

Reactive extrusion of poly (butylene succinate-co-adipate) and poly (ϵ -caprolactone) biodegradable blends through titanium-based transesterification catalyst

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ABSTRACT

This article addresses the development of biodegradable blends of poly (butylene succinate-co-adipate) (PBSA) and poly (ϵ -caprolactone) (PCL) processed by reactive extrusion in the presence of titanium butoxide (TiOBu_4) (TBT) in twin-screw equipment. The PBSA/PCL concentration was set to 60/40 (wt.%), and 0%, 0.1%, 0.3% and 0.5% of TBT were added to the polymer weight. FTIR analysis revealed slight changes around the carbonyl peak correlated to the generation of copolymers. The results of MFR showed an increase in viscosity for higher TBT concentrations, and tensile tests indicated improved yield stress and yield elongation from up to 0.3% TBT concentration, with similar Young modulus. The storage modulus was similar at room temperature for blends with and without TBT. The thermal properties showed insignificant changes among the formulations. The crystallization behavior seemed to be influenced by a chain scission and copolymer generation competition promoted by transesterification, and altered the microbial susceptibility to a certain extent. PLOM and SEM results showed a blend morphology evolution from a co-continuous-like to a co-continuous-to-dispersed-like when the TBT concentration increased. Overall, TBT was an effective transesterification catalyst for the generation of a cohesive morphology with good mechanical properties, with no loss of microbial susceptibility.

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1. Introduction

Global warnings on environment plastic residues have become usual, but not neglected, and several institutions and researchers have published studies and reports on the issue every year [1–3]. Among the solutions proposed to the problem with plastic residues, biodegradable plastics can reduce the adverse environmental impacts; therefore, biodegradable polymers have drawn the attention of academia, industries and governments [4]. The most studied type of biodegradable polymers is the aliphatic polyester class, which includes poly (butylene succinate-co-adipate) (PBSA) and poly (ϵ -caprolactone) (PCL), among others. Although both polymers represent good alternatives to conventional plastics [5], they have faced several challenges to be introduced in the market, due to some drawbacks (e.g., poor mechanical and barrier properties, and high price) in comparison to conventional polymers.

Blending polymers are an excellent alternative for the development of new materials and overcoming of the aforementioned drawbacks. However, most polymers are immiscible and the resulting blend morphology may exhibit poorer properties in comparison to neat polymers. Compatibilization methods have been developed in an attempt to deal with this issue, and several studies have explored blending aliphatic polyesters and their promising applications, especially in agriculture, packaging and biomedical sectors [5–10].

Compatibilization can occur by non-reactive and reactive methods. The former involves the addition of compatibilizing agents - generally block copolymers - which are miscible to the polymers present in the blend and promote some degree of interaction among them, whereas the reactive method generates compatibilizing agents in-situ by the addition of a chemical compound that interacts with polymers during blending. The reactive method offers a good advantage to polyesters blends due to the easy catalysis of transesterification reactions, which can generate copolymers between phases, and the convenience of application of a single step

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process [9,11,12]. Titanium-based catalysts show high catalytic activity in transesterification reactions in comparison to other metal catalysts, especially titanium butoxide (TBT) [13]. Furthermore, the literature reports several cases of compatibilization induced by the transesterification catalyzing effect of TBT [13–19].

PBSA and PCL are flexible thermoplastic polyesters of reasonable mechanical properties and processing window; they are biodegraded by a large variety of microorganisms in several media, however publications on their blend system are still scarce [20,21]. It is well known that PCL has low melting point (at around 60 °C), which may hinder its use in many applications [22]. Therefore, it is generally employed as a blending partner for other biodegradable polymers of higher T_m . Moreover, PBSA and PCL have been used in blends or multilayered films with polysaccharides or proteins for overcoming the processing difficulties of natural polymers and reducing the higher costs of biodegradable polyesters in comparison to non-biodegradable polymers [22–24]. Martin et al. [25] showed the better adhesion of PBSA and PCL to thermoplastic starch compared to poly (lactic acid) (PLA), and Avérous and Fringant [26] concluded associations of wheat starch to aliphatic polyesters, such as PBSA and PCL, avoid the main drawbacks of starch. Reddy et al. [22] demonstrated the blending of thermoplastic soy meal to poly (butylene succinate) (PBS) and PCL together enhanced the mechanical properties of the blends.

Another disadvantage for biodegradable applications is the high crystallinity of PCL, which slows the biodegradation process. Chen et al. [27] demonstrated that blending PCL with other aliphatic polyesters, such as PBS, reduces its crystallinity enhancing biodegradation conditions and giving rise to promising applications (e.g., carriers for controlled release systems).

Previous studies on solvent casting and single screw extrusion of PBSA/PCL blends conducted by our research group showed the concentration of polymers can be a good adjustable parameter for tuning the blend properties [28]. According to the results, PBSA/PCL 60/40 (wt.%) blend exhibited similar to, or even higher mechanical properties than those of neat PBSA and other PBSA/PCL blends concentrations, and improved susceptibility to biodegradation in comparison to neat homopolymers. Herein, the authors focus on the incorporation of a compatibilizing agent into this polyester concentration towards obtaining the best properties.

The compatibilization of this blend system can enhance the blend morphology promoting good performance and fast biodegradability, and the understanding of the blending and compatibilizing behavior of PBSA/PCL systems opens new possibilities for research on biodegradable blends, since their properties enable specific applications, or even their use as components for a new polymer material. This study investigates the effect of concentration of transesterification catalyst titanium butoxide (TBT), $Ti(OBu)_4$, on the reactive extrusion of PBSA/PCL 60/40 (wt.%) blend.

