Review

Comprehensive exploration of natural degradation of poly(lactic acid) blends in various degradation media: A review

Noor Afizah Rosli [a], Mehlika Karamanlioglu [b], Hanieh Kargarzadeh [c], Ishak Ahmad [a],[*]

[a] *Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia*
[b] *Biomedical Engineering Department, Faculty of Engineering and Architecture, Istanbul Gelisim University, 34310, Istanbul, Turkey*
[c] *Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza, 112, 90-363 Lodz, Poland.*

A B S T R A C T

Poly(lactic acid) (PLA), a bio-based polyester, has been extensively investigated in the recent past owing to its excellent mechanical properties. Several studies have been conducted on PLA blends, with a focus on improving the brittleness of PLA to ensure its suitability for various applications. However, the increasing use of PLA has increased the contamination of PLA-based products in the environment because PLA remains intact even after three years at sea or in soil. This review focuses on analyzing studies that have worked on improving the degradation properties of PLA blends and studies how other additives affect degradation by considering different degradation media. Factors affecting the degradation properties, such as surface morphology, water uptake, and crystallinity of PLA blends, are highlighted. In natural, biotic, and abiotic media, water uptake plays a crucial role in determining biodegradation rates. Immiscible blends of PLA with other polymer matrices cause phase separation, increasing the water absorption. The susceptibility of PLA to hydrolytic and enzymatic degradation is high in the amorphous region because it can be easily penetrated by water. It is essential to study the morphology, water absorption, and structural properties of PLA blends to predict the biodegradation properties of PLA in the blends.

1. Introduction

Thermoplastic poly(lactic acid) (PLA) is a member of the aliphatic polyester family that is obtained from the polymerization of lactic acid via fermentation of simple sugars from agricultural by-products [1]. The outstanding renewability of PLA can be attributed to the use of these agricultural by-products, which consequently reduces the dependence on petroleum-based polymers; this, in turn, contributes to reducing problems related to the environment and air quality [2]. PLA has received significant research attention in recent decades owing to its appealing features, such as excellent biocompatibility, decent transparency, and high tensile strength and modulus. Key factors such as favorable government policies promoting biodegradable plastic packaging have increased the global demand for PLA production; moreover, its applications have attracted significant global research-based attention. The biodegradability of PLA have facilitated its widespread use in applications involving packaging, disposable goods, automobile components, electronic parts, clothing, and medical equipment.

Despite these promising properties, PLA possesses several disadvantages, such as high brittleness, low thermal stability, low crystallization rate, poor barrier properties, and low biodegradation rate [3–5]. Although PLA is categorized as a biodegradable polymer, recent studies have revealed certain problems related to its disposal, owing to its poor degradation properties [6–8]. ISO and ASTM standards define degradable polymers as materials that undergo mechanical and physical deterioration due to changes in their chemical structures under specific environmental conditions. Accordingly, biodegradable polymers are defined as substances that undergo degradation via the action of microorganisms at ambient temperatures; water and carbon dioxide are released as the final products in this process [9]. However, PLA does not adhere to this definition of biodegradation. PLA is unusual in that the biodegradation occurs in two steps: hydrolytic degradation followed by microbial attacks [10] and the degradation of other biodegradable polyesters via a single-stage microbial attack [11].

Several studies have reported on the possibility of PLA biodegradation. However, the degradation rate of PLA is extremely low at ambient temperatures because the hydrolytic mechanism occurs at temperatures above the glass transition temperature ($T_g \sim 55\ °C$) of PLA [12,13].

Fig. 1 shows the results of our study, in which PLA exhibited significant differences between burial temperatures. Although PLA remained intact after one year of soil burial at 25 °C with no change on the surface other than some soil debris (Fig. 1(a)), the disintegration of PLA was visible, with holes appearing on the surface only after 1 month of burial in soil at 50 °C (Fig. 1(b)). The biodegradation of PLA via microbial attacks is also complicated because of the scarcity of PLA-degrading microorganisms in soil [14,15]. In addition, proteinase K, which successfully degrades PLA, is rarely found in nature. Therefore, PLA degradation in soil typically occurs via the hydrolytic rather than the microbial route [16]. In addition, PLA is known to not degrade in artificial or fresh seawater at 25 °C for ~400 d, and it does not exhibit any mass loss [17]. Therefore, it is crucial to educate consumers about the negative effects of random disposal of PLA-based materials in the environment, as PLA has a low degradation rate, both on land and in the sea.

Among the limitations of PLA, the improvement in the brittleness and degradation properties of PLA have been the focus of recent studies. The disadvantages of PLA have led researchers to conclude that the future of PLA is highly dependent on the use of polymer blending and copolymerization methods to improve its properties [18]. The blending process is one such method employed to improve the properties of PLA. Various PLA blends prepared using different types of rubbers [19,20], aliphatic polyesters [21,22], synthetic polyesters [23], and synthetic polymers [24–26] have been investigated to enhance the properties of PLA. The increase in the number of studies related to PLA, especially those concerning its various polymer blends, indicates the existence of an environmental issue.

To the best of our knowledge, there are no reports in the literature that compile findings regarding the degradation of PLA blends in three different media. Thus, it is essential to present an analysis of factors improving the degradation rate of PLA blends to explain their degradation properties and determine how different types of polymer matrices with and without additives affect the rate of degradation. Although PLA shows deficiencies with respect to biodegradation properties, the addition of inducers can improve these properties. The analysis of approaches employed for enhancing and accelerating the degradation rate of PLA, especially that with high L-lactide content, is the main focus of this review. PLA blends with high L-lactide content have received significant research attention because they are cost-effective compared to PLA with high D-lactide content. However, L-lactide is less susceptible to hydrolytic degradation, which causes PLA with high L-lactide content to exhibit poor degradation properties [12,27]. Additionally, because abiotic and biotic factors are both present under natural environmental conditions, factors that influence the improvement of the degradation properties of PLA blends in three different media (abiotic, biotic, and natural) are elucidated in this review.

2. Typical degradation of PLA

The first degradation step of PLA involves the hydrolysis of the hydrolyzable ester groups on its backbone. As a heterochain polymer, the oxygen and carbon atoms on the PLA backbone facilitate hydrolysis, thereby increasing its vulnerability to biodegradation. The cleavage of the PLA ester linkage chain via hydrolysis occurs randomly in the presence of water, as shown in Fig. 2. The degradation of PLA through hydrolysis has been confirmed by FTIR analysis, in which the absorption peak corresponding to the ester group in PLA was noted to decrease after several months of burial in soil [28]. After the ester linkage breaks, the carboxylic end groups tend to self-catalyze, which directly increases the degradation rate of PLA [29].

