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Biodegradable poly(3-hydroxybutyrate-co-3-hydroxyvalerate) /
thermoplastic polyurethane blends with improved mechanical and
barrier performance

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Abstract

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) polymers pose a green alternative to fossil-fuel derived polymers, as they exhibit good biocompatibility, biodegradability and outstanding barrier performance compared to other biopolyesters. However, their excessive brittleness has not yet been overcome without compromising barrier performance. In this work, a native ester-based thermoplastic polyurethane (TPU) not stabilised against hydrolysis, has been thoroughly assessed for the first time as an additive in melt blends with PHBV. Phase segregation in scanning electron microscopy (SEM) confirmed the immiscibility of the two polymers, however a degree of interaction has been found. Wide-angle X-ray scattering and differential scanning calorimetry revealed no major effect of the TPU on the crystallinity of the PHBV phase. The onset and kinetics of thermal degradation was not altered by the presence of the TPU up to 50 wt% content. Blends with increasing TPU contents showed a gradual decrease in the modulus of elasticity and tensile strength, while a substantial increase in elongation at break has been found for contents of TPU above 20 wt%, which resulted in an improvement in the overall toughness of the blends. The excellent barrier performance of the PHBV against water vapour and aroma compounds was shown to be unaffected by TPU loads of ≤ 30 wt%. Full decomposition of neat PHBV and PHBV/TPU blends below 50 wt% TPU content was achieved after 40 days according to biodisintegration standards (ISO 20200). The study puts forward the potential use of TPU to improve the mechanical performance of these natural biopolyesters without compromising the barrier properties or the biodisintegrability of the melt blends.

Keywords

PHBV, TPU, biodisintegration, melt blending, biodegradable polymers

1. Introduction

Polyhydroxyalkanoates (PHAs) are a family of naturally occurring storage biopolyesters synthesised by more than 300 species of Gram-positive and Gram-negative bacteria. [1] Among the various biodegradable polymers, PHAs provide a good alternative to fossil-fuel based plastics as they possess thermoplastic properties similar to conventional polyolefins, with the advantage of being 100% biodegradable, compostable and produced from renewable resources. [2-5] Another key advantage of PHAs is their excellent barrier properties, which are similar to those of polyethylene terephthalate (PET), [6] and are much better than other biopolyesters such as poly(lactic acid). [7] In the areas of food and cosmetic packaging, PHAs are already commercialised as cosmetic containers, shampoo bottles, covers, milk cartons, films, moisture barriers in nappies and sanitary towels, pens and combs, among others (reviewed by [8]).

Nevertheless, PHAs have a very narrow processing window, are excessively brittle, and currently constitute a more expensive alternative to other commonly used materials in the packaging sector. These application limitations have been confronted by using different approaches, including the addition of plasticisers, enhancing the synthesis of poly(3-hydroxybutyrate-co-3-hydroxyvalerate; PHBV) heteropolymers, or blending with other polymers. Although increasing valerate contents in PHBV results in higher flexibility, higher strength and a lower melting temperature, [9] high contents of hydroxyvalerate (HV) lead to a decrease in the barrier properties. [10] Moreover, the improvement in elongation at break with HV wanes with storage time. [11] Therefore, low HV-content grades might still be more suitable for packaging applications. A recent work reported the effect of different plasticisers on the mechanical and barrier properties of PHBV. [12] Researchers found that, although the barrier properties could be maintained with the addition of some plasticisers, the elongation at break of PHBV could not be substantially modified. The authors thus concluded that it is questionable whether plasticised PHBV may be used in larger scale packaging applications in the near future. [12] The approach of blending it with other polymers by melt compounding is a very convenient method since it uses conventional polymer processing equipment widely used in the packaging industry. This strategy has also been assessed for the PHBV copolymers. [13-15] Biodegradable polyesters [13] such as polylactides, polycaprolactone, polybutylene succinate (PBS) [16] and butylene (adipate-co-terephthalate) (PBAT) [17] have been studied in this sense. However, the barrier properties of the blends were found to be considerably lower than that of the pure PHBV. [18]