2. Experimental

2.1. Materials

An injection grade PBSA, Bionolle® 3020MD ($M_n = 60$ kg/mol), was supplied by Showa Denko K. K. (Japan), injection grade PCL, CAPA® 6500 ($M_n = 50$ kg/mol) was provided by obtained from Perstorp, and titanium tetrabutoxide (TBT), $Ti(OBu)_4$, reagent grade (97% purity) was supplied by Sigma Aldrich and used as received.

2.2. Blend preparation and processing

The mixing ratio of PBSA and PCL was fixed at 60 wt.%/40 wt.% in all blend systems, due to their improved properties, as reported in [28]. PBSA and PCL pellets were dried at 40 °C for

24 h, and four portions of PBSA/PCL were pre-mixed prior to the TBT addition, which occurred in 0 wt.%, 0.1 wt.%, 0.3 wt.% and 0.5 wt.% polymer mass by a plastic pipette. They were manually mixed again before feeding into the extruder, and their portions are referred to as T00, T01, T03 and T05, respectively. The materials were then introduced into a B&P corotating twin-screw extruder (MT19TC) of 19 mm screw diameter (D) and 25 L (length)/D. The melt blending temperatures were set at 90 °C (feeding zone), 100 °C, 110 °C, 110 °C (melting zone) and 115 °C (die) by an 80 rpm rotor speed. Each extrudate was quenched in water bath at room temperature and then granulated. The granules were dried at 40 °C for 12 h, and the injection molding process was conducted in a Thermo Scientific Haake Minijet II, of barrel and mold temperatures of 102 °C and 33 °C, respectively. The heating and cooling stages took 120 s and 50 s, and the samples dimension followed Type V geometry, according to ASMT D638. All extruded pellets and injection-molded samples were dried at 40 °C under vacuum for 24 h prior to tests for preventing hydrolysis.

2.3. Blends characterization

The extruded materials were characterized by melt flow rate (MFR), Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and polarized light optical microscopy (MOLP). Dynamic-mechanical thermal analyses (DTMA), scanning electron microscopy (MEV) and biodegradation essays were performed with the injection-molded samples.

Melt flow rate (MFR) measurements were taken at 105 °C by MI-2 equipment commercialized by Göttfert, since higher temperatures significantly decreased the polymers viscosity, and 1.2 kg load. The evaluation followed ASTM D1238 procedure B.

Fourier-transform infrared spectroscopy (FTIR) was performed by Spectrum 100 (Perkin Elmer), and FTIR spectra were recorded according to an attenuated total reflection (ATR) method, with 16 scans, 4000 to 600 cm^{-1} wavenumber, and ± 4 cm^{-1} resolution. 1 mm thickness samples were directly placed onto the ZnSe ATR cell.

Tensile tests were performed by an Instron universal tensile testing machine, model 5969, of 1 mm/min speed, according to ASTM D638. At least five specimens were tested for each blend formulation.

Dynamic-mechanical thermal analyses (DMTA) were conducted in a DMA 8000 (Perkin Elmer) at – 90 to 60 °C temperature, 1 Hz frequency, 2 °C/min heating rate, and with a single bending type cantilever and tensile mode of 0.01% maximum strain. The storage modulus (E') and $\tan \delta$ were recorded as a function of temperature.

Differential Scanning Calorimetry (DSC) was performed in a DSC 8000 (Perkin Elmer), under 20 ml/min nitrogen flow. The sample (~8 mg) was first heated up to 140 °C for 1 min for the elimination of the previous thermal history; it was cooled to – 70 °C and kept for 1 min, and then reheated to 140 °C. The heating and cooling processes were set to 10 °C/min rate. All DSC curves refer to the second heating towards minimizing the thermal history effect. The degree of crystallinity (X_c) was calculated by Equation > 1:

$$X_c(\%) = \frac{(\Delta H_m - H_{cc})}{(\Delta H_m^0 \times W)} \times 100 \quad (1)$$

where ΔH_m is the melting enthalpy, ΔH_{cc} is the cold crystallization enthalpy, ΔH_m^0 is the melting enthalpy of 100% crystalline polymer (PBSA \Rightarrow 116.9 J/g [29], PCL \Rightarrow 136 J/g [30]), and W is the weight fraction of the blend component.

Polarized light optical microscopy (PLOM) was conducted on a Leica LEITZ DMRXP coupled to a Carl Zeiss Microimaging GmbH/AxioCam ERc 5 s and AxioCam ERc 5 s Rev.1–2 software.

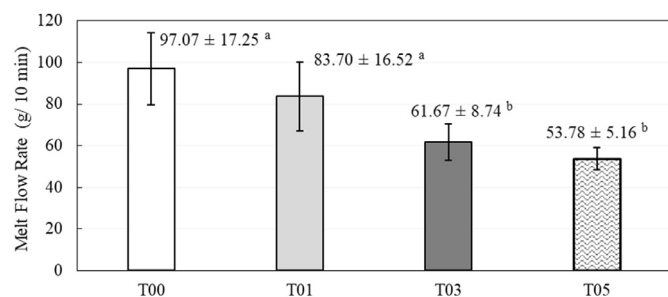


Fig. 1. Melt flow rate of PBSA/PCL/TBT blends. Means followed by the same letter in the columns did not differ in Tukey's test at 95% confidence level.

The 2 > mm thick sample was placed between glass slides onto the heating plates of a Cambridge Shearing System CSS450 and then heated to 120 > °C for the accommodation of the material. It was cooled down to room temperature for crystallization monitoring. The cooling rate could not be controlled; however, it was established between 10 and 20 > °C/min

Scanning electron microscopy (SEM) was performed on an In-spect F50 (FEI Company) of 3 > kV. The sample was fractured in liquid nitrogen, and the fractured ends were sputter-coated with platinum and then examined.

