



Tailoring Biodegradability of Poly(Butylene Succinate)/Poly(Lactic Acid) Blends With a Deep Eutectic Solvent

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Biodegradable polymers concern an important topic for innovation in materials, as they are supposed to contribute to the reduction in the amount of waste materials, which lead to microplastics with similar properties as conventional polymer materials. Poly(butylene succinate) and poly(lactic acid) blends are polymers with interesting properties offering possible alternatives to some conventional petrochemical-sourced polymers. Some of the physical properties of such blends can be tailored from the addition of small amounts of deep eutectic solvents (DESs) that can act as compatibilizers, i.e., interfacial agents between poly(butylene succinate) (PBS) and poly(lactic acid) (PLA). In our study, materials formulated with a DES having a coarse morphology according to the dispersed particle sizes display thermal and mechanical properties rather close to the non-compatibilized PBS/PLA blends but a higher ability to biodegrade. In comparison with PBS/PLA blend, biodegradation experiments show that PBS/PLA/DES blend exhibits higher weight losses and faster fragmentation under conventional conditions. A significant decrease in PLA melting temperature under composting conditions, i.e., at 58°C, is observed indicating that PLA phase is the component mainly concerned. As a conclusion, this work demonstrates that morphologies as well as the biodegradability process can be tailored by adding a small amount of a DES in such biosourced polymer blends. Indeed, designing polymer materials, for which degradation processes are targeted in the dispersed phase, i.e., in multiple locations of the material, can be an efficient route to “predegrade” phases in a polymer matrix to accelerate macroscopic biodegradation.

Keywords: polymer, polyester, deep eutectic solvent, biodegradation, composting

INTRODUCTION

Plastics are everywhere in our everyday life and, unfortunately, in our natural environment, where their chemical stability can be considered as a main drawback. As a consequence, combination of life properties, i.e., properties required for their use and controlled end-of-life, is a major scientific challenge offered to polymer scientists. In this perspective, bio-based polymers such as poly(butylene succinate) (PBS) and PLA can offer a good balance between mechanical and thermal properties and ability to biodegrade as they are dispersed in air, soil, or water media.

PBS, produced by polycondensation of fossil or bio-based succinic acid and 1,4 butanediol, can substitute low-density polyethylene or even poly(butylene-adipate-co-terephthalate) (PBAT) in many applications. PBS and its copolymers are also of interest as they are able to biodegrade in various environments (Xu and Guo, 2010; Zeng et al., 2016). Their biodegradation rate can be tuned via synthesis conditions, i.e., copolymerization or from their formulation. For mechanical reinforcement, PBS can be blended with PLA, with which it is partially miscible, to associate the properties of both polymers (Shibata et al., 2006; Bhatia et al., 2007; Deng and Thomas, 2015). PBS/PLA material that are at least partially bio-sourced and biodegradable can be used as agricultural mulching films, stretch films, bags, and kitchenware, for example (Livi et al., 2018).

Morphologies, thermal, and mechanical properties can be tuned from a relevant choice of the formulation compositions (Livi et al., 2015). The capacity for hydrolysis is often correlated with material properties as well as natural conditions.

Biodegradation corresponds to the degradation of organic matter into water, CO₂ and/or CH₄, and biomass, by the action of microorganisms. At first, fragmentation increases the surface area, enabling microorganisms to attach. Physical means such as grinding and/or chemical degradation (such as hydrolysis), leading to lower molecular weight polymer, which are more easily assimilated by microorganisms (Witt et al., 1996), are responsible for fragmentation. Then, microorganisms mineralize fragments and oligomers into simple molecules and biomass (Witt et al., 1996; Castelan, 2010). Concerning the environment, higher temperatures, if they do not kill microorganisms, often lead to faster degradation, and a degradation temperature close or higher than the glass transition temperature (T_g) favors the biodegradation process. Indeed, at temperatures above the T_g of a polymer, increased chain mobility facilitates access to enzymes (Weinberger et al., 2017), as well as water absorption (Siparsky et al., 1997). This explains that, at temperatures under their T_g , polyesters such as PLA are not likely to degrade, whereas they significantly age at temperatures close to their T_g (Agarwal et al., 1998; Itävaara et al., 2002; Yagi et al., 2009; Karamanlioglu and Robson, 2013). Humidity fosters the degradation by increasing the hydrolysis rate and by favoring microorganisms activity and transport (Gu et al., 1994). pH influences the degradation, and PLA chains degrade more rapidly in alkaline conditions than in neutral or acidic conditions (Makino et al., 1986; Schliecker et al., 2003).

Material properties are also key parameters influencing biodegradation. Synthetic polymers can be manufactured with different properties such as crystallinity, glass transition, and melting temperatures, and their ability for versatility can be considered as an advantage over natural polymers like chitosan, gelatin, starch, etc. (Vieira et al., 2013; Díaz et al., 2014; Pellis et al., 2016).

Polymers, with hydrolysable bonds, such as polyesters, are likely to degrade in presence of enzymes naturally present in the environment. In addition to lower volumes of discarded plastic materials, degradation in natural environment can contribute to soil fertility.

Parameters such as morphology, crystallinity, hydrophilicity, and molar masses can significantly influence biodegradation in natural media. Husarova et al. observed that, under composting conditions, PLA having a high specific surface area degrade faster in biotic media. Rudnik observed the same tendency under soil burial conditions with PLA (Rudnik and Briassoulis, 2011; Husárová et al., 2014). Moreover, degradability decreases when increasing hydrophobicity (Höglund et al., 2010). Morphologies with multiphase materials can also favor bacteria and enzyme activities from the creation of pathways made after the disappearance of the easiest phase to be biodegraded (Delamarche et al., 2020).

The degradation rate is smaller for polymers with high degrees of crystallinity, as crystallites are less accessible to enzymes and to water. Thus, amorphous PLA degrades faster than semi-crystalline PLA both in abiotic medium and in aerobic condition under composting conditions (Zhou and Xanthos, 2008; Pantani and Sorrentino, 2013).

Hydrophilic character is preferred for improving affinity with bacteria and enzymes that can catalyze hydrolysis of the polyester chains. Lower molecular weight are in favor of faster degradation and Husarova et al. showed that, under composting conditions and in abiotic aqueous conditions, low molecular weight PLA degrades faster than high molecular weight PLA (Husárová et al., 2014).

The first part of this work considers the design and characterization of PBS/PLA blends with and without a small amount of a deep eutectic solvent (DES). DESs prepared by mixing two components display a melting temperature lower than the ones of the individual components. DESs exhibit similar properties to few ionic liquids and are widely studied, as they are considered to contribute to environment-friendly solutions. For such a route, choline chloride/glycerol DES exhibits a low toxicity and can be considered relevant for “green” applications (Radošević et al., 2015). In the present work, this DES is expected to act as an interfacial agent in PBS/PLA blends. Considering a similar way, PBAT/PLA or PP/PA blends were studied with considering phosphonium-based ionic liquids (Yousfi et al., 2014; Lins et al., 2015). For thermoplasticization of starch, Decaen et al. showed that choline chloride permits a good compromise between limited chain scission and thermomechanical properties (Decaen et al., 2017).

