, enhancing interfacial adhesion, and thereby forming ligament-like fibers between the phases. The blend showed an increase in impact strength from 6 to $16 \text{ kJ}\cdot\text{m}^{-2}$ and in elongation at break from 6% to 37%. The toughness of the compatibilized blend improved, and the tensile strength and thermal stability did not significantly reduce.

Ma et al. (80) introduced TPP into the PLLA/PBS system through reactive blending for toughening. The participation of TPP in the reaction induced the highly elastic PBS to form elastic microfibrils that firmly combined with the PLLA matrix. As a result of the improvement in compatibility, the size of the dispersed phase tended to decrease, and the impact strength of the blend reached $28.7 \text{ kJ}\cdot\text{m}^{-2}$, which was nearly 100% higher than that of the blend without TPP. Zhu et al. (81) used TPP as a chain extender in the reaction. The relative molecular weight of the blend system could be improved without changing the crystalline structure, and tensile strength and impact strength reached 63.7 MPa and $4.56 \text{ kJ}\cdot\text{m}^{-2}$, respectively.

The addition of a small amount of BPO, DCP, and TPP can cause cross-linking in polymer blending and greatly improve the toughness of PLA/PBS blends. The cross-linked/branched structure generated in the mixture can act in heterogeneous nucleation; increase crystallization rate, crystallinity, and nucleation density; and improve chain mobility. Given that DCP is highly reactive and has a strong capability to initiate branching reactions, it can effectively promote the adhesion between the two phases. In applications, DCP is also highly effective in improving the compatibility of PLA/PBS.

4 Degradation performance of PLA/PBS blends

The degradation of polymers can be induced by thermal activation, oxidation, photolysis, or hydrolysis processes. In polymer degradation chain scission occurs, and oligomers, monomers, and other low molecular weight species are formed (82,83). The maintenance of degradation performance of PLA/PBS blends is also an important part of evaluating the comprehensive performance of blends. Degradation of these two polymers is usually caused by hydrolysis reaction; after water permeates into the blends, molecular chains are

Figure 8: Mechanism of the formation of a cross-linked network and chain scission between PLA and PBS by DCP (73). Copyright 2018. Reproduced with permission from Elsevier.

broken and a large number of carboxyl groups are formed, and the rate of hydrolysis and degradation of the blends are accelerated (84,85).

Zhang *et al.* (86) studied the degradation behavior of PLA/PBS blends buried for 60 days, and the degradation behavior of PLA and PBS in soil was similar to a certain extent, with the extension of degradation time, the average molecular weight of the blends decreased exponentially. Zhou *et al.* (87) and Wang *et al.* (84) studied the hydrolytic degradation behavior of PLA/PBS blends and found that with the process of degradation, the tensile properties of the blends were all lost earlier than their parent polymers. During the degradation process, both the blends and their parent polymers underwent a slow-to-fast transition in their hydrolysis rates, the reason is that the immiscible

binary blend system causes phase separation, introduces a large number of voids, enhances the hydrophilicity of the blend, and accelerates the hydrolysis of PLA/PBS blend interface region. The hydrolysis and degradation rate of PLA can be controlled by modification. Compared with pure PLA, the weight loss rate of acetylated PLA decreased from 28% to 18% after 60 days of degradation. Moreover, the addition of organic clay made the blends exhibit overall corrosion, and the hydrolysis and degradation of a single polymer film exhibited surface corrosion (88).

Mulchandani and Katiyar (89) simulated and predicted the thermal degradation mechanism of PLA/PBS blends, and pointed out that in PLA/PBS blends, the existence of polymer crystal impurities and some defects became the nucleation part, the thermal degradation

Figure 9: Possible *in situ* reactions among PLA, PBS, and EGMA during melt compounding (77). Copyright 2019. Reproduced with permission from Elsevier.

started from the nuclear site as the growth center, and the thermal degradation mechanism would also change with the addition of nanomaterials and the generation of cross-linking structure. Srimalanon et al. (90) studied the biodegradation activities of *Pseudomonas genisae* and *Stenotrophomonas pavanii* on *in situ* PLA/PBS films doped with 2-hydroxypropyl-3-piperazinyl quinoline carboxylic acid methacrylate (HPQM). The residue of HPQM in the blend can inhibit the growth of bacteria, delay the enzymatic degradation process under buried soil conditions, and reduce the biodegradation rate by 1.4–1.8 times compared with that of PBS/PLA blend without HPQM. However, with the increase in PBS content in the blend, the biodegradation rate will also increase.