The microbial susceptibility of the blends was assessed by laboratory soil burial according to ASTM G160 standard. Both humidity and temperature of the greenhouse environment were measured by an Incoterm thermo-hygrometer, and the soil humidity and pH were evaluated every 30 days. The samples used were composed of half of the tensile testing samples, and their geometry followed ASTM D638 type V. Four samples of each PBSA/PCL blend were used for each burial period (30, 60, 90, 120 and 150 days), and their masses were measured prior to the tests (m_i). After the corresponding period, the samples were collected, gently washed and dried for 24 > h in an oven at 45 > °C under vacuum for the final mass measurement (m_f). The weight loss percentage (WL%) was calculated by Equation > 2:

$$WL\% = \left(\frac{m_i - m_f}{m_i} \right) \times 100 \quad (2)$$

All statistical analyses were conducted by One-way (ANOVA) software Origin 2019 9.6.0.172 (OriginLab Corporation), and the results were expressed as mean ± errors. Statistically significant differences (p), i.e., when $p > \leq 0.05$, were analyzed by ANOVA with Tukey's testing.

3. Results and discussion

Fig. > 1 displays the melt flow rate data of the PBSA/PCL/TBT blends. The results show a decreasing trend in the MFR values as the TBT concentration increased, which indicates the transesterification catalyst affected the rheological behavior of the blends increasing their melt viscosity. Utracki [31] correlated the viscosity increment to the reactive compatibilization of blends due to increased interactions between the two phases. The transesterification catalyst acts as a Lewis acid, coordinating the carbonyl groups and activating them for nucleophilic attacks [32]. Such a mechanism fractures the macromolecular backbone into shorter fragments (degradation step), which may reconnect randomly through interchange reactions (compatibilizing step) [14]. Coltelli et al. [33] observed the same tendency in reactive PLA/ PBAT blends in the presence of TBT, and concluded the catalyst affected their rheological behavior, hypothesizing the predominance of transesterification onto degradation. Wang and coworkers [19] studied PLA and poly (propylene carbonate) (PPC) blends with and without TBT and observed the transesterification catalyst promoted the formation

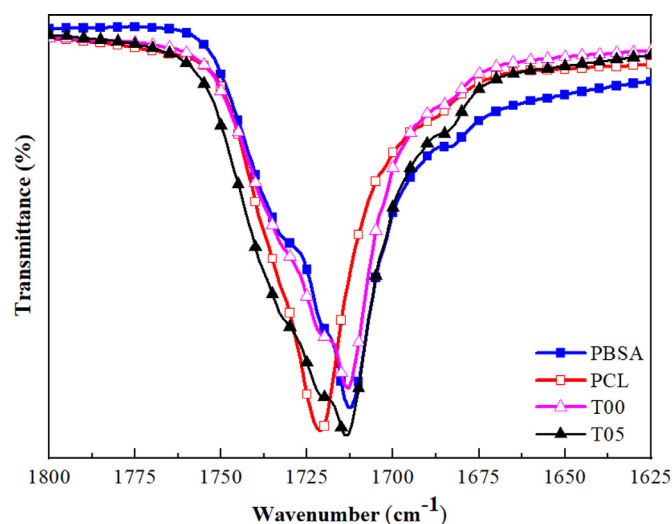


Fig. 2. FTIR spectra of PBSA, PCL, T00, and T05.

of block copolymers, which increased the viscosity of the blend, hence, the interaction between PLA and PPC, since they acted as compatibilizers. The authors also highlighted a limit for TBT concentration, from which the chain scission reaction became dominant, thus decreasing viscosity. Likewise, Muthuraj and coworkers [34] extruded PBS and PBAT blends in various proportions with no use of catalysts. Measurements of their MFR showed higher flow values in comparison to neat polymers, attributed to the degradation during the process. Therefore, it is reasonable to assume TBT acted over PBSA/PCL blend rheology, since the compatibilization mechanism prevailed over the degradation one.

The compatibilization mechanism proposed in this study derives from transesterification reactions that probably occur at the interface of polyesters PBSA and PCL, thus originating copolymers with chain segments similar to those of their precursors and enhancing compatibilization [35]. The FTIR analysis revealed some peak shifting that might be related to such reactions. Fig. > 2 shows the FTIR spectra of PBSA, PCL, T00, and T05 samples of the area of interest corresponding to the carbonyl groups (C=O) vibration band, from 1800 to 1625 cm^{-1} . The spectra of T01 and T03 blends were omitted for a better observation.

The carbonyl group peaks of neat polymers PBSA and PCL were observed at 1713 and 1721 cm^{-1} , respectively, whereas those of T00 and T05 were detected at 1713 and 1714 cm^{-1} , respectively. Although no significant peak frequency shift was observed, the width of the T05 carbonyl vibration band may be larger than those of neat polymers and T00. Such a result may be attributed to the fact the carbonyl group, present in T05 blend, is surrounded by more different carbon segments due to the ester-ester interchange reaction. The broadening of the carbonyl band as a result of the blending process is reported in [20,36].

The mechanical properties of PBSA/PCL/TBT blends are shown in Figs. 3 and 4, and Table > 1 displays a summary of the data. The stress-strain representative curves of each blend concentration are available as supplementary data S1. Fig. > 3 shows the average values of Young modulus (E) and yield stress (σ_y). The incorporation of TBT in the blend system decreased the Young modulus initially at 0.1 and 0.3 > wt.% concentration; however, this trend was not observed in TBT higher concentrations, since T05 showed Young modulus statistically similar to all other blends. On the other hand, the presence of TBT in the blend system increased the yield stress, whereas the resistance of T05 blend was 25% higher than that of T00. Some authors ascribed such a mechanical behavior to the competition between chain scission and transesterification reac-

Table 1
Mechanical properties of PBSA/PCL/TBT blends.