A conventional approach for increasing elongation at break in brittle polymers is the addition of an elastomeric second phase. This is commonly known as rubber toughening of polymers and has been successfully carried out for many years, leading to many engineering materials such as high impact polystyrene (HIPS), acrylonitrile-butadiene-styrene (ABS) or styrene-butadiene-styrene copolymers (SBS). Recently, interest in this approach to increase the toughness of biopolyesters has grown, as brittleness is one of the main drawbacks in their application in the packaging field. In this regard, intense work in toughening polylactic acid (PLA) has been

conducted in recent years. [19-23] Toughening PHBV with elastomers such as ethylene vinyl acetate, [24] epoxidized natural rubber [25] and poly(butadiene-co-acrylonitrile) [26] has also been investigated. In most cases, the addition of the elastomeric phase showed either no great improvement [26] or loss of the desired biodegradability. [24, 26] In line with blending with an elastomeric material, the use of a biodegradable thermoplastic polyurethane is proposed in the present work. Thermoplastic polyurethanes (TPUs) are a widely used class of polymers with excellent mechanical properties and good biocompatibility, which have already been successfully evaluated in a number of biomedical applications. [27] Although conventional TPUs are typically not intended to degrade quickly, they are susceptible to hydrolytic, oxidative and enzymatic degradation, which could be deliberately exploited to design biodegradable systems. [28] In fact, good biodegradability of TPUs has been reported under composting conditions, [29] especially when the TPU comes from an ester diol. [30] In this sense, the use of TPU for the development of biodegradable blends has been already explored with other biopolyesters such as PLA. [31-33] Moreover, the use of TPU to increase the elongation at break of PHBV has already been explored by solvent casting. [34] In this work, Wang et al. obtained blends of PHBV/TPU with an increased elongation at break of up to 6% for TPU contents of 40%. The addition of the TPU by solvent cast resulted in a decrease in the crystallinity of PHBV by close to 20%, which may lead to a drop in the gas barrier performance.

In the present work, the use of a native ester-based TPU (not stabilised against hydrolysis) has been assessed for the first time in melt blends with PHBV as an additive for decreasing the brittleness of these natural biopolyesters without compromising the barrier properties or the biodegradability of the PHBV. A thorough study on the effect of the interaction of the two polymers in the blends behaviour has been carried out, as well as an assessment of the final biodegradability of the system by measuring the biodegradation of the blends under standard conditions.

2. Experimental

2.1. Materials

Commercial grade PHBV with 3 wt% valerate content was purchased from Tianan Biopolymer (Ningbo, China) in pellet form (ENMAT Y1000P). The native thermoplastic polyurethane Elastollan[®] 880AN was kindly supplied by BASF (Germany).

2.2. Blend processing

Prior to the blending step, both the PHBV and TPU pellets were vacuum dried at 80°C for 3 hours. The PHBV blends were obtained by mixing different amounts of pellets of both polymers in a Brabender Plastograph mixer (Brabender, Germany) for 8 min at 100 rpm and at 175°C. To avoid severe thermal degradation during blending, the melt temperature was not allowed to reach 185°C. The batches were subsequently compression moulded into films using a hot-plate hydraulic press (Carver 4122, USA) at 177°C, 2 MPa and 4 min to produce films with

a thickness of 200 μm . All the samples were stored in a vacuum desiccator at ambient temperature for 2 weeks to allow full crystallisation to take place. [35] Blends containing 5 wt% (95/5), 10 wt% (90/10), 20 wt% (80/20), 30 wt% (70/30), 40 wt% (60/40) and 50 wt% (50/50) of TPU were obtained. For the sake of comparison, the pure PHBV (100/0) and TPU (0/100) were also processed under identical conditions and used as reference materials.

2.3. Morphology

Scanning Electron Microscopy (SEM) of all the samples was conducted using a high-resolution field-emission JEOL 7001F microscope. The samples were fractured in liquid nitrogen and then were coated by sputtering with a thin layer of Pt prior to SEM observation. The size of the dispersed phase (i.e. diameter of the spheres) was measured in the SEM microphotographs by using ImageJ software (the number of spheres measured for each sample was never below 200).