The present study aims to investigate the relationships between physical properties and biodegradation for these polymer blends and to investigate the role of the addition of a DES. Material data such as molar masses, crystallinity yield, morphologies, and surface properties are reported, as these ones are known to control biodegradability (Delamarche et al., 2020).

To assess biodegradability, 3-month degradation essays were conducted, i.e., under composting conditions at 58°C (higher than PBS glass transition temperature, T_g , and close to the one of PLA) in deionized water and NaOH solution, under soil burial conditions, as well as in humid atmosphere at room temperature. Weight loss data, ¹H NMR, and differential scanning calorimetry (DSC) measurements were considered to follow the biodegradation of PLA.

TABLE 1 | Formula of studied polymers and deep eutectic solvent.

Abbreviation	Full name	M_n (g mol ⁻¹)	Melting temperature T_m (°C)	Structural formula
PBS	Poly(butylene succinate)	50 kDa	113	
PLA	Poly(lactic acid)	34 kDa	170	
DES	Choline chloride/glycerol	231.72	-	

MATERIALS AND METHODS

Materials

The various polymers used in this study are listed in **Table 1**. PBS and PLA were supplied as pellets by Natureplast (denoted PBE 003 and PLA 005 grades, respectively). L-Lactic acid/D-lactic acid contents for the considered PLA is 94:6 mol-% (Dorigato et al., 2012). Choline chloride/glycerol (1:2 mole ratio), a hydrophilic DES, was supplied by Scionix Co.

Processing of PBS/PLA Blends

Polymer pellets were dried in an oven at 70°C for 12 h. Pellets and additives were extruded using a 15-g capacity DSM microextruder (Midi 2000 Heerlen, NL) with corotating screws (L/D ratio equal to 18) at 190°C with a 100-rpm speed for 3 min. PBS/PLA (60:40 wt ratio) and PBS/PLA/DES (60:40:1 wt ratio) were extruded. Extruded coupons were injected in a 10-cm³ mold at 30°C to obtain 2-mm thick and 4-mm wide dumbbell-shaped specimens. Thin films (0.2 mm) were processed under compression at 210°C and considered for aging experiments.

Characterization Experimental Techniques

Molar Masses

Molar masses were determined using a size exclusion chromatography (SEC) equipment, comprising Agilent Technologies columns, a light scattering detector, and a Shimadzu RID-10A detector. Three milligram samples were cut and dissolved in chloroform (1 mg/ml). Analysis took place at 30°C under a 1-ml/min flow. $\frac{dn}{dc}$ used was 0.06 ml/g for PBS and 0.0237 for PLA (Malmgren et al., 2006).

¹H NMR

One-dimensional ¹H NMR spectroscopy was used to determine the PBS and PLA contents of the blends (see formula, **Figure 1**). Samples, cut from films, were dissolved in CDCl₃ and analyzed at 25°C using a Bruker Advance III spectrometer (400 MHz), equipped with a 5-mm multinuclear broadband probe (BBFO+). To evaluate the weight percentage of PBS and PLA in the blends, peak resonance (a) of PLA (CH) at 5.1 ppm and resonance peak

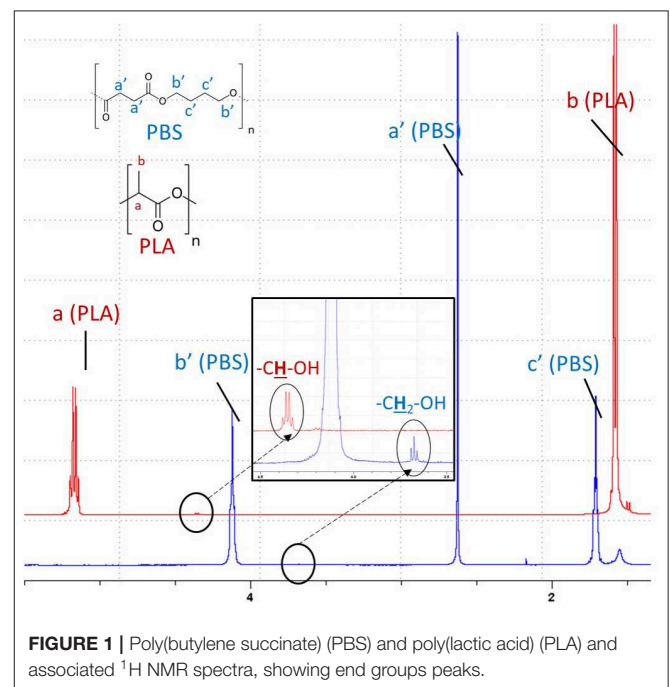


FIGURE 1 | Poly(butylene succinate) (PBS) and poly(lactic acid) (PLA) and associated ¹H NMR spectra, showing end groups peaks.

(a) of PBS (CH₂) at 2.6 ppm were considered to calculate the weight content of PBS:

$$f_{(PBS)} = \frac{\frac{I_{a(PBS)}}{4}}{\frac{I_{a(PBS)}}{4} + I_{a(PLA)}}$$

$$wt\%(PBS) = \frac{f_{(PBS)} \times M_{PBS}}{f_{(PBS)} \times M_{PBS} + [1 - f_{(PBS)}] \times M_{PLA}} \times 100$$

with $f_{(PBS)}$ the molar fraction of PBS and $wt\%(PBS)$ the weight content of PBS.

End group analysis was carried out to calculate mean molar masses of PBS. It was assumed that each polyester chain exhibits one hydroxyl and one carboxylic end groups. Resonance peak

of hydroxyl end group (CH₂-OH) of PBS, appearing at 3.7 ppm (Labruyère et al., 2014), was integrated as well as CH₂ (a) one in the monomer repeating unit at 2.6 ppm. \overline{M}_n was determined as follows:

$$\overline{M}_n = \frac{I_a}{4} \times \frac{2}{I_{\text{CH}_2\text{-OH}}} \times M_{\text{PBS}}$$

with $M_{\text{PBS}} = 172.2 \text{ g/mol}$, I_a the integral of resonance peak CH₂ in the polymer repeating unit, and $I_{\text{CH}_2\text{-OH}}$ the integral of resonance peak of hydroxyl end group (CH₂-OH).

To evaluate the molar mass of PLA phase after processing, the hydroxyl end group of PLA (CH-OH) signed at 4.34 ppm and CH (a) of the monomer at 5.1 ppm were analyzed to calculate the molar mass. However, this peak is close to peak (b) of PBS. Hence, PLA end-chain titration was carried out after extracting PLA from the PBS/PLA blend with the following protocol. First, samples were dissolved in CHCl₃. Then, tetrahydrofuran was added to induce precipitation of PBS. After filtration and solvent evaporation, the remaining PLA and PBS oligomers (soluble in THF) were analyzed by NMR in CDCl₃. \overline{M}_n was determined as follows:

$$\overline{M}_n = \frac{I_a}{1} \times \frac{1}{I_{\text{CH-OH}}} \times M_{\text{PLA}}$$

with $M_{\text{PLA}} = 72.1 \text{ g/mol}$, I_a the CH peak integral in the polymer repeat unit, $I_{\text{CH-OH}}$ the integral of peak of hydroxyl end group (CH-OH). Spectra of pristine PBS and PLA are displayed in **Figure 1**.