Blend	Young's modulus (MPa)	Yield stress (MPa)	Elongation at break (%)	Elongation at yield point (%)
T00	616.93 (± 26.67) ^a	12.82 (± 2.78) ^a	20.89 (± 9.58) ^a	2.45 (± 0.56) ^a
T01	579.11 (± 17.04) ^b	14.10 (± 1.12) ^{a,b}	21.42 (± 5.92) ^a	2.89 (± 0.42) ^{a,b}
T03	580.13 (± 21.94) ^b	14.00 (± 0.52) ^{a,b}	44.52 (± 14.46) ^b	2.83 (± 0.12) ^{a,b}
T05	588.17 (± 7.06) ^{a,b}	16.07 (± 0.62) ^b	47.75 (± 8.10) ^b	3.28 (± 0.16) ^b

Means followed by the same letter in the columns did not differ in Tukey's test at 95% confidence level.

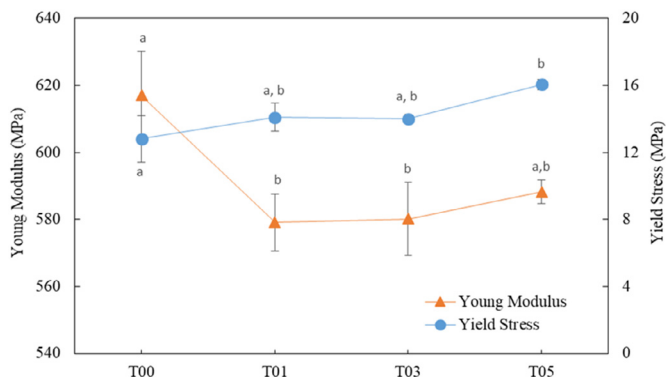


Fig. 3. Young modulus and yield stress curves of PBSA/PCL/TBT blends. Means followed by the same letter in the columns did not differ in Tukey's test at 95% confidence level.

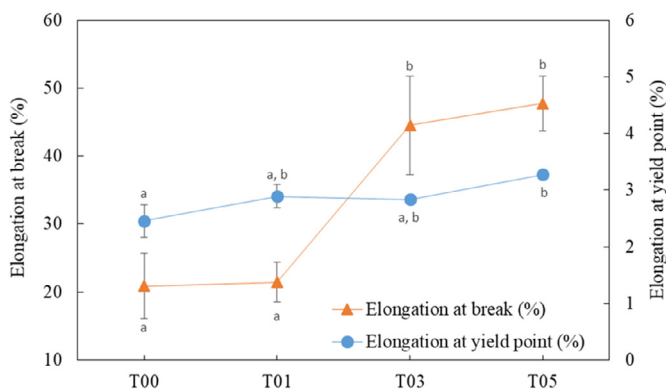


Fig. 4. Elongation at break and yield point curves of PBSA/PCL/TBT blends. Means followed by the same letter in the columns did not differ in Tukey's test at 95% confidence level.

tions, both catalyzed by TBT [14,19]. The former can be translated into plasticization of short chains, lowering the Young modulus, whereas the latter can be transposed into compatibilization of copolymers, which promotes more entanglements between phases. Wang et al. [19] presented a TBT incorporated polyester blend with increased low shear viscosity to a certain point (0.5 > wt.% TBT) accompanied by a Young modulus decrease. Since they used 1 > wt.% of TBT, the chain scission prevailed over compatibilization, thus reducing viscosity and modulus. The MFR behavior corroborated the mechanical properties results and the hypothesis of copolymer generation mechanism prevailing over chain scission.

Fig. 4 displays the average values for elongation at break (ϵ_r) and elongation at yield point (ϵ_y) of PBSA/PCL/TBT. The incorporation of 0.3 > wt.% and 0.5 > wt.% of TBT duplicated the elongation at break of the blends when compared to T00. On the other hand, the elongation at yield (ϵ_y) did not show any significant change. The increase in elongation at break in transesterification-catalyzed blends was reported in several studies [15,35,37], which assigned it to the interlocking effect through chains interpenetration and entanglements. PBSA-co-PCL might have been generated in situ dur-

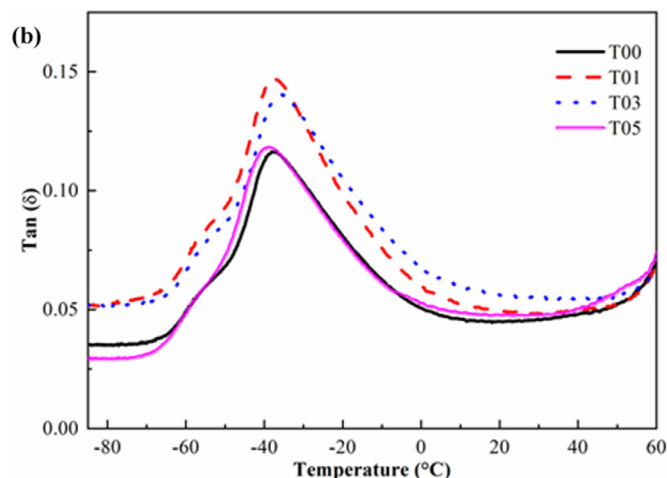
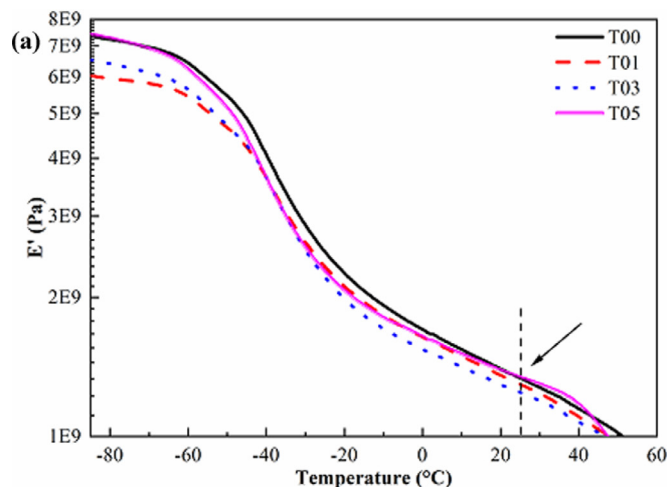