Upon hydrolytic degradation, low-molecular-weight PLA and oligomers diffuse out of the bulk PLA and are consumed by microorganisms, a process which is also known as enzymatic or catalytic degradation. PLA molecules with a molecular weight of approximately 10 kDa and below can be consumed by microbes through enzymatic degradation [12,30,31]. A schematic diagram of the enzymatic degradation reaction, which yields carbon dioxide, water, and humus, is shown in Fig. 3.

Enzymatic processes can be divided into two categories: (i) enzymatic oxidation by aerobic microorganisms and (ii) enzymatic hydrolysis by aerobic and anaerobic microorganisms [12]. Enzymatic reactions occur in compounds with particular chemical structures and bonds wherein enzymes can only attack certain functional groups at specific sites. Different enzymes possess varying active-site shapes, and therefore, can only biodegrade specific polymers [12]. Therefore, various microorganisms consume PLA at different rates depending on the shapes of their respective active sites. Proteinase K, pronase, and bromelain are popular enzymes that are known to degrade PLA [32].

3. Natural degradation properties of PLA blends

The degradation rate of PLA is relatively low, particularly in soil and marine environments, and is significantly influenced by environmental factors, such as temperature, water content, type of available carbon sources, and pH [33]. The typical disintegration rate of PLA is low, especially during the initial months of burial [34,35]. The degradation of commercially available high-molecular-weight PLA proceeds slowly in a marine environment, mainly because of the low temperature of water (<~30 °C) [36–38]. The degradation rate of PLA is low in marine conditions, similar to that in soil conditions, because the T_g of PLA is typically higher than the water temperature [17,39,40]. Likewise, PLA does not degrade during 400 days in seawater at 25 °C [17]. The primary degradation mechanism of PLA in marine conditions involves photo-oxidative degradation because the carbonyl group in the PLA structure absorbs ultraviolet light at wavelengths below 280 nm [36,41]. The degradation of PLA through photo-oxidative or photolytic degradation
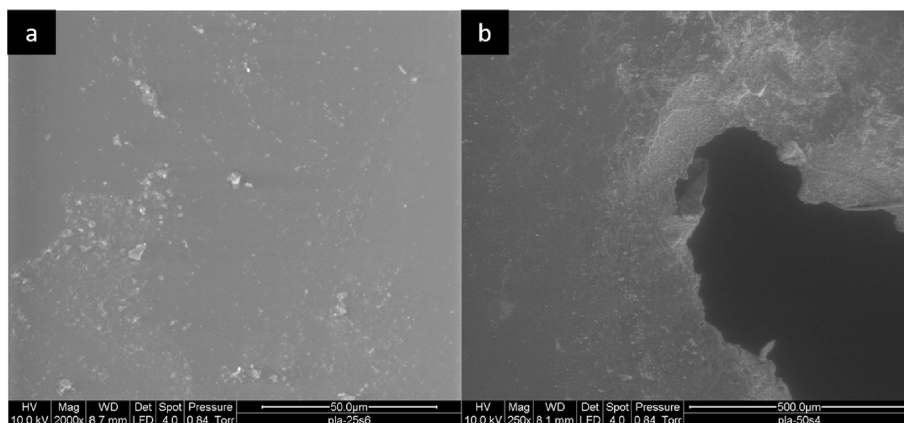

Fig. 1. Micrograph of PLA at (a) 25 °C after one year and (b) 50 °C after one month of soil burial.
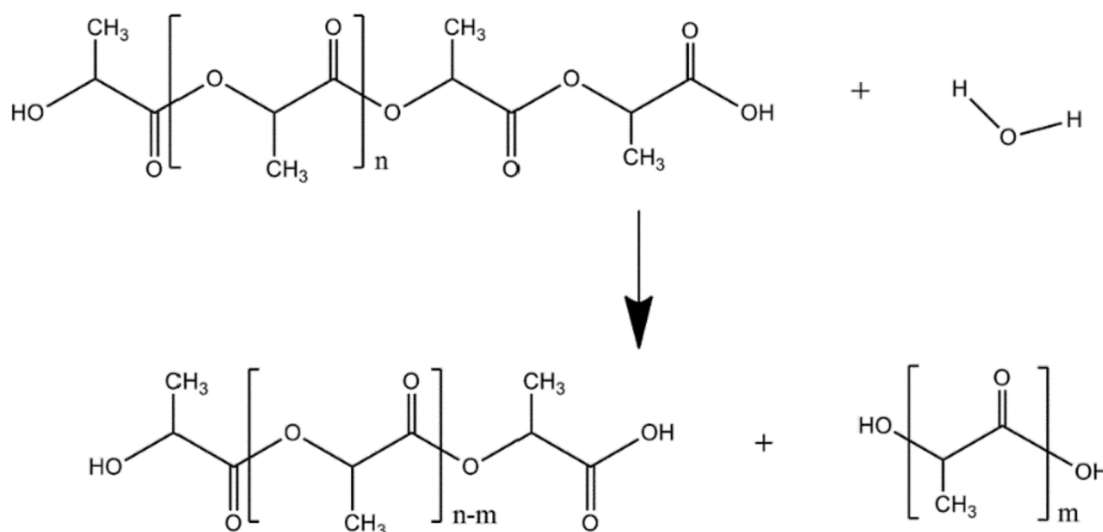
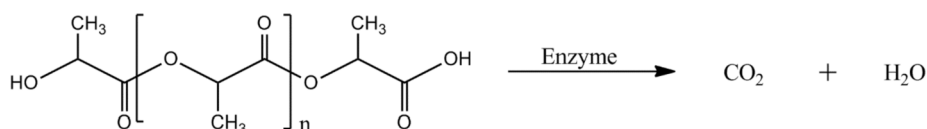**Fig. 2.** Hydrolytic degradation of PLA in the presence of water.

Fig. 3. Enzymatic degradation of PLA in the presence of microorganisms.

mainly involves the Norrish II mechanism [36]. The absorption of photons results in C—O bond dissociation [41]. Nevertheless, like hydrolytic degradation, random chain scission occurs more readily in amorphous regions [42]. The methine group produced through the Norrish II mechanism further degrades into carboxylic acid, anhydride, and diketones [43].