Wide-angle X-ray diffraction (WAXS) measurements were performed using a Bruker AXS D4 ENDEAVOR diffractometer. The samples were scanned at room temperature in reflection mode using incident Cu K-alpha radiation ($k = 1.54 \text{ \AA}$), while the generator was set at 40 kV and 40 mA.

2.4. Thermal properties

The thermal stability of the blends was investigated by means of thermogravimetric analysis (TGA) using a TG-STDA Mettler Toledo model TGA/SDTA851e/LF/1600. The samples were heated from 50°C to 900°C at a heating rate of 10°C /min under nitrogen flow. The characteristic temperatures $T_{5\%}$ and T_{max} corresponded, respectively, to the initial decomposition temperature (5% of weight loss) and to the maximum degradation rate temperature measured at the derivative thermogravimetric (DTG) peak maximum.

Differential scanning calorimeter (DSC) experiments were conducted using a DSC2 (Mettler Toledo) with an intracooler (Julabo model FT900). The weight of the DSC samples was typically 6 mg. Samples were first heated from -20°C to 200°C at 10°C/min, kept for 1 min at 200°C, cooled down to -20°C at 10°C/min, and then finally reheated to 200°C at 10°C/min. The crystallisation temperature (T_c), melt temperature (T_m), melting enthalpy (ΔH_m) and crystallisation enthalpy (ΔH_c) were determined from the cooling and second heating curve. The crystallinity (X_c) of the PHBV phase was calculated by the following Equation (1), where (ΔH_m) (J/g) is the melting enthalpy of the polymer matrix, (ΔH_m^0) is the melting enthalpy of 100% crystalline PHBV (perfect crystal) (146 J/g), and w is the weight fraction of PHBV in the blend. [36]

$$X_c (\%) = \frac{\Delta H_m}{w \cdot \Delta H_m^0} \times 100 \quad (1)$$

The DSC instrument was calibrated with an indium standard before use.

2.5. Mechanical properties

Tensile tests were conducted in a universal testing machine (Instron 4469) at a crosshead speed of 10 mm/min and at room temperature. Tests were conducted according to ISO 527:2012 using films prepared by hot press moulding and subsequently conditioned as previously detailed. A minimum of five specimens of each sample were tested and the average results with standard deviation were reported.

2.6. Permeability measurements

The water vapour permeability (WVP) of the PHBV/TPU blends was measured according to the ASTM E96 (2011) gravimetric method, using Payne permeability cups (Elcometer, Hermelle Argenteau, Belgium). Distilled water was placed inside the cup to expose the film (the exposed area was $9.6 \times 10^{-4} \text{ m}^2$) to 100% relative humidity on one side. Once the films were secured, each cup was placed in an equilibrated relative humidity desiccator at 24°C. Relative humidity at 0% was held constant using silica gel. The cups were weighed periodically ($\pm 0.0001 \text{ g}$), at least twice a day for 7 days. Aluminium foil was used as a control to rule out vapour loss through the seal. WVP was calculated from the steady-state permeation slopes obtained from the regression analysis of weight loss data over time. The permeability to D-limonene (Panreac, Barcelona, Spain) was measured analogously, filling the cups with the volatile compound instead of distilled water. The lower limit of vapour permeability detection of the permeation cells was $\sim 1.10^{-17}$ and $5.10^{-17} \text{ kg}\cdot\text{m}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$ for water vapour and D-limonene, respectively, based on the weight loss through the seal in the aluminium samples. All measurements were performed in triplicate. The diffusivity coefficients of both permeants in the studied blends was calculated according to Equation (2), where P is the permeability, D the diffusivity and S , the solubility of the permeants as evaluated from the steady-state vapour sorption mass increase in the studied conditions.