Thermal Properties

DSC analyses were carried out using a TA Instruments equipment. Samples were subjected twice to a thermal cycle considering heating and cooling ramps of 10 K min^{-1} , from -70 to 200°C and from 200 to -70°C .

Crystallinity yields were calculated according to the following equation:

$$\chi_{c,p} = \frac{\Delta H_m}{wt_p \times \Delta H_{0,p}} \times 100$$

where wt_p is the weight fraction of the polymer (PBS or PLA), and $H_{0,p}$ is the enthalpy of 100% crystalline polymer (Marten et al., 2003; Shi et al., 2012).

$$\begin{aligned} \Delta H_{0,\text{PBS}} &= 110.3 \text{ J/g} \\ \Delta H_{0,\text{PLA}} &= 93 \text{ J/g} \end{aligned}$$

Thermogravimetric analyses were carried out using a TA Instrument equipment. Samples were subjected to a heating rate of 20 K min^{-1} under nitrogen atmosphere from 25 to 600°C . Temperatures at which 1% of the initial weight was lost $T_{1\% \text{deg}}$ ($^\circ\text{C}$) and degradation temperatures T_{degPLA} and T_{degPBS} (obtained from the maxima of the derivative curves of the weight loss as a function of temperature) were determined.

Morphologies

Transmission electron microscopy was carried out at the Technical Center of Microstructures of Lyon using a Philips CM 120 microscope with an accelerating voltage of 80 kV . Samples ($80\text{--}100 \text{ nm}$ thick) were cut using an ultramicrotome equipped with a diamond knife and set on copper grids.

Dynamic Mechanical Spectroscopy

Dynamic mechanical measurements were carried out using an ARES G2 rheometer. The heating rate was 3 K min^{-1} from -60 to 90°C at a frequency of 1 Hz . The change in shear storage modulus, G' , and shear loss modulus, G'' , were determined. $\tan(\delta)$ was considered to determine the alpha-relaxation temperatures, T_α , related to T_g of PBS and PLA. T_α was considered as the difference between $T_{\alpha(\text{PBS})}$ and $T_{\alpha(\text{PLA})}$.

Mechanical Properties

Uniaxial tensile tests were conducted using an INSTRON 33R4469 tensile machine at 25°C . Dumbbell specimens were tested for a 50-mm/min elongation speed. Young's modulus and maximum and average strain at break were determined.

Degradation Experiments

Degradation experiments for 3 months were performed considering films exposed to various environments. Every month, two samples of each formulation were recovered, washed with deionized water, and gently dried on absorbent paper. Then, they were dried in a vacuum oven at 30°C for 12 h and kept in a closed desiccator. Weight losses were calculated as follows (W_0 being the weight before degradation experiment and W_t the weight after degradation experiment):

$$\text{Weight loss (\%)} = \frac{W_0 - W_t}{W_0} \times 100$$

Abiotic Hydrolysis

Abiotic hydrolysis was conducted at 58°C in deionized water and in alkaline solution (NaOH 0.01 M). Films ($1.25 \times 1.5 \times 0.02 \text{ cm}^3$) were disposed in 10 ml of aqueous solution in individual closed flasks.

Composting

Composting was conducted at 58°C in open containers. Compost was from composting facility of Racine—Ecopole la Rize (Décines-Charpieu, France). Organic matter percentage was obtained by calcination of dry samples and was found to be $58.2 \pm 0.3 \text{ wt-\%}$. The water content and ability to retain water were analyzed. Polymer samples ($2.5 \times 1.5 \times 0.02 \text{ cm}^3$) were buried 15 cm beneath the surface. Moisture content was regularly adjusted to be 90% of the maximum capacity of water retention.

Soil Burial

Soil burial experiment was conducted at room temperature in open containers. Soil was from LyonTech Campus La Doua, Villeurbanne, France. Organic matter percentage was obtained by calcination of dry samples and was found to be $21 \pm 3 \text{ wt-\%}$. Water composition and ability to retain water of the soil were analyzed as well. Polymer samples ($2.5 \times 1.5 \times 0.02 \text{ cm}^3$) were

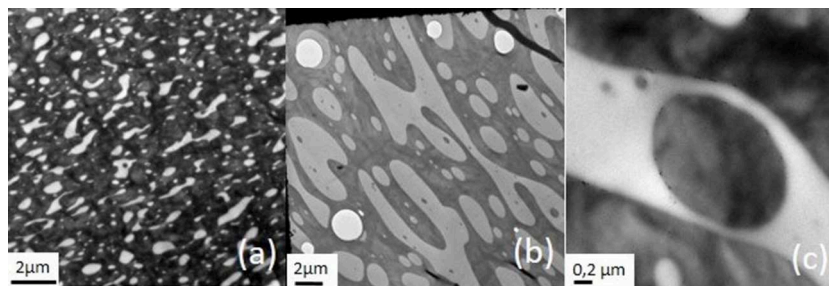


FIGURE 2 | TEM images of (a) poly(butylene succinate) (PBS)/poly(lactic acid) (PLA) (60:40) wt phr, (b,c) PBS/PLA/deep eutectic solvent (DES) (60:40:1) wt phr.

buried 10 cm beneath the surface. Moisture content was regularly adjusted to 90% of the maximum capacity of water retention.

Humid Atmosphere

Polymer samples ($2.5 \times 1.5 \times 0.02$ cm) were disposed in a closed transparent chamber with humidity-saturated air at room temperature.

RESULTS AND DISCUSSION

DES as Interfacial Agents in PBS/PLA Blends

TEM images (Figure 2) confirm that PBS matrix and PLA (appearing as white domains of the dispersed phase) are not miscible (Bhatia et al., 2007). PLA in PBS/PLA blends are irregularly dispersed (Figure 2a). Adding DES (Figure 2b) leads to the formation of a PBS-rich continuous phase and the presence of larger PLA domains (up to $45 \mu\text{m}^2$). In addition, inclusions of PBS are observed in PLA-dispersed domains, indicating the start of phase inversion (Figure 2c). In fact, Wu et al. reported that, as the weight fraction of PBS is up to 60 wt-%, PBS becomes the continuous phase and the inversion content is close to 50 wt-% (Wu et al., 2012). At molecular scale, eutectic solvent is observed at the interface.

The fact that the addition of DES, which is made of an ionic liquid and a solvent, induces larger PLA domains was not expected regarding our earlier studies. Indeed, Lins et al. added 1% of phosphonium-based ionic liquids in PBAT/PLA blends and observed smaller PLA droplets as well as a rather homogeneous size distribution. This phenomenon suggests that IL locates in the interfacial zones due to strong interactions with the ester groups leading to a decrease in the interfacial tension (Lins et al., 2015). Furthermore, Leroy et al. studied the addition of choline chloride/glycerol in PBS–zein blends and showed that DES behaves as a compatibilizing agent leading to a finer dispersion of zein in the PBS matrix (Leroy et al., 2012).