PLA degrades faster under composting conditions than in soil or seawater [44,45]. Compost is a biological environment in which organic material is decomposed into carbon dioxide, water, mineral salts, and humus [30]. Typically, PLA is reported to degrade between 45 and 60 d at 50–60 °C under composting conditions [46]. Compost possesses high temperatures equal to or greater than the T_g of PLA, specifically during the thermophilic phase (~60 °C), which can enhance the PLA degradation rate. There are two types of composting: industrial and home composting. Sedničková et al. [47] concluded that PLA blends with high PLA percentages are not suitable for home composting and should be treated in industrial composting systems as the temperature and stability of the compost can be strictly maintained in industrial composting. Moreover, there are various types of microorganisms in compost because of the availability of carbon and other energy sources, which consequently enhance the degradation capacity of the polymer [30]. Therefore, the degradation rates of different PLA blends in soil, compost, and seawater environments are discussed in detail.

Generally, high humidity (60%) and high water absorption facilitate the hydrolysis reaction and increase the degradation rate of PLA [48]. However, PLA has a high water resistance owing to the steric shielding effect and hydrophobicity of its methyl side group (–CH₃) [28,49]. Blends of PLA with starch, a natural and inexpensive biopolymer, have been investigated to improve biodegradability and reduce the production costs of PLA [45,50]. PLA blends with thermoplastic starch (TPS) are known to disintegrate after 21 d in compost [50]. The addition of 50% starch to ternary blends of PLA/poly(caprolactone) (PCL)/starch results in an increase in the weight loss from 20 to 80% after 16 weeks in soil [51]. PLA blends with starch were found to absorb more water than PLA, indicating that starch increases the hydrophilicity of PLA blends [51]. This consequently increases water absorption, which causes the

polymer to swell and enhances the biodegradation rate.

In addition to increasing the hydrophilic properties, the addition of starch also disrupts the crystalline structure of PLA, thereby increasing the degradation rate of the PLA blends [49]. The rate of reaction of hydrolysis in the crystalline region is significantly lower than that in the less-organized amorphous region. The effortless penetration of water into the amorphous region compared to that in the crystalline region increases the susceptibility to hydrolysis in the former. Therefore, the degree of crystallinity of PLA can be altered via blending, which can yield samples with several degradation rates. An increase in the amorphous regions of PLA/natural rubber (NR) blends has been reported by Rosli et al. [28]. A high content of NR increased the biodegradation rate of PLA/NR blends in soil. As the content of the amorphous phase increased, the blend became more flexible, which increased the water diffusion. The effects of the crystalline and amorphous structures on the water absorption rate in the PLA blend is shown in Fig. 4. The image shows high water diffusion in the amorphous region, which ultimately increases the degradation rate of the PLA blend.

The degradation rate of PLA/starch/gelatin blends assessed in seawater under laboratory conditions was determined to be higher than that of commercially available biodegradable polymers [52]. The blend disintegrated after 4 weeks in seawater [52]. Similar to starch, gelatin also enhanced the biodegradability of the PLA blends owing to its higher fragmentation. An amorphous phase was observed around crystalline PLA in the microstructure of the blends, which enabled water diffusion and quicker degradation. Consequently, a PLA/starch/gelatin blend has been proposed for fabricating short-shelf-life packaging materials [52,53]. High- and low-molecular-weight linear PLLA and three-armed *star*-shaped poly(DL-lactic acid) (PDLLA), respectively, have been combined into amorphous *all*-PLA blends [38]. These samples were immersed in bottles containing seawater and biodegradation was assessed using a biochemical oxygen demand test [38]. The biodegradation of *all*-PLA blends in seawater increased with the amount of three-armed star-shaped PDLLA, whereas the biodegradation of linear PLLA was insignificant [38]. The high content of amorphous three-armed star-shaped PDLLA in the blend decreased the crystallinity of the *all*-PLA
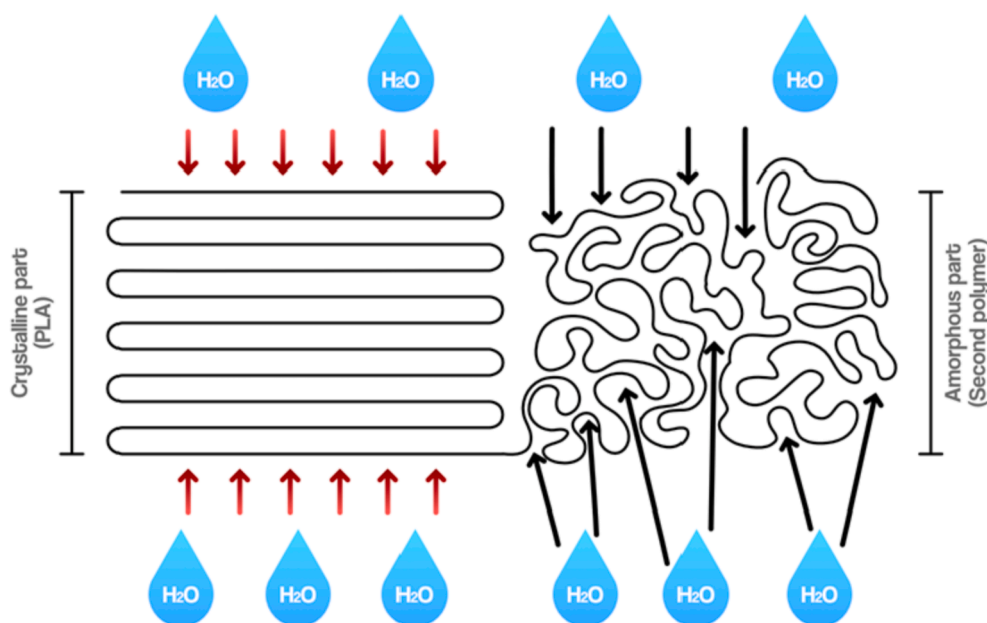
Fig. 4. Relationship between PLA blend structure with water absorption.

blends, and consequently enhanced water diffusion.

Certain chemical components of the second-phase matrix are also known to contribute to an increase in the PLA biodegradation rate upon blending [37,38,54]. Glucose in starch is an extremely efficient carbon source because it promotes the soil-based biodegradation of PLA/starch blends by microorganisms [54]. Moreover, the presence of numerous hydroxyl groups (–OH) with high levels of amorphous and three-armed star-shaped PDLLA in *all*-PLA blends can enhance the activity of the biological agents, thereby increasing the biodegradation rate [38]. PLA blends with poly(lactic-*co*-glycolic acid) (PLGA) have been proposed for use in triboelectric nanogenerators (TENGs) [37]. The use of dielectric polymers in TENG-based applications increases plastic pollution in marine environments. The PLA/PLGA blends degraded entirely in natural seawater after nine months [37]. However, neat PLA exhibited a weight loss of only 1% after nine months in seawater. The PLGA content facilitated the seawater-based degradability of the PLA/PLGA blend because neat PLGA completely degraded in seawater after one month. PLGA was noted to be initially hydrolyzed in the blends to produce acidic end groups, which subsequently catalyzed the degradation of PLA [37]. The –OH group on the starch, three-armed star-shaped PDLLA, and PLGA increases the number of hydrogen bond formed with the water –OH group, thus increasing the degradation rate of the PLA blends. The relationship between the chemical components in the PLA blend and the water permeability rate is shown in Fig. 5.