$$P = DS \quad (2)$$

2.7. Biodisintegration in composting conditions

Disintegrability of neat PHBV and PHBV/TPU films, as well as neat TPU, was assessed by means of a disintegration test under lab-scale composting conditions according to the ISO 20200 standard, "Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test". [37] For the preparation of solid synthetic waste, 10% of activated mature compost (VIGORHUMUS H-00, purchased from Burás Profesional, S.A., Girona, Spain) was mixed with 30% rabbit food, 10% starch, 5% sugar, 1% urea, 4% corn oil and 40% sawdust. The water content of the substrate was around 55 wt% and the aerobic conditions were guaranteed by gently mixing the compost and periodically adding water according to the standard requirements. The samples were cut from hot pressed plates ($10 \times 10 \times 0.2 \text{ mm}^3$) and buried inside iron mesh bags to simplify their extraction and

allow the contact of the compost with the specimens, and were incubated at 58°C for 41 days. At different composting times samples were recovered for analysis, washed with distilled water, dried at 40°C under vacuum for 24 h, and weighed. The degree of disintegration was calculated by normalising the sample weight, at different days of incubation, to the initial weight with Equation (3), where m_i is the initial dry mass of the test material and m_f is the dry mass of the test material recovered at different incubation stages.

$$D = \frac{m_i - m_f}{m_i} \times 100 \quad (3)$$

Photographs of samples were taken for visual evaluation.

3. Results and discussion

3.1. Morphological characterisation

Figure 1a-f presents the cryofractured surfaces of the PHBV/TPU blends with different TPU contents. A first observation shows that, in all cases, the morphology of the blends revealed the presence of a two-phase morphology, thus revealing an immiscible polymeric system. Hence, the TPU microstructure shows the TPU dispersed within a PHBV continuous matrix, thus revealing a characteristic discrete-phase structure (DPS, or drop-in matrix). [38] For all the studied compositions, the TPU is found to be homogeneously dispersed throughout the PHBV matrix, forming spheres which increase in size with a greater TPU content. Figure 1g shows the size distribution of the dispersed phase as a function of the TPU content, while Figure 1h plots the D10, D50 and D90 values determined as the size below which 10%, 50% and 90% of the spheres respectively are comprised, respectively. In samples with TPU contents ≤ 10 wt%, the segregated TPU phase is observed to be confined in spheres of close to 1 μm on average (0.9 μm and 1 μm for 5 wt% and 10 wt% respectively). When the amount of TPU is increased, the size of the dispersed phase is also gradually increased. Mean values of droplet size for 80/20, 70/30, 60/40 samples are 2.4 μm , 3.6 μm and 3 μm in diameter, respectively. However, the d10 value seems unaffected, indicating the abundance of small particles is not altered. On the other hand, the number of spheres with a size ≥ 2 μm increases with TPU content. This behaviour could be explained by a droplet-droplet coalescence mechanism. Finally, for 50/50 samples, larger domains of both PHBV and TPU can be observed. These domains reveal a co-continuous morphology, i.e. the TPU content is above the percolation threshold. Moreover, a phase reversion effect can be seen in Figure 1f, as TPU and PHBV spheres are forming part of the dispersed phase.