Fig. 5. DMTA results of PBSA/PCL/TBT blends: (a) Storage modulus curves and (b) Tan δ curves.

ing the reactive blending process, lowering the interfacial tension and reducing the size of dispersed domains, thus enhancing the material yielding [33]. Although deeper understanding is necessary, TBT can potentially tune the mechanical properties of the PBSA/PCL blend system.

The DMTA results of storage modulus (E') and $\tan \delta$ are displayed in Figs. 5 (a-b). The E' obtained from the dynamic-mechanical thermal analysis followed the same trend observed for Young Modulus in tensile tests, i.e., T01 and T03 show lower E' than T00. However, the T05 E' is similar to that of T00 at room temperature, as indicated by the arrow in Fig. 5(a). This behavior may be explained by the competition between chain scission and transesterification, whereas T01 and T03 show increased mobility due to the plasticizing effect of shorter polymer chains (lower E'), and the chain mobility of T05 is similar to that of T00 probably due to PBSA-co-PCL generated by transesterification [14].

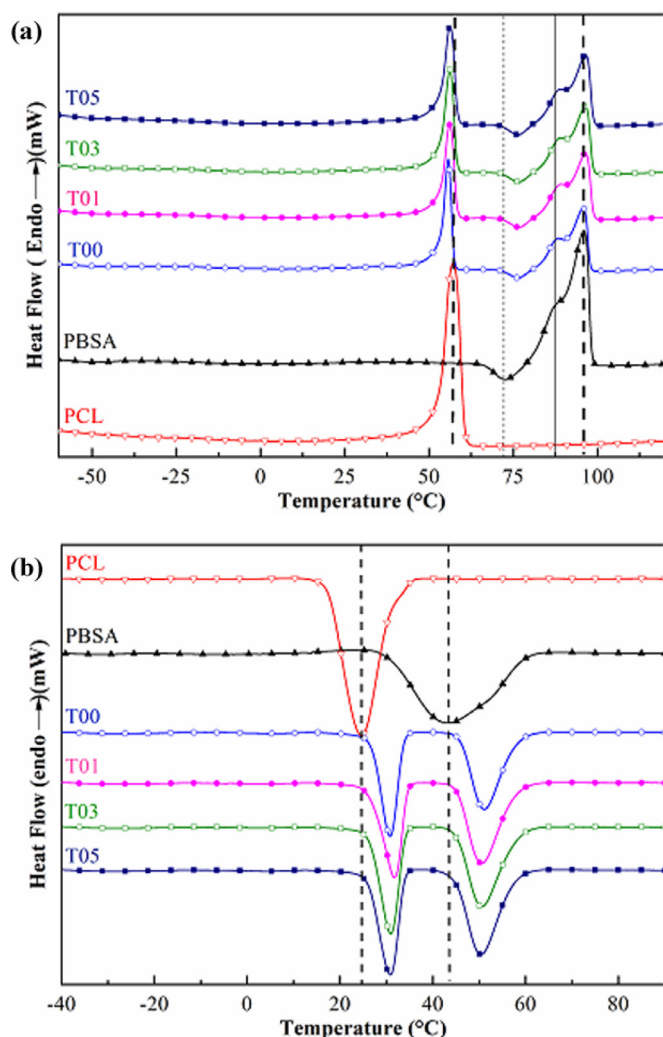


Fig. 6. DSC results of neat polymers and PBSA/PCL/TBT blends: (a) Second heating curves and (b) cooling curves.

According to Fig. 5(b), all PBSA/PCL blends showed 2 glass transition temperatures (T_g). The peak around $-38 > ^\circ\text{C}$ refers to the T_g of PBSA, while the shoulder at $-58 > ^\circ\text{C}$ is associated with the T_g of PCL [28]. The TBT concentration did not vary T_g significantly, which means the reactive process did not induce miscibility to the blends. The literature reports some studies in which reactive compatibilization through TBT was achieved, even without modifications in the polymers T_g [13,14,38].

Since PBSA is a copolymer formed by poly (butylene succinate) (PBS) and poly (butylene adipate) (PBA), the calculation of its crystallinity percentage by Eq. (1) depends on the composition of each homopolymer. DMTA results showed $-38 > ^\circ\text{C}$ T_g for PBSA, as displayed by $\tan \delta$ peak, which corresponds to a copolymer containing 75% of PBS and 25% of PBA, according to the mixture rule, taken into account in the choice of the 100% crystalline PBSA melting enthalpy value proposed as $116.9 > \text{J/g}$ [28,29].

The melting and crystallization behaviors of the blends and pure polymers were evaluated by DSC. Fig. 6 shows the DSC (a) second heating and (b) cooling thermograms of neat polymers and PBSA/PCL/TBT blends. The thermal properties displayed in Fig. 6(a) and degree of crystallinity of the samples are shown in Table 2.