In addition to introducing polymer matrices for synthesizing flexible PLA blends, plasticizers have also been employed to improve the flexibility of PLA. Plasticizers such as poly(ethylene glycol) (PEG) are known to increase the biodegradation rate of PLA/TPS blends in soil [55]. The addition of tributyl citrate as a plasticizer in a low-molecular-weight PDLA-b-PEG copolymer was found to increase the biodegradation rate of the PLA matrix in compost at 60 °C for 54 days, where the plasticized PLA degrades faster than neat PLA [56]. Epoxidized palm oil (EPO) has also been employed in PLA/starch blends as a plasticizer [57]. After five months of the soil burial test in this study, the weight loss and physical appearance of neat PLA remained unchanged [57]. The addition of 5 wt % starch increased the degradation rate of PLA by 2% [57]. Furthermore, the degradation rate increased to 17.35% with the addition of 20 wt% EPO [57]. PEG, EPO, and tributyl citrate are hydrophilic plasticizers with low molecular weights. Typically, the addition of a hydrophilic plasticizer increases the hydrophilicity of the blends and provides
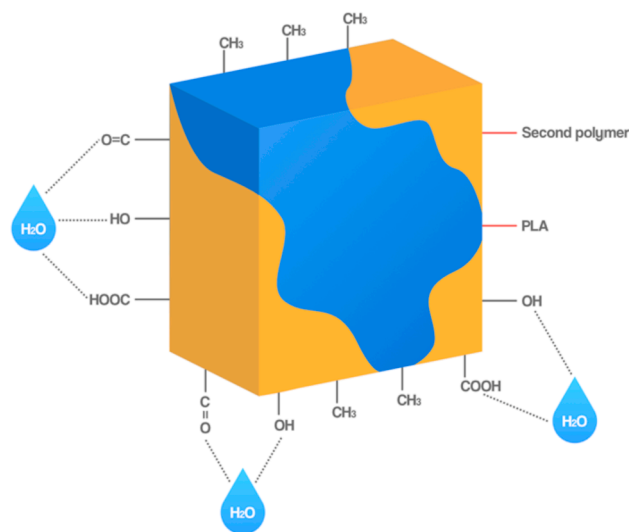

Fig. 5. Chemical interaction between the chemical components in PLA blend with water.

free volume, thereby increasing the rate of water diffusion [58]. These hydrophilic and low-molecular-weight compounds are typically leached out, absorbed by the soil, and metabolized by microbes [58].

Blend morphology is a critical factor that influences the biodegradation rate of PLA in blends. Typically, PLA is incompatible with other polymer matrices, resulting in the formation of an immiscible blend [59,60]. The immiscibility of the blend components leads to the formation of a separate phase within the polymer matrix, which also assists in increasing the biodegradation rate [28]. Fig. 6 reveals the immiscibility of PLA/NR blends from our findings. PLA and PLA/NR blends were buried in soil for 180 d at 24 °C [28]. Owing to the phase separation, NR was found to provide a pathway for water to enter, thereby improving the degradation rate of PLA. The formation of this separate phase facilitates the movement of water into the blend, thereby increasing its degradation rate. Shi et al. [61] revealed that the weak interface between PLA and starch enhanced the biodegradation of their blends with increasing starch content. Scanning electron microscopy (SEM) revealed
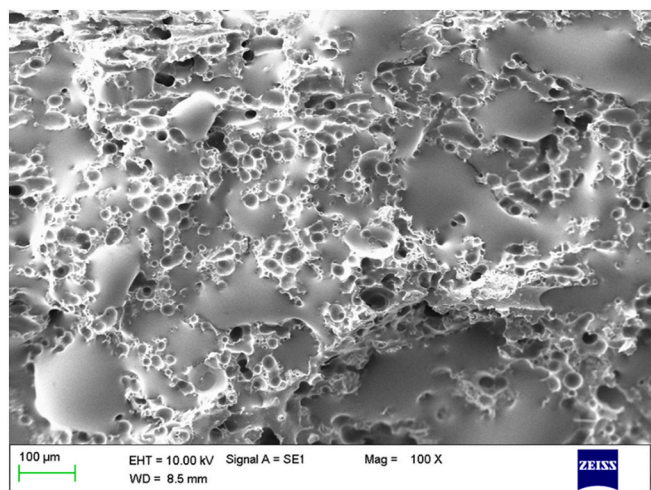
Fig. 6. Phase separation of PLA and NR in a PLA/NR blend.

that the starch phase disappeared after the biodegradation of the blends. Additionally, Xue et al. [55] found that increasing the content of TPS in PLA/TPS blends caused numerous cracks and voids on the surface of the films, which led to increased water diffusion and a consequent increase in the degradation rate [55]. The PLA blends and poly(butylene succinate) (PBS) blends were buried in soil at ~37 °C, and it was found that high PBS content contributed to the highest weight loss after 60 d of burial in soil [62]. In contrast, pure PLA showed the lowest weight loss among all blend compositions [62]. The presence of two T_g values in the PLA/PBS blend indicates that these two components are immiscible, as evidenced by increased phase separation with the increase in PBS content [63]. The phase separation contributes to the increased water absorption and degradation rate of the PLA/PBS blends. The biodegradation of a PLA/poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHHx) blend in seawater at 27 °C was determined [64].

After 28 d in seawater, 1 and 33% of the neat PLA and 20/80 wt% PLA/ PHBHHx blend degraded, respectively [64]. The degradation of PHBHHx in seawater was quicker than that of PLA [64]. SEM revealed that biodegradation increased when the surface of the blend was covered more with PHBHHx than with PLA [64].