Tensile properties analyses of PBS/PLA blends reported in Table 2A show that the PLA phase, having a higher modulus compared to PBS, acts as a reinforcing component leading to higher Young's modulus (Qiu et al., 2016). The strain at break is slightly improved with the addition of DES, which can be explained by better adhesion between PBS and PLA, provided by DES acting as an interfacial agent.

TABLE 2 | (A) Mechanical properties of neat poly(butylene succinate) (PBS) and poly(lactic acid) (PLA) and PBS/PLA blends (uniaxial tension; 50 mm min^{-1}) and (B) dynamic mechanical analysis of PBS/PLA blends without and with deep eutectic solvent (DES) (1 wt phr) at 1 Hz, 3 K/min.

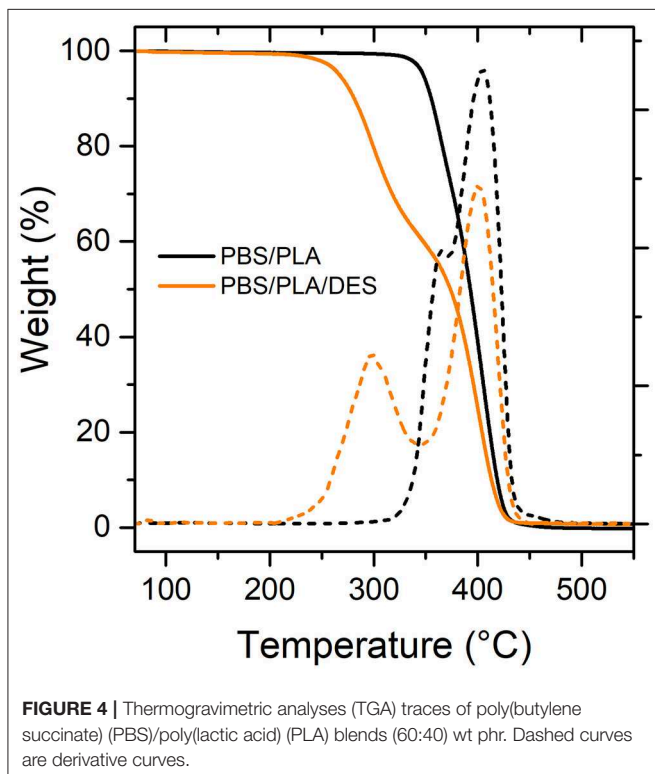
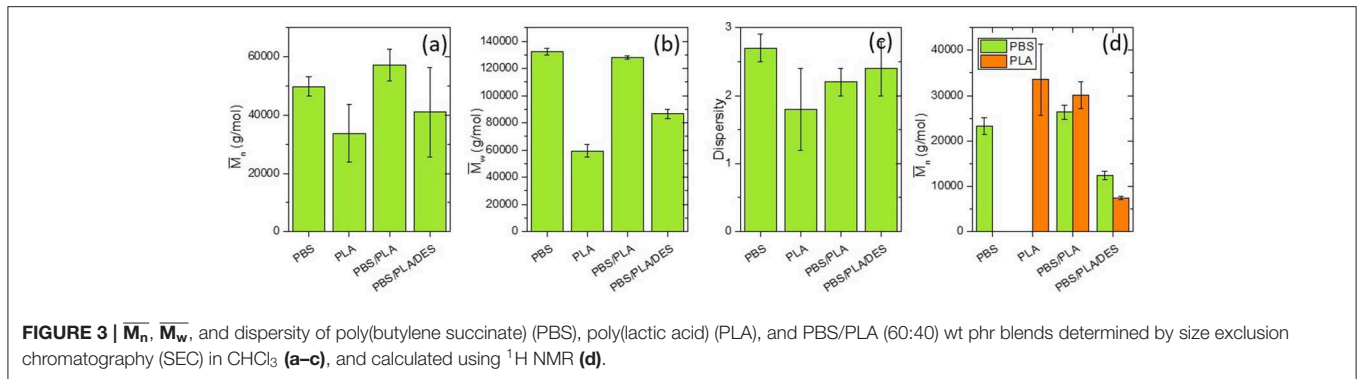
(A)			
Material	Young's modulus (MPa)	Strain at break (%)	Maximum strain at break (%)
PBS	320 ± 27	310 ± 90	385
PLA	3,500*	5*	–
PBS/PLA	603 ± 57	391 ± 84	418
PBS/PLA/DES	619 ± 17	424 ± 66	490
(B)			
Material	$T_{\alpha, \text{PBS}} (\text{°C})$	$T_{\alpha, \text{PLA}} (\text{°C})$	$\Delta T_{\alpha} (\text{°C})$
PBS/PLA	–25.6	61.1	86.7
PBS/PLA/DES	–24.3	59.7	84.0

*Data provided in product datasheet.

Data from dynamic mechanical analyses are summarized in Table 2B. The observation of two distinct α -relaxation temperatures related to PBS and PLA phases confirm that PBS and PLA are not fully miscible (Deng and Thomas, 2015).

Number average molar mass, \overline{M}_n , weight average molar weight, \overline{M}_w , and dispersity, $\overline{M}_w/\overline{M}_n$, determined with SEC, are reported in Figures 3a–c. As PLA and PBS are not distinguishable on SEC chromatograms, \overline{M}_n of distinct PBS and PLA phases are determined by end group titration using ^1H NMR spectroscopy as well (Figure 3d). Average molar masses calculated using ^1H NMR titration (Figure 3d) are significantly lower than molar masses measured using SEC (Figure 3a). Since it is assumed that polymers are not branched, end-group titration may underestimate real values. Hence, instead of discussing absolute average molar masses, only trends are studied in this work.

PBS/PLA blends with DES exhibit significantly lower molar masses of involved polymer components. This suggests that the DES leads to chain scissions, as observed by Park and Xanthos for neat PLA (Park and Xanthos, 2009). This could be due to transesterification reactions leading to random chain scissions first (Lins et al., 2015). It was observed by Freyermouth that no or few transesterification reactions can take place



between PBS and PLA in PBS/PLA blends after 105 min at 180°C (Freyermouth, 2014); however, the addition of DES could lead to different results, given the important degradation phenomenon taking place during processing. Nevertheless, no additional resonance peak, which is a signature of a possible transesterification phenomenon, could be evidenced using ^1H NMR spectroscopy.

Hence, although transesterification is not observable, it is clear that DES causes thermal degradation during material processing, leading to lower molar masses. This seems to favor miscibility between PBS and PLA, as evidenced by the merging of alpha relaxation peaks in DMA spectra (Table 2B). These conclusions are in agreement with the ones issued from thermogravimetric analyses (Figure 4, Table 3), which show that PBS/PLA/DES blends degrade at lower temperature than PLA/PBS blend. They

TABLE 3 | Degradation temperatures of poly(butylene succinate) (PBS) and poly(lactic acid) (PLA) phases and degradation temperature for 1% wt loss from thermogravimetric analyses (TGA) (heating rate: 20 K min^{-1} ; nitrogen atmosphere).