The degradability of PLA/PBS blends under composting conditions simulates the degradation process of plastics after use, and tests and evaluates whether the samples can be completely decomposed without causing pollution to the environment. Tolga et al. (91) studied

that under the condition of compost, mineral filler in the influence of the PLA/PBS blend system disintegrating process, the use of chalky powder can produce more voids in the blend, improve the permeability of water to the matrix, and accelerate the hydrolysis degradation. However, the addition of talc powder causes less voids, and the degradation performance is not improved much. The feasibility of using fillers to control the degradation process was verified. Luzi et al. (36) studied that PLA/PBS blends added with CNC and s-CNC reached a disintegration degree of more than 90% after 17 days of compost. s-CNC modified with hydrophilic surfactant increased its dispersity and accelerated PLA disintegration in compost soil. This accelerated degradation behavior is related to different cross-sectional morphologies and the presence of hydrophilic surfactants.

Enzymatic degradation, biological composting, and microbial degradation are effective ways to degrade PLA/PBS materials. With the expansion of the application

Figure 10: Schematic of the morphological evolution of PLA/PBS blends in the presence of different loadings of EGMA (78). Copyright 2020. Reproduced with permission from John Wiley and Sons.

Figure 11: Interphase chain extension and compatibilization model of PLA/PBS blends (79). Copyright 2013. Reproduced with permission from American Chemical Society.

fields of PLA and PBS materials, various methods should be used to modify PLA/PBS blends to obtain excellent mechanical properties, while avoiding damaging their biodegradability. In addition, although PLA is a biodegradable material, it still takes some time for it to be completely degraded in nature. Therefore, it is of great significance to further explore the degradation mechanism of blends and improve the degradation efficiency of PLA/PBS blends.

5 Conclusion

PLA/PBS blends exhibit a broad application prospect as thermoplastic resins with excellent mechanical properties, biocompatibility, and processing performance, after their comprehensive material properties are greatly improved. The use of various compatibilizers to improve the compatibility of blends through physical or chemical blending is a common method for solving the problem of the poor compatibility of PLA/PBS blends. In the process of physical modification, the optimization of production technology and the addition of a third component can improve the toughness and crystallization properties of the blends. The addition of various types of graft and block copolymers as compatibilizers exerts a good compatibilization effect. New synthetic copolymers used as

compatibilizers may introduce new properties while optimizing the properties of blends and are thus worthy of in-depth exploration and research. When applied as compatibilizing agents, nanoparticles can considerably increase the mechanical strength and compatibilizing effect of materials. However, the description of the compatibilizing mechanism is imperfect, and further studies on the compatibilizing effect and the improvement in the various properties of the materials are needed. Chemical modification for enhancing compatibility involves the addition of highly active reactive polymers or compounds with low molecular weight that react with the polymer to form a cross-linked/branched chain structure at the phase interface. The representative reactive compatibilizers, such as ADR, BPO, and DCP, react with PLA and PBS to form branched copolymers that enhance the interfacial adhesion of the two-phase system and improve the strength, toughness, crystallization, and other properties of the blends. This method has considerable capacity for increasing efficiency and is suitable for industrial production after development. Degradation performance, as one aspect of the comprehensive performance of blends, needs to be considered. Enzyme degradation, biological composting, and other methods can make PLA/PBS blends have a good degradation effect. Therefore, it is necessary to consider the influence of various environmental factors and explore the degradation mechanism to fully demonstrate its biodegradability.

Given the trend of green development, improving the compatibility of blends to enhance the comprehensive performance of the blends while fully exploiting the degradation performance of PLA has become the current mainstream research direction. The use of simple compatibilizers that are highly suitable for commercial applications or green chemical reaction methods to improve compatibility and obtain blend materials with super toughness will be conducive to further breakthroughs in the application of PLA materials in the medical field, packaging, and daily life.

Acknowledgement: The authors express great thanks to the National Natural Science Foundation of China (51273060) and Hubei Provincial Key Laboratory of Green Materials for Light Industry (Hubei University of Technology, Wuhan 430068, China).

Funding information: The work is funded by National Natural Science Foundation of China (51273060) and Key Project of Science and Technology Research Plan of Hubei Provincial Education Department, the Open Fund of Hubei Provincial Key Laboratory of Green Materials for Light Industry.

Author contributions: Xipo Zhao and Dianfeng Zhang: writing – original draft, writing – review and editing, methodology, formal analysis, and conceptualization; Songting Yu and Hongyu Zhou: resources, visualization, project administration, investigation, and validation; Shaoxian Peng: resources and project administration.

Conflict of interest: Authors state no conflict of interest.

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