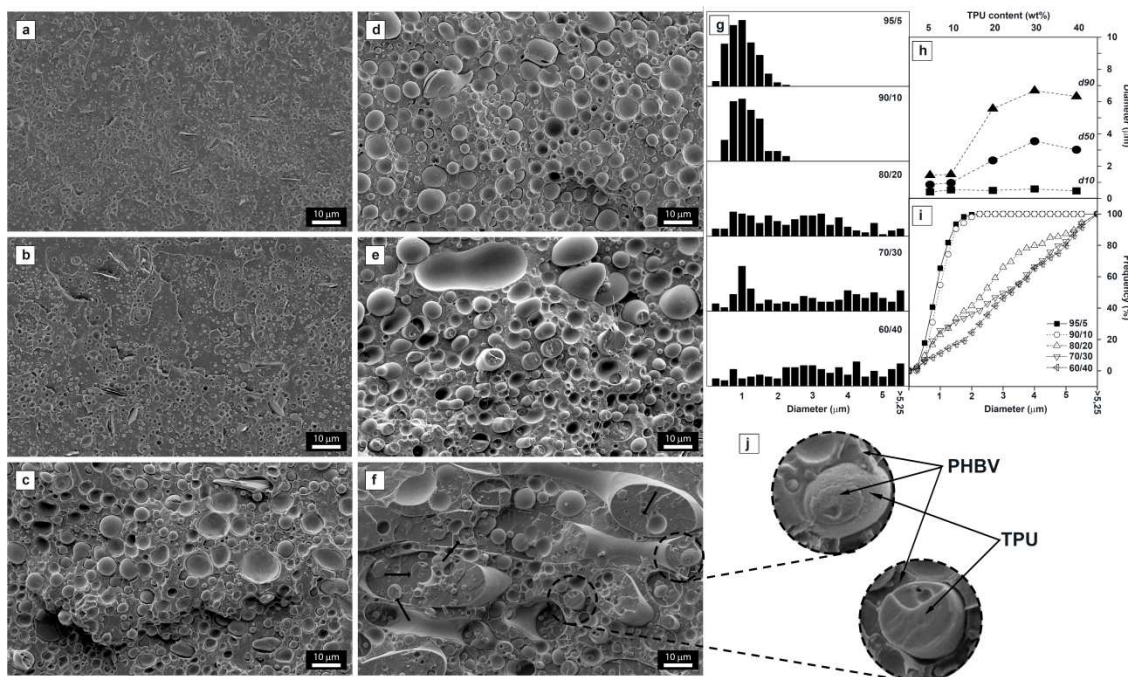


Figure 1. Morphology of PHBV/TPU blends. Figure 1a-1f: Scanning electron images of 95/5 (a), 90/10 (b), 80/20 (c), 70/30 (d), 60/40 (e) and 50/50 (f). Particle size distribution for the PHBV/TPU blends (g). D10, D50 and D90 values of the PHBV/TPU blends (h). Accumulated frequency of particle sizes in the ester-blends (i). Detail of PHBV/TPU blend interfaces (j).

As far as phase interaction is concerned, from a theoretical point of view and according to the literature, [31, 32, 34] some degree of interaction should be expected between the PHBV and the TPU since both are polyesters. Moreover, as discussed in the following sections, the mechanical behaviour of the blends implies that a certain degree of adherence should exist on the interface between the two polymers. Additionally, the gas barrier performance results (see section 3.4) clearly reveal a continuous interface. For all these reasons, an immiscible system with good interfacial interaction should be expected. However, direct observation of the morphology by SEM, does not seem to corroborate this, as clear detachment of the spheres from the continuous matrix can be detected throughout the whole range of studied materials. This debonding of the TPU particles could be explained by the SEM sample preparation procedure rather than by an actual lack of adhesion on the interface between the two polymers. Quenching in liquid nitrogen can provoke high thermal stresses in heterogeneous systems when there is a difference in the coefficient of linear thermal expansion (CLTE) of the involved materials. In this case, the PHBV is a highly crystalline polymer with a relatively low CLTE, while TPU is an elastomer with a high CLTE. [39] Hence, during fast cooling, the TPU spheres would shrink in such a way that the interface adhesion would be exceeded and consequently, a pull-out effect is observed throughout the fracture. On the other hand, in a phase reversion situation in which the TPU is surrounding the PHBV, the relative shrinkage of the TPU will lead to a compressive strength over the PHBV spheres therefore, the adhesion at the interface will not be

significantly affected by the fracture. This is illustrated in Figure 1j (upper image), where the detail of a PHBV sphere in a TPU region can be seen interacting at the interface and the debonding of a TPU particle surrounded by PHBV is observed in the lower image. The black arrows indicate PHBV spheres in TPU regions where the fracture has taken place in a cohesive mode, probably due to adhesion at the interface (Figure 1f).