Material	$T_{1\% \text{ deg.}} (^\circ\text{C})$	$T_{\text{deg PLA}} (^\circ\text{C})$	$T_{\text{deg, PBS}} (^\circ\text{C})$
PBS	304	–	409
PLA	319	379	–
PBS/PLA	324	365	405
PBS/PLA/DES	228	298	401

Degradation temperatures $T_{\text{deg PLA}}$ and $T_{\text{deg PBS}}$ were obtained from the maxima of the derivative curves of the weight loss as a function of temperature.

are also in agreement with DSC results (Table 4), which show a lower crystallization temperature (T_c) when DES is present in the blends.

Degradation Mechanisms Observed at Microscale

Fragmentation process to small fragments of samples is reported in Figure 5.

PBS/PLA/DES blends exhibit fringes after degradation in alkaline environment (Figure 5B). TEM images showed that PLA domains are elongated in PBS/PLA/DES materials (Figure 2b). Assuming that the microstructure is similar whatever the processing conditions, this phenomenon can be explained by a faster degradation of PLA phase compared to the PBS one. Weight loss data (Figure 6) also supports the proposed mechanism. In fact, in alkaline medium at 58°C , PBS/PLA/DES blend exhibits a higher weight loss during the first month of exposure, i.e., up to 20 wt-% loss compared to non-modified PBS/PLA blend. After 3 months exposure, data cannot be provided for PBS/PLA/DES blends as not all fragments could be recovered (which means leading to very efficient biodegradation). In deionized water, PBS/PLA blend containing DES shows a higher weight loss compared to neat PBS/PLA blend. In a similar way, under composting conditions at 58°C , PBS/PLA/DES blend undergoes a rather high weight loss, i.e., 18% after 2 months exposure.

As a conclusion, PBS/PLA blends modified with a DES degrade faster than neat PBS/PLA blends, but it is expected that $T_{1\% \text{ deg.}}$ at 228°C does not significantly disturb extrusion

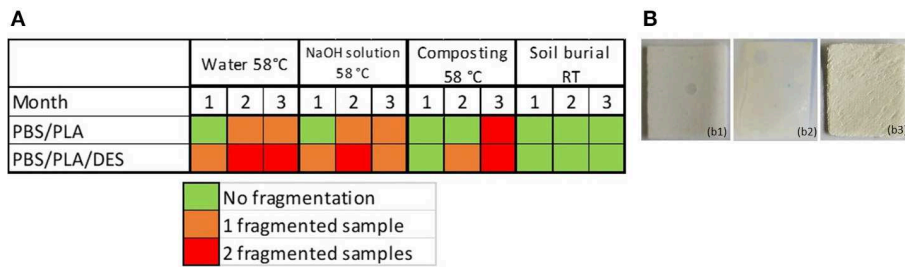


FIGURE 5 | (A) Fragmentation observed during aging experiments after various exposure times: 1, 2, and 3 months. **(B)** Photographies of poly(butylene succinate) (PBS)/poly(lactic acid) (PLA) blend (60:40) wt phr after 1 **(b1)** and 3 **(b2)** months of exposure and PBS/PLA/deep eutectic solvents (DES) (60:40:1) wt phr **(b3)** after 3 months of exposure in NaOH solution at 58°C.

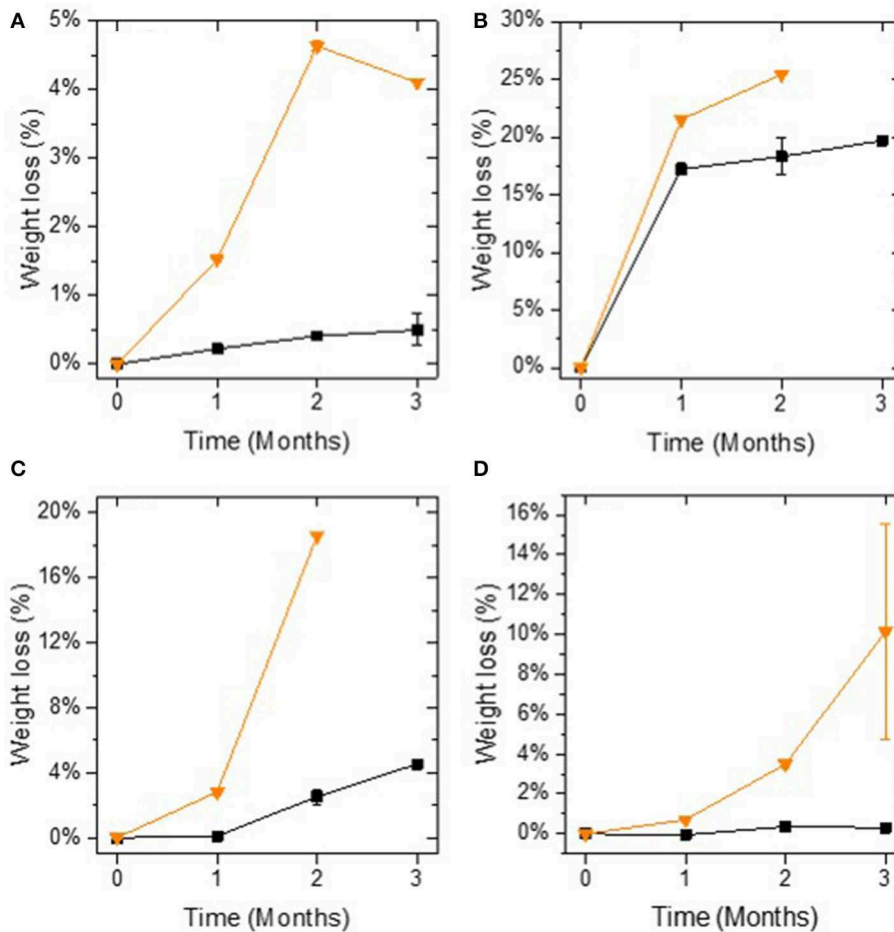


FIGURE 6 | Weight loss (%) of poly(butylene succinate) (PBS)/poly(lactic acid) (PLA) (60:40) wt phr (black) and PBS/PLA/deep eutectic solvents (DES) (60:40:1) wt phr (orange) in deionized water at 58°C **(A)**, in 0.01 M NaOH solution at 58°C **(B)**, under composting conditions at 58°C **(C)**, and under soil burial conditions at room temperature **(D)**. Results are given with standard deviation. If not shown, only one sample could be recovered and weighted.