The phase separation between PLA and other polymer matrices in their blends necessitates the use of compatibilizers [65,66]. The primary function of compatibilizers is to improve the mechanical properties of the blends by reducing the phase separation in PLA blends. This, in turn, causes a decrease in water diffusion, which leads to a decrease in the biodegradation rate of the blend. PLA/PBAT blend films with different ratios have been compatibilized using chain extenders [67]. The compatibilized blends were found to possess a higher degree of crystallinity than that of neat polymers, thereby decreasing the degradation rate [67]. PLA/PBAT blend films containing chain extenders were still present in the soil after 360 d because the chain extenders reduced the degradation rate of the blends [67]. The soil-based biodegradation of PLA was therefore not enhanced by a compatibilized blend with PBAT [67]. However, the addition of a compatibilizer to certain formulations can improve the biodegradation properties of the blends [28]. For example, liquid natural rubber (LNR)-compatibilized PLA/NR blends were buried in soil for 180 d [28]. The weight loss was noted to increase with a high content of LNR (8 wt%) [28]. An excessive amount of compatibilizer caused the formation of a third phase (agglomerations) between the matrix phases [59]. The formation of agglomerates or a new third phase increases the domain size and consequently increases the water absorption and degradation rate, as shown in Fig. 7. [28].

4. Degradation properties of PLA blends in biotic media

Until recently, the functions of microorganisms during environmental degradation were not well understood because of the limited number of studies on the subject [11,46]. The presence of microorganisms in degradation media is the most crucial factor that affects the enzymatic degradation of PLA. The population and distribution of PLA-
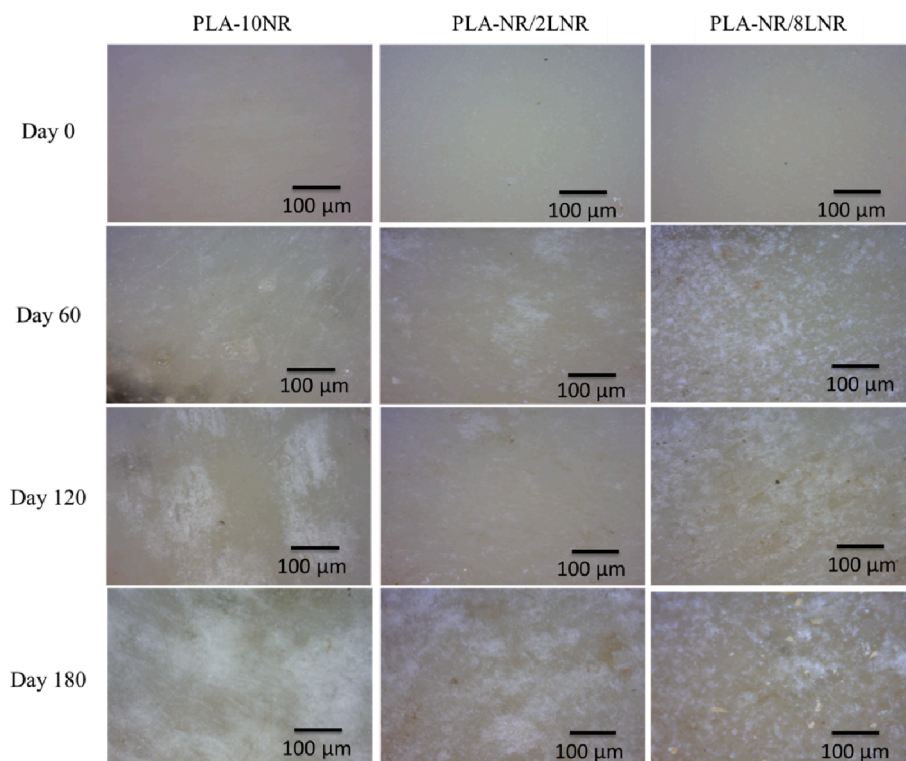

Fig. 7. Optical micrographs of compatibilized PLA/LNR blends [28].

degrading microorganisms in the ecosystem depend on the degradation environment, such as the type of soil, compost, or seawater [12]. Microorganisms utilize oxygen and consume carbon from PLA as a food source.

Enzymes primarily attack the amorphous parts of a polymer because their loose packing makes them susceptible to biodegradation. Therefore, the degradation rate of PLA decreases with an increase in its crystallinity [68,69]. High-molecular-weight PLA (>20 kDa) is typically resistant to microbial attacks; its high molecular weight (and large molecular size) does not facilitate its entrance into the microorganism cells [12]. Moreover, water is required for microbes to grow and reproduce. Therefore, an increase in water absorption increases the microbial activity, thereby increasing the polymer degradation rate. Various factors affecting the degradation of PLA blends in biotic media are discussed henceforth.

Blends of PLA with ethylene-vinyl acetate (EVA) prepared and buried in agricultural soil in Vietnam featuring *Rhizobium* sp. and *Alpha proteobacterium* sp. were investigated [70]. An increase in the EVA content (40 wt%) of the blends enhanced the degradation of PLA, as determined by the weight loss data after 15 months. *Rhizobium* sp. and *Alpha proteobacterium* sp. were identified as biodegraders of PLA-like polymers (polyesters) that possessed structures similar to that of PLA [70]. The increase in the weight loss of the PLA/EVA blend is influenced by the crystalline properties and phase separation between PLA and EVA. Singla et al. [71] found that the addition of EVA reduces the crystallinity of PLA, and the T_g of PLA decreases with the addition of EVA. The low crystallinity then causes an increase in water absorption rate and increases microbial attack in the amorphous phase. Moreover, high EVA content increased the number of EVA droplets dispersed in the continuous PLA phase [71]. The increase in EVA droplets separated from the PLA phase facilitates water diffusion and increases microbial activity.

Porous films produced using blends of PLLA and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P(3HB-co-4HB)) via selective enzyme methods were investigated by Ju et al. [72]. Two types of enzymes (lipase from *Pseudomonas mendocina* and proteinase K) were employed in the enzymatic degradation test. The test was performed in a Tris–HCl buffered solution medium at 45 °C. The attack of lipase, which is known to biodegrade P(3HB-co-4HB) on PLA was found to be insignificant [72]. Although proteinase K could not biodegrade P(3HB-co-4HB), the addition of P(3HB-co-4HB) increased the enzymatic degradation rate of PLLA [72]. The addition of 10–30 wt% P(3HB-co-4HB) succeeded in increasing the enzymatic degradation rate of PLA to a level higher than that of neat PLLA [72]. These results were possible owing to the formation of an immiscible blend of PLLA and P(3HB-co-4HB) [73]. The separation of polymer phases in the immiscible blend facilitated the diffusion of enzyme molecules into the interface, thereby increasing the microbial activity and rate of biodegradation. The immiscible blend also increased the water absorption rate, which increased the hydrolytic degradation of the blend.