Pure PBSA and PCL showed maximum melting temperatures of $96 > ^\circ\text{C}$ and $57.2 > ^\circ\text{C}$, respectively, are highlighted by the thick

dashed line in Fig. 6(a). PBSA/PCL/TBT blends showed no significant variation at such temperatures (see Table 2). The thin dashed line (Fig. 6(a)) indicates the cold crystallization temperature (T_{cc}) of PBSA, achieved for neat PBSA and blended PBSA. However, for the latter it takes place at slightly higher temperatures than neat PBSA. By comparing the blends to neat polymers, it can be hypothesized that PCL chains blocked the motion of PBSA chains that were able to crystallize, thus requiring more energy for the crystallization to happen [12].

The solid thin line in Fig. 6(a) refers to the duplicated melting behavior of PBSA exhibited by the presence of crystals of different sizes and T_m [34,39]. Such crystals were also observed in the PLOM results, Fig. 7. The double PBSA melting peaks were considered one in Equation 1.

Although the polymers melting enthalpy does not vary significantly, T05 showed the lowest value for both PBSA and PCL (Table 2), which is associated with an exchange reaction between polymer chains, whose rate also depends on the catalyst concentration [40]. The same trend was observed for total crystallinity, as T05 showed the lowest value, which leads to the hypothesis that transesterification prevails over the chain scission process, and the exchange reactions hinder crystallization due to the copolymer generation, which promotes phases' entanglement in T05 [19,41,42].

Table 3 shows a summary of the DSC results displayed in Fig. 6(b). The dashed lines highlight the crystallization temperatures ($24.6 > ^\circ\text{C}$ and $43.1 > ^\circ\text{C}$) of PCL and PBSA, respectively. When blended, both PBSA and PCL had their crystallization temperatures increased, in comparison to neat polymers, probably due to a nucleating effect of titanium alkoxide formed by the reaction of TBT and the carboxylic groups of the polymers [39]. On the other hand, the lowest ΔH_c for T05 corroborates the hypothesis of prevalence of copolymer generation by TBT catalysis, hindering crystallization [42].

The morphological and crystallization behaviors of PBSA/PCL/TBT blends were investigated by PLOM. Due to the low thickness of the PLOM samples, the crystallization temperatures of the polymers were higher than that of the DSC results. PBSA showed crystallization between $80 > ^\circ\text{C}$ and $45 > ^\circ\text{C}$, and PCL started to crystallize at around $50 > ^\circ\text{C}$ and finished at $40 > ^\circ\text{C}$. Fig. 7 displays PLOM micrographs of two steps of neat PBSA crystallization indicating the formation of PBSA spherulites of different sizes. Some small-sized spherulites nucleated at $70 > ^\circ\text{C}$ and grew up to $60 > ^\circ\text{C}$, Fig. 7(a), whereas larger spherulites nucleated and grew at $45 > ^\circ\text{C}$, Fig. 7(b). Such a behavior is probably the cause of the double melting temperature of PBSA.

Fig. 8 shows PLOM micrographs of the crystallization behavior of T00 and T05 blends. PBSA spherulites began to appear at around $75 > ^\circ\text{C}$ for both blends, however, T05 shows crystalline domains sparser than those of T00.

Figs. 9(a) and (b) show SEM micrographs of cryofractured surfaces of injection molding T00 and T05 samples, respectively. The rough regions surrounded by holes represent the PCL domains (highlighted by the white line), whereas smooth ones denote PBSA. Apparently, T00 sample formed a co-continuous morphology and T05 showed a transition from co-continuous to matrix-particle pattern, with PBSA as the matrix. T01 and T03 blends formed an intermediary morphology between those showed by T00 and T05 samples. The co-continuous pattern originates from the phase inversion process; since PCL has lower T_m , it melts first forming the matrix, and when PBSA begins to melt, its phase overcomes the PCL domains [43,44].

Although the morphology of T05 shows a large size distribution of PCL drops, it seems the increasing TBT concentration accelerated the formation of those domains, and the copolymers may have been generated at the interfaces [45].

Table 2

DSC thermal properties. Cold crystallization temperature (T_{cc}), melting temperature (T_m), melting enthalpy (ΔH_m), cold crystallization enthalpy (ΔH_{cc}), and degree of crystallinity (X_c).

Sample	T_{cc} PBSA ($^{\circ}\text{C}$)	T_m PBSA ($^{\circ}\text{C}$)	T_m PCL ($^{\circ}\text{C}$)	ΔH_m PBSA (J/g)	ΔH_{cc} PBSA (J/g)	ΔH_m PCL (J/g)	X_c PBSA (%)	X_c PCL (%)	Total X_c (%)
PBSA	71.0	96.0	–	60.7	4.2	–	48.3	–	48.3
PCL	–	–	57.2	–	–	50.6	–	37.2	37.2
T00	76.1	95.8	55.7	28.4	3.2	20.8	35.9	38.3	36.9
T01	76.5	96.5	56.1	28.7	3.2	19.9	36.3	36.5	36.4
T03	76.6	96.3	56.2	31.2	3.7	21.0	39.1	38.6	38.9
T05	76.3	96.5	56.2	27.2	4.3	19.5	32.7	35.8	33.9