(at 190°C) and compression molding (at 210°C) with short residence times. Moreover, the lower thermal stability in the presence of DES should not reduce the applications profile. Considering the fact that the molar masses of the polyesters in

the presence of DES are lower than for unmodified PBS/PLA blends, PBS/PLA/DES blends are susceptible to lose integrity faster. Furthermore, it is known that PLA degrades well at 58°C (Agarwal et al., 1998; Itävaara et al., 2002; Yagi et al., 2009). It can

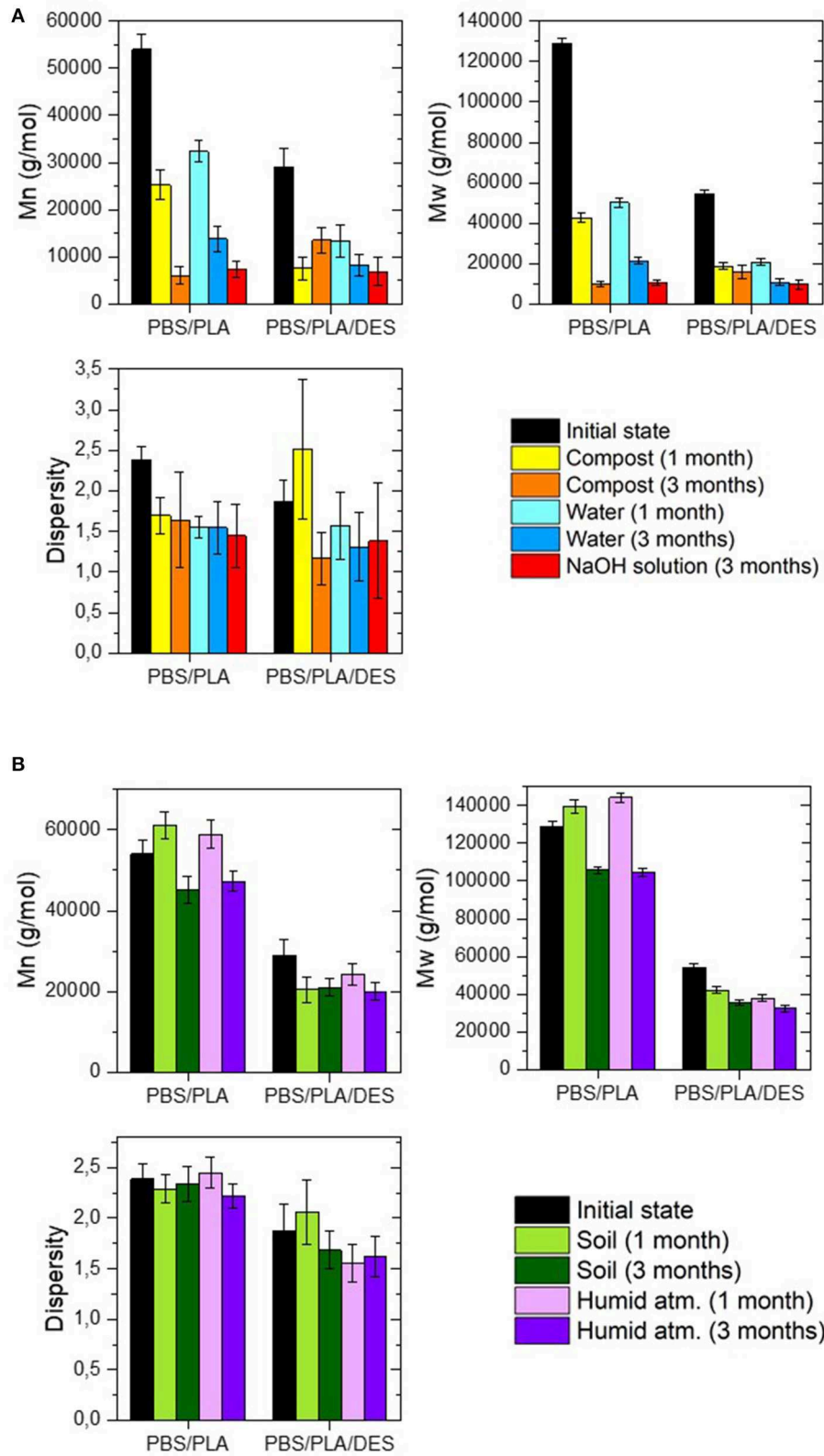


FIGURE 7 | \overline{M}_n , \overline{M}_w , and dispersity of poly(butylene succinate) (PBS)/poly(lactic acid) (PLA) blends measured with CHCl_3 -deep eutectic solvents (DES), after degradation under composting conditions, in water, and in NaOH solution at 58°C (A), and under soil burial conditions and in humid atmosphere at room temperature (B).

be supposed that PLA chains are the weakest component in the materials at such temperature.

At room temperature under soil burial conditions, PBS/PLA/DES blends show a larger weight loss, but this phenomenon cannot be reproduced after 3 months exposure. For choline chloride/glycerol, having a low toxicity (Radošević et al., 2015) and being hydrophilic, it might improve surface affinity with microorganisms, whereas it might not be the case for PBS/PLA blend. Nevertheless, heterogeneities of composition could occur in the biodegradation medium regarding the populations of microorganisms, i.e., depending on the location in the container. Specimens left under humid atmosphere did not exhibit any weight loss after 3 months exposure.

Molar Masses Changes During Biodegradation

Molar masses determined using SEC are reported in Figure 7. As PLA and PBS are not distinguishable on SEC chromatograms, the variation of refractive index vs. concentration, dn/dc , of neat PBS (0.06) was used to calculate the average molar masses polymer in blends. Hence, the resulting \overline{M}_n were used to evidence the trends, as these ones are semiquantitative values.

\overline{M}_n of PBS phases only was determined by chain end titration using ^1H NMR spectroscopy (Table 5). As said earlier, molar masses determined using ^1H NMR titration might underestimate real values since it was assumed that polymer chains are not branched.

Under composting conditions and in deionized water at 58°C (Figure 7A), molar masses decrease is significant above 1 month of exposure and does not change afterwards for PBS/PLA blends including DES, suggesting that \overline{M}_n reaches a limit of $\sim 10,000$ g mol^{-1} . From this limit, polymer chains might diffuse into the biodegradation medium. Dispersity decreases with degradation

TABLE 4 | Glass transition, melting, and crystallization temperatures of poly(butylene succinate) (PBS), poly(lactic acid) (PLA), PBS/PLA (60:40 wt phr), PBS/PLA/deep eutectic solvents (DES) (60:40:1 wt phr) films determined using differential scanning calorimetry (DSC) (heating/cooling rate of 10 K min^{-1} under nitrogen atmosphere) before exposure.

Material	$T_{g,\text{PBS}}$ ($^\circ\text{C}$)	$T_{g,\text{PLA}}$ ($^\circ\text{C}$)	$T_{m,\text{PBS}}$ ($^\circ\text{C}$)	$T_{m,\text{PLA}}$ ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)
PBS	-29	-	116	-	92
PLA	-	60	-	177	95
PBS/PLA	-29	62	115	176	91
PBS/PLA/DES	-28	63	114	171	88–104

TABLE 5 | \overline{M}_n of poly(butylene succinate) (PBS)/poly(lactic acid) (PLA) and PBS/PLA/deep eutectic solvents (DES) blends determined using size exclusion chromatography (SEC) and ^1H NMR (PBS end group titration) after 3 months degradation.