Additionally, Shi et al. [23] studied the selective enzymatic degradation method in blends of PBS/PLLA using Proteinase K, which was one of the enzymes used in this study [23]. The enzymatic degradation was carried out at 37 °C in a phosphate-buffered saline solution (pH = 8.0). A blend with 20 wt% PBS exhibited a higher weight loss than that of neat PLA after 21 d [23]. PBS/PLLA blends have been shown to be incompatible despite an increase in the mechanical properties of the blends [63]. The immiscibility of the PBS/PLLA blend contributes to increasing the degradation rate [23]. The phase separation between the PBS and PLLA components in the matrix provides a pathway for the entry of enzymes from the surface into the blend. Moreover, the addition of PBS increases the specific surface area of PLA [74], which provides more area for microbial attack, thereby increasing the degradation rate of PLA. Meanwhile, Srimalanon et al. [75] also studied the degradation of PBS/PLA blends with the presence of *Pseudomonas geniculata* WS3 and *Stenotrophomonas pavanii* CH1 in soils under mesophilic (30 °C) conditions. After 28 d, a total of 0.27% and 0.11% weight loss of PLA were

recorded in soil inoculated with *P. geniculata* WS3 and *S. pavanii* CH1 bacteria, respectively. The addition of PBS at 40 wt% increased the degradation rate of the PLA blend; the weight loss increased to 2.28% and 1.31% in soil inoculated with *P. geniculata* WS3 and *S. pavanii* CH1, respectively [75]. Again, the phase separation between PBS and PLA was shown to contribute to the increase in weight loss of the blend, as it facilitated the entry of bacteria in the blend, thereby increasing bacterial attack.

A porous foam blend of PLA and gelatin was prepared as a drug delivery material via thermally impacted non-solvent-induced phase separation [76]. Gelatin acted as an additive for producing pores in PLA. Rarima et al. [76] investigated the enzymatic degradation of a PLA/gelatin blend in the presence of trypsin in a phosphate-buffered saline solution (pH 7.4) at 37 °C [76]. The trypsin enzyme was noted to successfully degrade the PLA/gelatin blend samples and pure PLA. After 28 d, the PLA/gelatin blend with the highest gelatin content exhibited a larger weight loss (100%) compared to pure PLA (56%) [76]. The enzymatic degradation of PLA occurred because of the adsorption of trypsin on the surface of PLA, which hydrolytically cleaved the ester group [76]. The increase in the enzymatic degradation rate of the PLA/gelatin blend was driven by factors such as porosity, water absorption, and crystallinity. The hydrophilic nature of gelatin increased the rate of water absorption of the blend. The addition of gelatin increased pore production [76], which also contributed to the increase in water absorption. In addition to increasing the hydrolytic degradation rate, the high-water absorption promoted the diffusion of enzymes into the blend and consequently increased the enzymatic degradation rate. Furthermore, the reduced crystallinity of PLA helped increase the degradation rate owing to the addition of gelatin. Both enzymatic and hydrolytic degradation were less effective in the crystalline areas. Therefore, the reduction in crystallinity in the PLA/gelatin blend increased the rate of biodegradation.

Zhao et al. [77] employed poly(ethylene-butylacrylate-glycidyl methacrylate) (PTW), a highly reactive elastomer consisting of a glycidyl epoxy group as a compatibilizer and toughening agent for PLA. The enzymatic degradation of the PLA/PTW blend was tested using proteinase K in a Tris–HCl buffered buffer solution (pH = 8) at 37 °C. The addition of PTW successfully increased the enzymatic degradation rate of PLA [77]. The degradation rate of the blend increased with increasing content of PTW. Although the PLA and PTW components in the blend were compatible, morphological analysis revealed the presence of two distinct phases [77]. This phenomenon increased the rate of water absorption, thereby increasing the enzyme diffusion and hydrolytic degradation. The relationship between the separated phases in the PLA blend is illustrated in Fig. 8.
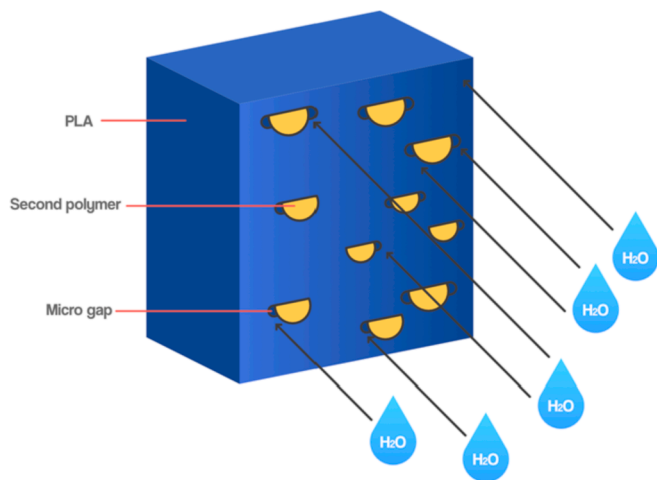

Fig. 8. Easy water penetration through micro-gap between PLA and second polymer in the phase-separated blend.

5. Degradation properties of PLA blends in abiotic media

The degradation rate of PLLA in water and in the human body is extremely low, and PLLA materials often remain in these environments for years without bioresorption; in vitro tests have shown that PLA crystalline residues remain intact for over five years [78]. Four essential parameters control the hydrolytic degradation of PLA particles in an aqueous solution: quantity of absorbed water, diffusion rate, coefficient of chain fragments within the polymer, and solubility of degradation products [79]. Other factors, such as the type of solvent, may also affect the degradation rate of PLA. A faster rate of degradation has been detected in PLA immersed in 50% ethanol because ethanol molecules diffuse more rapidly within the polymer matrix than water molecules [80]. Various factors affecting the hydrolytic degradation of PLA blends in abiotic media are discussed henceforth.

The blending of PLA with other polymers can accelerate or inhibit the hydrolytic degradation rate, depending on several factors. The chemical and physical properties of the second blend phase and its quantity play an essential role in affecting both the degradation rate and mechanical properties of the blend. Blending PLA with an amorphous polymer with a low T_g, such as polyethylene carbonate (PEC), improved the toughness of a 50/50 wt% PLA/PEC blend by 584% [81]. The PLA/PEC blend films were subjected to an alkaline hydrolysis test in sodium hydroxide (NaOH) aqueous solution at 37 °C. The neat PLA and PLA/PEC blends at 90 and 60 wt% of PLA completely hydrolyzed in alkaline solution; the degradation rates of the blends were higher than those of neat PLA [81]. Therefore, the hydrolytic degradation of PLA/PEC blends in an alkali solution was noted to depend on the inherent properties of the second phase and quantity of PEC. The hydrolytic degradation mechanism of the PLA/PEC blends involved surface erosion, and the reaction proceeded from the chain end to produce ethylene glycol and CO_2 [81]. However, the degradation of PLA started from the amorphous phase and involved either a carbonyl or hydroxyl end group [81].