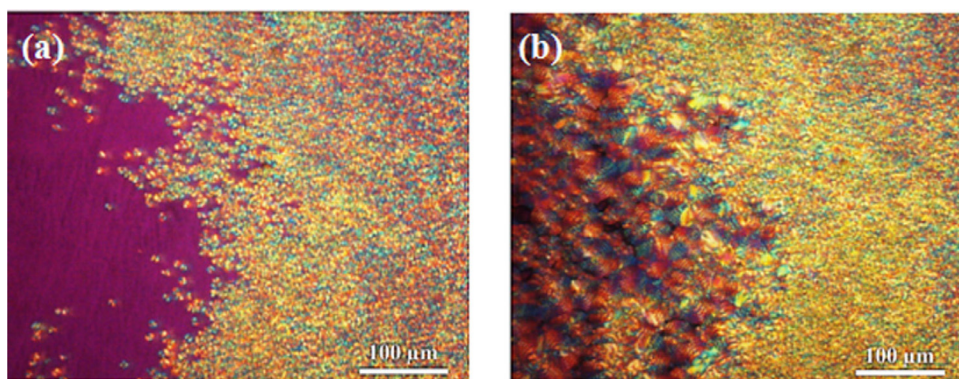


Fig. 7. PLOM micrographs representing two steps of PBSA crystallization behavior: (a) at $60 > ^{\circ}\text{C}$ and (b) at $45 > ^{\circ}\text{C}$.

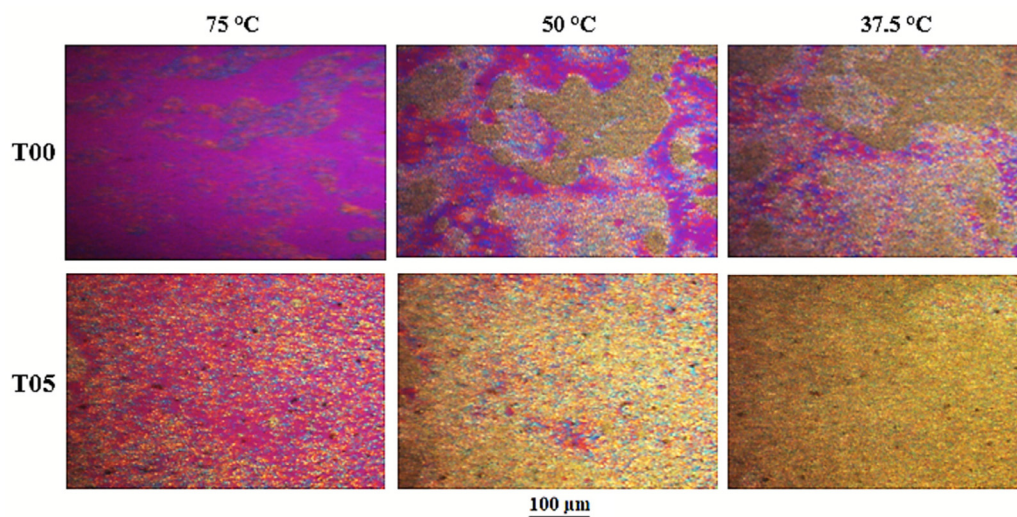


Fig. 8. PLOM micrographs of the crystallization behavior of T00 and T05 blends at $75 > ^{\circ}\text{C}$, $50 > ^{\circ}\text{C}$ and $37.5 > ^{\circ}\text{C}$.

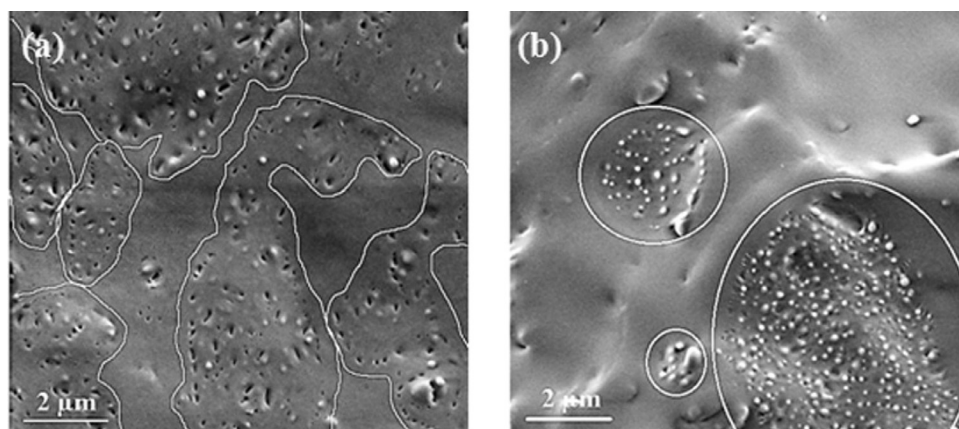


Fig. 9. SEM micrographs of (a) T00 and (b) T05 blends. White lines denote PCL domains.

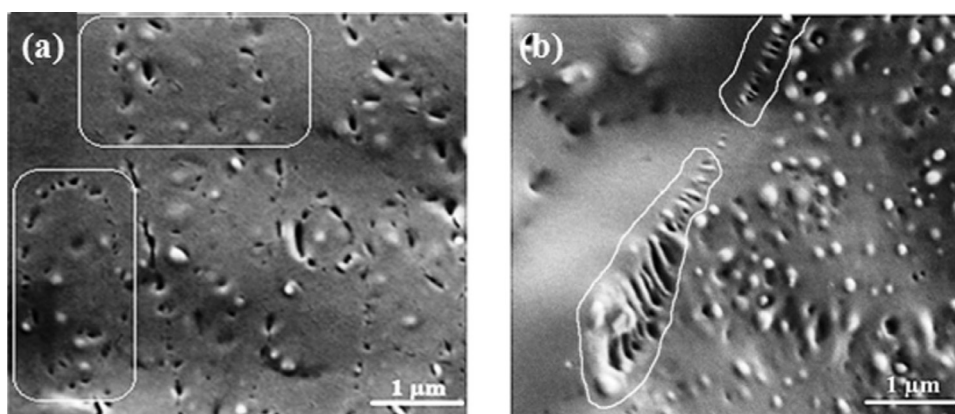


Fig. 10. SEM micrographs representing the interface between PBSA and PCL domains of (a) T00 and (b) T05 samples. Rounded rectangles highlight PCL domains, whereas circles denote a micro-fibril-like structure.