\overline{M}_n (kgmol^{-1})	Initial state		Compost		Water		NaOH		Soil	
	SEC	^1H NMR	SEC	^1H NMR	SEC	^1H NMR	SEC	^1H NMR	SEC	^1H NMR
PBS/PLA	54.0 ± 3.4	27.9 ± 1.6	6.1 ± 2.0	3.5 ± 0.2	13.9 ± 2.8	6.6 ± 0.4	7.4 ± 1.8	6.0 ± 0.3	45.2 ± 3.3	24.9 ± 1.7
PBS/PLA/DES	29.0 ± 4.0	12.4 ± 1.0	13.6 ± 2.7	$5.8 \pm 0.3^{**}$	8.2 ± 2.3	5.7 ± 0.3	6.9 ± 3.1	3.4 ± 0.2	21.0 ± 2.2	14.5 ± 1.0

^{**}Determined at the second month.

time. The molar mass loss under composting conditions is similar to its loss after exposure in deionized water, suggesting that the main degradation mechanism under composting conditions is abiotic hydrolysis. If biotic degradation occurs, it does not induce a significant loss of molecular weight at the core of the samples, but may be responsible for surface etching.

At room temperature, under humid atmosphere and soil burial conditions (Figure 7B), PBS/PLA blends modified with DES exhibit a molar mass loss after the first month of exposure. After 3 months of exposure, all the blends exhibit a loss of molar mass. The molecular weight loss after exposure under soil burial conditions is similar to that after exposure under humid atmosphere conditions, suggesting again that the main degradation mechanism, causing a loss of molar mass under soil burial conditions, is abiotic hydrolysis.

Molecular Scale Analysis of the Degradation Mechanisms

After 3 months of exposure, materials were analyzed in CDCl_3 using ^1H NMR spectroscopy, to observe the changes in PBS and PLA contents (Figure 8). PLA and PBS weight contents in PBS/PLA/DES blends were found to be 68:32 after 3 months of exposure under alkaline conditions, 72:28 after exposure under composting conditions, and remained unchanged otherwise. This result is in agreement with the fact that PLA phase degrades faster than PBS and then diffuses out of the material at 58°C .

Melting and crystallization of PBS and PLA in the blends were studied using DSC (Figures 9, 10). Owing to the occurrence of the cold crystallization exothermic peak of PLA overlapping the

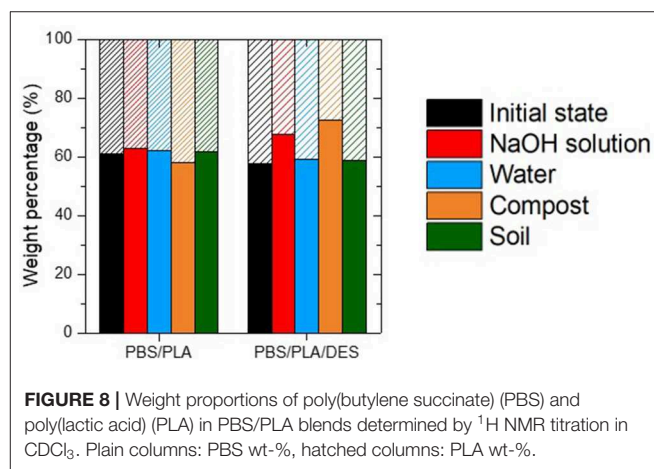
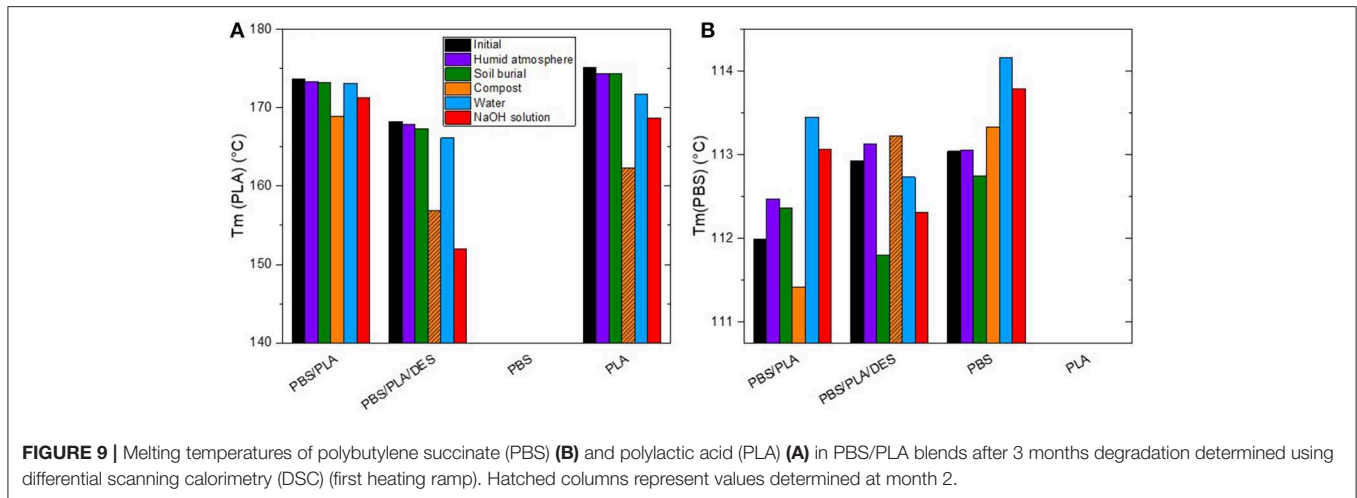


FIGURE 8 | Weight proportions of poly(butylene succinate) (PBS) and poly(lactic acid) (PLA) in PBS/PLA blends determined by ^1H NMR titration in CDCl_3 . Plain columns: PBS wt-%, hatched columns: PLA wt-%.



endothermal melting peak of PBS, the changes in enthalpy were difficult to assess. Hence, the data are not reported in this article.

For PBS/PLA/DES blends, the melting temperature of PLA (Figure 9A) slightly decreases after exposure in deionized water, but significantly lower values were measured after degradation in NaOH solution and compost. This decrease in melting temperature of PLA during degradation has been observed by Pantani and Sorrentino and was attributed to the presence of low molar mass chains (Pantani and Sorrentino, 2013). The melting temperature attributed to PBS phases does not change significantly after degradation experiments (Figure 9B). These observations are in agreement with the fact, as said earlier, that PLA domains are significantly degraded in PBS/PLA blends containing DES during exposure at 58°C.

The crystallization phenomena in the PBS/PLA blends was studied with considering a 10 K min⁻¹ cooling ramp from molten state (Figures 10C,D). PBS/PLA blends without DES show no change in their crystallization behavior after degradation at room temperature (under soil burial conditions and humid atmosphere). The crystallization temperature remains unchanged, i.e., ~94°C. However, after degradation at 58°C, a separation of the two peaks can be observed. A first peak, close to 103°C could be attributed to the PLA crystallization and a second one at lower temperatures to PBS crystallization. This second peak reaches its maximum at ~71°C after degradation in NaOH solution and under composting conditions, while it was at ~84°C after degradation in deionized water.