WAXS experiments were conducted on both the neat polymers as well as on all the studied PHBV/TPU blends. The diffractograms are shown in Figure 2. Three characteristic peaks of PHBV were detected in the pure PHBV diffractogram: $13.4^{\circ} 2\theta$, $16.9^{\circ} 2\theta$ and $21.5^{\circ} 2\theta$. According to the literature, these peaks correspond to the (0 2 0), (1 1 0) and (1 0 1) lattice planes of the orthorhombic unit cell of PHB lattices. [36, 39] The PHB crystal lattice is characteristic for the PHBV with HV contents below 37%. [40] The most intense peak at $2\theta = 26^{\circ}$ corresponds to the (0 0 2) reflection of boron nitride, which is present as a nucleating agent in the commercial grade PHBV used in this work. There were no changes in position or in relative intensities of the PHBV diffraction peaks throughout the whole range of PHBV/TPU blends. This suggests that the crystalline structure of PHBV does not change with the addition of the elastomer. The pure TPU pattern does not show any peaks, but a single amorphous hump. Therefore, the decrease in the absolute intensity of the peaks with increasing TPU content can mostly be explained by a dilution effect.

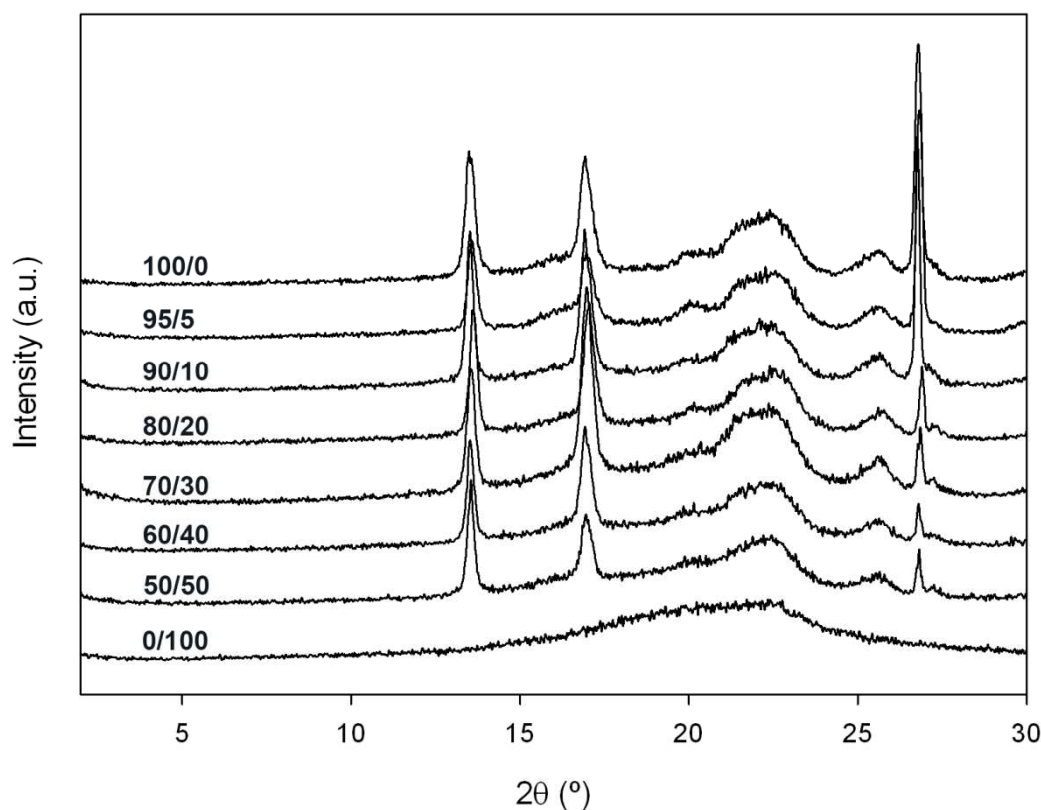


Figure 2. WAXS patterns of neat PHBV, TPU and PHBV/TPU blends.