Table 3

DSC thermal properties. Crystallization temperature (T_c) and crystallization enthalpy (ΔH_c).

Sample	T_c PBSA (°C)	T_c PCL (°C)	ΔH_c PBSA (J/g)	ΔH_c PCL (J/g)
PBSA	43.1	–	51.4	–
PCL	–	24.6	–	58.0
T00	51.1	30.8	28.3	22.0
T01	50.6	31.8	28.8	20.9
T03	50.6	30.4	30.9	23.1
T05	50.4	30.9	27.8	20.5

Figs. > 10(a) and 10 (b) show the interfaces between PBSA and PCL domains of T00 and T05 blends, respectively. The PCL domain of T00 is surrounded by holes, as highlighted by the rounded rectangles, (Fig. > 10(a)), while T05 displays a micro-fibril-like structure linking the immiscible polymer domains, as outlined by circles (Fig. > 10(b)). The same type of structure was obtained for the PLA/PPC system blended in the presence of TBT [19], and PLA/PBAT blended in the presence of triphenyl phosphite [12]. In both studies, the authors attributed those structures to the formation of in situ copolymers by transesterification reactions, which increased the entanglement of the domains, thus generating a more cohesive morphology. Such a behavior may explain the improved performance of the mechanical properties of T03, and especially T05.

The analysis of microbial susceptibility in soil aimed to verify if the addition of TBT would not compromise the responsiveness of the blended polyesters to biodegradation. To the best of our knowledge, the biodegradation capacity of polyester blends incorporated with TBT has not been evaluated. The weight loss of the blend systems has been calculated towards confirming the microbial susceptibility. Fig. > 11 shows the average weight loss (WL%) for each blend in each burial period, calculated by Equation > 2.

The results of the 90-day burial period were discarded due to an excessive experimental deviation. After a proper cleaning and drying process, the samples showed a moderate to heavy biofilm coverage on their surfaces and a small weight loss. A previous study of PBSA/PCL blend films fabricated by solvent casting pointed to an average weight loss of 30% to 40% for a 90-day burial in soil [28]. However, in the present study, no significant weight loss was observed for the injection molding samples until the end of the experiment, i.e., 150 days; the results show a 2% to 3% weight loss (Fig. > 11) due to the less specific area of the injection molded samples, since the biodegradation process starts at the material's surface [46]. In 120 and 150 burial days' periods, T05 showed a slightly higher, but not significantly expressive, weight loss, probably caused by its lower total degree of crystallinity in compari-

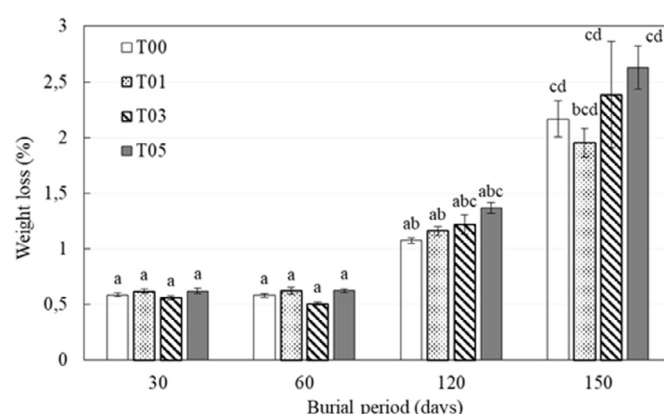


Fig. 11. Percentage of weight loss of PBSA/PCL/TBT blends as a function of burial time. Means followed by the same letter in the columns did not differ in Tukey's test at 95% confidence level.

son to the other samples, since degradation occurs preferentially in amorphous domains [47,48]. Although longer tests on biodegradation and assessments of CO_2 release are required, it seems TBT not only enables microbial susceptibility, but also exerts an indirect effect on the sample's weight loss by tuning the crystallinity of the blend.

4. Conclusions

The presence of transesterification catalyst TBT in the blending of PBSA and PCL polymers promoted some degree of compatibilization, since a finer morphology (PLOM and SEM results) and better mechanical properties (tensile tests and DMTA results) were exhibited mainly by a higher TBT concentration in the blends. Broad carbonyl peaks observed in FTIR results indicated the occurrence of transesterification between PBSA and PCL phases, and the MFR results showed higher viscosity for blends with increased TBT concentration. The thermal properties of PBSA/PCL/TBT blends did not suffer significant changes; however, the crystallization behavior from the presence of TBT showed the catalyst may act as a crystallization modifier in PBSA/PCL blends. The mechanical properties and microbial susceptibility of the blends can be adjusted by the tuning of the TBT concentration, without affecting other properties negatively. This study has demonstrated $\text{Ti}(\text{OBu}_4)$ – TBT – can act as a simple-use chemical for modifying and compatibilizing polyester blends' properties.

5. Credit author statements

Marcos V. B. Nicolino: Methodology, Investigation, Validation, Writing - original draft preparation. Alessandra A. Lucas: Resources, Writing - review & editing. Marcia C. Branciforti: Funding acquisition, Conceptualization, Supervision, Resources, Writing review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.polyimdegstab.2020.109320](https://doi.org/10.1016/j.polyimdegstab.2020.109320).

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