PBS/PLA/DES exhibits two distinct crystallization peaks before degradation experiments. No significant change is observed after degradation at room temperature. However, after exposure at 58°C, the small peak, attributed to PLA crystallization, broadens and its intensity diminishes, which is in agreement with the fact that PLA chains degraded and the shorter ones diffused out of the matrix during degradation. The crystallization peak of PBS is slightly shifted to lower temperatures after degradation exposure. PLA melting peak (Figures 10A,B) appears to be broad. After degradation at 58°C, this melting phenomenon is hardly observable. As seen earlier, this observation could be associated with the PLA

degradation with diffusion out of the PBS continuous phase. Furthermore, enthalpy of crystallization increases significantly after degradation in NaOH solution.

CONCLUSION

In this study, PBS/PLA blends were processed with addition of a DES, i.e., choline chloride/glycerol, which could act as a compatibilizer (interfacial agent). It was observed that the PLA dispersed phase in the PBS matrix exists as larger domains when DES is added to the PBS/PLA blends compared to the neat PBS/PLA blend. DES addition leads PBS/PLA/DES blend to display some decrease in molar mass values, similar mechanical properties, and decrease in thermal stability. Degradation tests under different conditions show improved degradation of PBS/PLA blends in the presence of DES, which enhances chain scissions (Decaen et al., 2017). Nevertheless, from molar masses measurements, it can be concluded that DES induces a significant decrease in PLA molar masses and consequently a lower thermal stability.

It is assumed that the good stability of PBS and degradation of mainly PLA during processing is associated with maintenance of mechanical properties and higher ability to biodegrade.

Biodegradation experiments performed at 58°C show that the PBS/PLA blends degrade faster. It is also observed that PLA phase undergoes the most important degradation phenomenon during exposure. In fact, this phenomenon is evidenced by the slight decrease in PLA melting temperature as well as of the PLA weight content. Therefore, at macroscale, a significant weight loss and fragmentation process are demonstrated. Thus, it can easily be assumed that the PLA phase is the weakest component in such blends, leading to a fast loss of integrity. This shows that designing polymer materials, for which degradation processes are targeted in the dispersed phase, i.e., in multiple locations of the material, can be an efficient route to accelerate macroscopic biodegradation.

However, PLA dispersed phase is not affected to the same extent after exposure at room temperature. In fact, it is well-known that PLA does not easily degrade under mesophilic

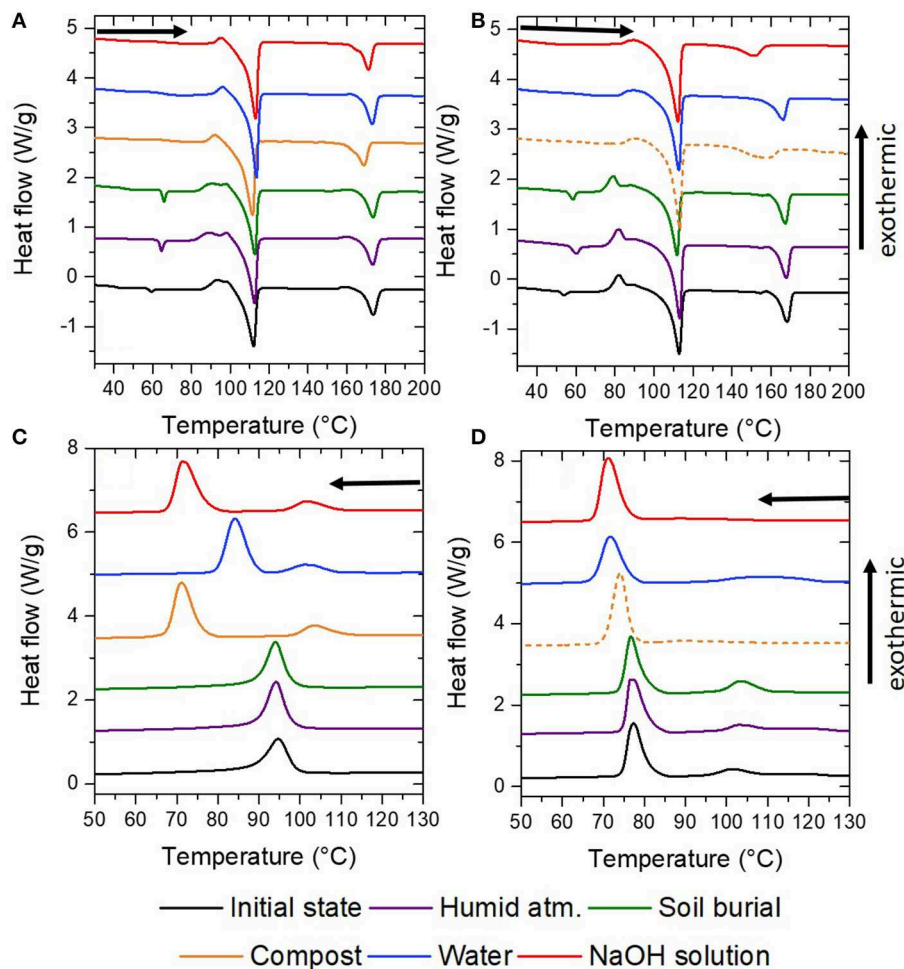


FIGURE 10 | Crystallization and melting curves of poly(butylene succinate) (PBS)/poly(lactic acid) (PLA) blends during cooling and heating ramps at 10°C/min, before and after degradation. (A,C) PBS/PLA, (B,D) PBS/PLA/deep eutectic solvents (DES). Dashed curves were acquired after 2 months because samples could not be studied in third month.

conditions (Agarwal et al., 1998; Itävaara et al., 2002; Yagi et al., 2009). At room temperature, it is difficult to identify which polymer, if any, constitutes a weak component as no significant change is observed using DSC. ¹H NMR does not evidence large changes in PBS/PLA contents, even though PBS/PLA/DES blend exhibits an important weight loss under soil burial conditions. Nevertheless, under soil burial conditions, blend containing DES shows a larger weight loss than the neat PBS/PLA blend.

Regarding molar masses analyses, it is observed that the molar mass decrease remains very similar under abiotic and biotic conditions at a same temperature. This suggests that hydrolysis remains the main degradation mechanism for polyester-based blends. However, blends including DES exhibit surprisingly higher weight loss than without additive under soil burial conditions at room temperature, showing that biotic degradation probably occurs at the surface of the exposed coupons. This phenomenon can be due to the choline chloride/glycerol nature, which has a hydrophilic character and displays a low toxicity.

This study shows that eutectic solvents can be used to tune mechanical properties of polymer blends as well as their biodegradability in the environment. Furthermore, degradation products must be identified and their eco-toxicity should be studied. Affinity with microorganisms of the DES is being studied and will be reported later.

DATA AVAILABILITY STATEMENT

The datasets generated for this study are available on request to the corresponding author.

AUTHOR CONTRIBUTIONS

SL, VM, and J-FG: conceptualization. SL, AM, ED, VM, and RB: methodology. AM, ED, VM, and SL: formal analysis and investigation. ED, AM, and VM: visualization. ED, VM, and SL: writing—original draft preparation. SL, J-FG, RB, and VM:

resources. SL, VM, and RB: project administration. All authors: data curation, validation, writing—review, and editing.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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