Serra et al. [82] studied the in vitro degradation of PLA/PEG blends with the addition of 5, 10, and 20 wt% PEG. The degradation of blends was performed in a simulated body fluid at 37 °C [82]. PLA showed an insignificant weight loss after 8 weeks, whereas the 80/20 wt% PLA/PEG blend started to degrade only after 2 weeks [82]. The sudden degradation of the PLA/PEG blend (80/20) prevented weight loss measurements because of difficulties in measuring the weights of the sample pieces [82]. The presence of PEG increased the hydrophilicity of PLA blends, as proved by the decrease in the values of the water contact angle [82]. PEG is a low-molecular-weight polymer that is commonly used as a plasticizer for PLA. Polymers with a low molecular weight and high hydrophilicity typically undergo degradation first in a blend. This was evidenced in a study where the T_g and crystallinity of PLA/PEG blends increased with degradation time [82].

The degradation of PLLA/segmented poly(ester urethane) (PHD) blends was studied by Montini-Ballarin et al. [83]. PLLA/PHD blends with ratios of 90/10 and 50/50 wt% were immersed in a phosphate-buffered saline solution (pH = 7.4) at 37 °C [83], after which the average molecular weight (M_n) of PLLA decreased by ~59%, whereas PLA blends with 10 and 50 wt% of PHD decreased by 74% and 90%, respectively [83]. Several factors improved the degradation of PLA in the PLA/PHD blends. The factors involved the degradation of PHD products, which accelerated the degradation of PLLA in the blend [83]. The insoluble cleaved chains from degraded PHD were presumed to produce a local acidic environment, thereby catalyzing PLA and increasing the degradation rate [83]. Crystallinity and hydrophilicity were also suggested as factors that could contribute to the degradation behavior of the blend. The 50/50 PLA/PHD blend exhibited the highest degradation rate owing to the highly amorphous PHD phase, which enhanced the hydrophilic properties.

Rahmani et al. investigated the in vitro degradation of poly(mannitol sebacate) (PMS)/PLA blends in a phosphate-buffered saline solution (pH $\cong$ 7.4) containing sodium azide at 37 °C [84]. The final degradation rate of PLA was 4.10%, whereas those of the PMS/PLA blends with mass ratios of 60/40, 50/50, and 40/60 were 43.99, 43.46, and 32.92%, respectively, over 35 days [84]. The high levels of mass loss revealed that PMS could improve the biodegradability of PLA. PMS is also a biodegradable polyester with a high degradation rate compared to that of PLA. PMS contains hydroxyl groups of mannitol moieties in its polymer chain, thereby increasing the hydrophilicity of the PLA blends. The increased hydrophilicity of PLA blends was proven through water contact angle analysis, where the angle reduced with increasing content of PMS [84]. The high level of hydrophilicity increased the water permeability and consequently increased the biodegradation rate of PLA.

The effect of morphology on the hydrolytic degradation of an immiscible blend of PLA and thermoplastic polyurethanes (TPU) in an alkaline solution (pH = 12) at 30 °C was studied by Buys et al. [85]. The relationship between blend composition and hydrolytic degradation behavior was noted to be nonlinear, and the 50/50 PLA/TPU blend exhibited the fastest degradation rate compared to those of other compositions [85]. This acceleration in the degradation rate resulted from the immiscibility of PLA/TPU blends, which was proved by the presence of two T_g peaks. The immiscibility between PLA and TPU was observed based on the morphological analysis, where TPU droplets dispersed in the PLA phase [85]. The phase separation resulted in easy entry of water into the blend, thus increasing the hydrolytic degradation.

The hydrolytic degradation of PLA/poly(dodecafluorheptyl methylacrylate) (PFA) blends and PFA-coated PLA was comparatively investigated by Huang et al. [86]. The blend samples exhibited a higher water absorption rate owing to the phase separation of the blend, in which gaps are produced between PLA and PFA [86]. The effect of the resulting gap between PLA and PFA on the water absorption rate can be understood through the illustration in Fig. 8. The higher the water infiltration rate, the higher the hydrolytic degradation rate. The hydrolytic degradation rate of the PLA/PFA blend was greater than that of neat PLA during the initial 20 d [86]. However, the hydrolytic degradation of PLA in the PLA/PFA blend and PFA-coated PLA was delayed because of the autocatalytic effect [86]. Nevertheless, this effect was limited because it was negligible after 40 d [86].

The effect of PBS on the hydrolytic degradation of PLA was studied by Wang et al. [87]. The samples were hydrolytically degraded in an NaOH solution (pH = 13) at 37 °C. From a morphological point of view, a typical sea-island structure of PLA/PBS was observed [87]. The gaps between the PLA matrix and dispersed PBS particles provided a pathway for water diffusion, which accelerated hydrolytic degradation. However, PBS did not alter the hydrolytic degradation mechanism of PLA, and the degradation mainly occurred on the surface of the sample [87]. Moreover, PBS remained unattacked after 312 h of degradation [87]. Although PBS could degrade in an alkaline solution, the degradation rate of PBS was much lower than that of PLA, and thereby required a longer incubation time [87]. Zhou et al. [88] also investigated the hydrolytic degradation of PBS/PLA blends in a simulated body fluid (pH = 7.4 ± 0.1) at 37 °C with penicillin and streptomycin. Pure PLA was found to exhibit insignificant degradation until 16 months, when a mass loss of only 2.2 ± 1.0% was recorded. However, the addition of 40 wt% PBS increased the degradation rate of the PLA blend with a mass loss of 25.4 ± 9.6% [88]. The PLA-rich blends were found to degrade faster than the PBS-rich blends [88]. The enhancement in degradation properties resulted from the phase separation between PLA and PBS, which increased the water absorption rate and thereby increased the degradation rate of the blends.