3.2. Thermal characterisation

Differential Scanning Calorimetry

Second phase additives can often affect the crystallinity of binary polymer blends with semicrystalline polymers such as PHBV. Table 1 gathers the crystallisation (ΔH_c) and melting enthalpies (ΔH_m) and crystallisation and (T_c) melting temperatures (T_m) of PHBV and PHBV/TPU blends as a function of the blend composition. The corresponding thermograms are presented in Figure S1 in the Supplementary Materials. The appearance of two melting peaks in the thermograms is the result of melt-recrystallisation mechanisms that are typical for this type of biopolymer and has been reported in previous works dealing with PHBV blends. [36, 41] A gradual decrease in both crystallisation and melting temperatures can be observed as the TPU concentration is increased (see Table 1). The slight decrease in the melting temperature accounts for $\leq 2^\circ\text{C}$ for TPU contents up to 30 wt%. This points towards a crystallite population of slightly decreasing size or decreased lamellar thickness. The crystalline fraction, as calculated from the melting enthalpies of the blends, is also shown to decrease with increasing TPU content, indicating that the presence of TPU might interfere with the crystallisation process to some extent.

Table 1. Thermal properties of the PHBV/TPU blends.

PHBV/TPU (%)	TGA			DSC				
	$T_{5\%}$ ($^\circ\text{C}$)	T_{\max} ($^\circ\text{C}$)	Res (wt.%)	T_c ($^\circ\text{C}$)	ΔH_c (J/g)	T_m ($^\circ\text{C}$)	ΔH_m (J/g)	X_c (%) [*]
100/0	277 \pm 0	296 \pm 0	1.1 \pm 0.0	118 \pm 0	89.1 \pm 0.9	171 \pm 1	98.1 \pm 0.9	67.2 \pm 0.6
95/5	280 \pm 2	296 \pm 3	1.1 \pm 0.0	111 \pm 0	79.1 \pm 0.8	170 \pm 0	90.3 \pm 1.5	65.1 \pm 1.1
90/10	281 \pm 2	296 \pm 3	1.3 \pm 0.1	110 \pm 0	71.5 \pm 2.4	170 \pm 0	83.6 \pm 1.9	63.7 \pm 1.5
80/20	279 \pm 1	296 \pm 1	1.6 \pm 0.2	106 \pm 0	62.3 \pm 0.5	169 \pm 1	73.9 \pm 2.2	63.3 \pm 1.9
70/30	282 \pm 2	296 \pm 2	2.0 \pm 0.1	103 \pm 0	53.7 \pm 1.4	169 \pm 0	65.8 \pm 0.7	64.3 \pm 0.7
60/40	281 \pm 2	296 \pm 0	2.4 \pm 0.0	99 \pm 1	41.8 \pm 0.4	168 \pm 0	55.2 \pm 0.6	63.0 \pm 0.7
50/50	281 \pm 3	296 \pm 2	2.9 \pm 0.1	97 \pm 0	31.5 \pm 0.6	167 \pm 0	44.5 \pm 0.9	61.0 \pm 1.2
0/100	324 \pm 1	407 \pm 1	4.7 \pm 0.3	-	-	-	-	-

^{*}For the calculation of crystallinity (X_c), only the PHBV fraction was considered.

Thermogravimetric analysis

The thermal degradation behaviours of neat PHBV and TPU, as well their blends were examined using TGA under N_2 flow. The original thermogravimetric curves are shown in Figure 3, while their respective first derivative curves are presented in the inset. Experimental replicates are also shown on the graph to demonstrate the excellent reproducibility of the results. Data, including the onset of degradation ($T_{5\%}$), temperature for the maximum weight loss rate (T_{\max}), and residual charge (Res), are shown in Table 1. It is well reported that PHB and its copolymers easily undergo thermal degradation involving random chain scission in a

one-step process with an onset between 270°C and 300°C. [42, 43] Degradation of the TPU proceeds at a later stage in a two-step process, in which it has been suggested that urethane linkages and unstable side chains degrade at temperatures of 300°C–400°C, followed by chain scission at the β -position to the carbon–carbon double bond occurring at around 450°C. [44, 45] The residual charges in the tested specimens can be ascribed to the presence of boron nitride as a nucleating agent in the commercial grade PHBV and to the char formation of methylene diphenyl diisocyanate. [46] The onset of thermal degradation in all the PHBV/TPU blends was comparable to that of the neat PHBV (Table 1). Moreover, the temperature for the maximum rate of degradation in all the blends was the same as for neat PHBV. This indicates degradation in the blends is governed by the presence of the more labile PHBV and that TPU does not have an impact on this parameter. It is also remarkable that the degradation rate of the blends was reproducible and decreased linearly with an increasing TPU content, while the two-stage degradation of the TPU analogously increased together with the final residual charge. These results suggest neither component has any impact on the other's degradation kinetics, so that thermal degradation of the blends might be predicted a result of their separate combination.