Oyama et al. [89,90] studied the effect of blending oligomeric poly(aspartic acid-*co*-lactide) (PAL) on the hydrolytic degradation of PLLA under various experimental conditions. PAL is a high hydrophilic polymer due to the presence of aspartic acid units and terminal carboxylic groups. Degradation tests were performed in a phosphate-buffered saline solution (pH = 7.3) at 40 °C and NaCl salt solution (pH = 3.4, 7.4, 10.4 and 12.0) at 40 °C. The hydrolysis notably

accelerated upon the addition of PAL when the blend was exposed to the buffer saline solution [89]. Meanwhile, PLA did not show any weight loss after 100 d in low or high concentrations of NaCl solution except at pH 12.0 [90]. The addition of PAL increased the hydrolysis of the PLA/PAL blends, where the weight loss increased in all NaCl solutions. Moreover, 100% weight loss of the blends was observed in a medium with pH 10.4 and 12.0 after 40 d and 25 d, respectively [90]. The opening of the succinimide ring led to the formation of aspartic acid. The resultant carboxylic acid from PAL was found to facilitate acid catalysis and efficient hydrolysis of the ester linkages in PLA. Therefore, PAL can be considered as a potential degradation accelerator for PLA which works in a water-based solution.

The effect of both PAL and poly(malic acid-*co*-L-lactide) (PML) on PLA blends in a ratio of 80/20 has also been analyzed [91]. Films were hydrolytically degraded at 40 °C in a phosphate-buffered solution. The annealed films with high initial crystallinity were noted to lose their mass more quickly at an earlier degradation stage compared to the quenched film with a low degree of crystallinity [91]. The analysis suggested that the amorphous region contained concentrated PAL and PML as a result of displacement from the crystalline region; moreover, the terminal carboxylic acid group of the PLA chain functioned as an acidic catalyst for PLA hydrolysis, which enhanced and intensively accelerated the volume of the amorphous region [91]. However, between 40 and 60 d, the hydrolytic behavior differed depending on the degradation rate [91]. Highly developed crystals that were formed at a high degradation rate or via annealing exhibited a hydrolysis resistance significantly higher than that of less-developed crystals formed at a low degradation rate [91]. Therefore, the degree of crystallinity and crystal thickness of PLA were noted to be the determining factors in the hydrolytic degradation mechanism that accelerated or resisted the degradation rate.

Additionally, the pre-or post-treatment of PLA blend films, which directly affect the crystal size and crystal thickness of PLA, are essential factors in hydrolytic degradation. For example, the effect of annealing/quenching a 70/30 blend of PLA with poly(trimethylene terephthalate) (PTT) on hydrolytic degradation has been investigated [92]. Hydrolytic degradation tests were conducted in distilled water at 58 °C. The rate of weight loss of the annealed samples was found to be low and the samples possessed better hydrolytic stability owing to the higher crystallinity and thicker crystal size of the PLA formed via annealing [92]. In comparison, quenched samples with a low crystallinity and an amorphous structure exhibited faster degradation [92]. As shown in Fig. 4, the amorphous region is more easily penetrated by water than the crystalline region. This, in turn, increases hydrolytic degradation.

6. Comparison of PLA blend degradation rate in various media

The best medium for the degradation of PLA blends is challenging to determine as each medium has different experimental conditions. In addition, there is limited research on the degradation of PLA blends in certain media, such as in seawater. Nonetheless, this section will discuss the comparison of degradation of PLA/PBS blends in different media. The PLA/PBS blend was selected for comparison because of consistency in the experimental conditions, i.e., temperature and PLA/PBS composition at 80/20 wt%. Table 1 presents a summary of the degradation properties of PLA/PBS blends in different media.

Table 1 shows that the degradation rate of the PLA/PBS blend is almost the same in each case. However, it is interesting to note that the degradation rate of the PLA/PBS blend is slightly higher in the natural medium. This may be due to the difficulty in controlling the natural environment compared to the other two media. Aspects that are difficult to control include the presence of unknown microbes in the soil and differences in the components of different soils. This may be one of the factors that increase the rate of degradation. From this comparison, PLA blends that are degraded in biotic and abiotic media can potentially degrade in the natural environment. In addition, this comparison shows

Table 1
Summary of degradation properties of PLA/PBS blends in different media.

Medium	Experimental condition	Result	Ref
Natural	• In laterite soil at 28 to 38 °C	• ~0.6% and ~1.2% weight loss after 10 d and 20 d, respectively.	[62]
Biotic	• In agriculture soil mixed with compost inoculated with *P. geniculate* WS3 and *S. pavanii* CH1 bacteria at 30 °C	• 0.24% and 0.16% weight loss after 14 d in medium with *P. geniculate* WS3 and *S. pavanii* CH1 bacteria, respectively.	[75]
Abiotic	• In simulated body fluid at 37 °C • pH = 7.4 ± 0.1	• 2.4% weight loss after 10 months	[88]
	• In NaOH at 37 °C • pH = 13	• 0.032 g/cm^2 weight loss after 13 d	[87]

that the properties of PLA blends that contribute to the high water absorption rate play a more important role compared to the degradation medium in determining the rate of PLA degradation in the blend.

7. Conclusions

PLA is a bio-based polyester that has received significant attention owing to its outstanding properties. However, the future application of PLA depends on several strategies, such as blending or copolymerization, to overcome its high brittleness. Various types of PLA blends have been introduced, increasing the use of PLA and contributing to problems involving its disposal. The degradation rate of PLA is low under normal environmental conditions, even though it is classified as a biodegradable polymer. Hydrolytic degradation is the primary mechanism for PLA blends in various degradation media. Microbes in the degradation media accelerate the enzymatic degradation rate, and this typically occurs in the second stage. In both degradation methods, water is the fundamental component required for degradation. In enzymatic degradation, water is required for microbes to grow and provide a pathway for microbes to access the PLA blends. Therefore, factors that influence the water absorption rate play an essential role in determining the biodegradation properties of PLA. In all three types of media (natural, biotic, and abiotic), immiscible PLA blends form separate phases, thereby increasing water uptake and further increasing biodegradation rates. In addition to phase separation, the formation of pores in PLA blends contributes to the increase in water permeability. Therefore, the morphology of PLA blends is indicative of the biodegradation properties of PLA in the blends. The addition of a hydrophilic polymer matrix or materials such as plasticizers also increases the degradation rate of PLA. A low-molecular-weight hydrophilic plasticizer can easily dissolve into the medium from the blends, thereby providing an accessible volume that can facilitate the entry of water and microbes. Previous studies have suggested that the hydrolytic degradation of PLA blends depends on various factors. Although some mechanisms have been proposed with respect to PLA, it has not been possible to propose a specific rule or reaction conditions and mechanisms for controlling the hydrolytic degradation of PLA blends. The determinant factors vary from one blend system to another. It is worth noting that the hydrolytic degradation rate of PLA blends can be adjusted according to their applications by optimizing the degradation and blend processing conditions. Finally, the development of new PLA blends for improving specific properties and predicting their degradation in a particular environment must involve the study of the morphology and hydrophilicity of the blends.

Declaration of competing interest

None.

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