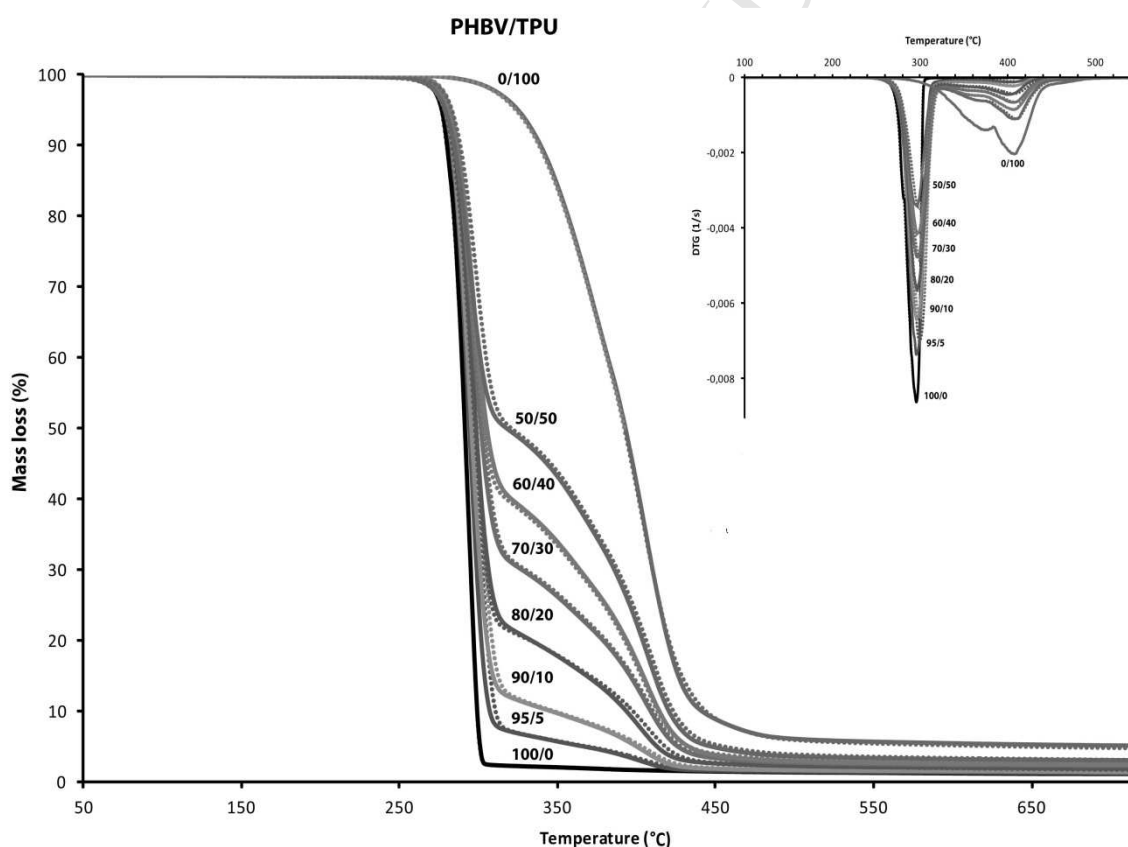


Figure 3. Weight loss versus temperature of the tested materials as analysed by TGA. Inset displays the DTG curves for the same samples.

3.3. Mechanical properties

In order to evaluate the effect of the addition of the TPU to the mechanical performance of the PHBV, tensile tests up to failure were conducted on the pure PHBV and TPU, as well as all the blends. The interaction of the two polymers has been analysed by using different mechanical models, assuming different degrees of adhesion on the interface to study how the mechanical properties of the blends vary with the addition of the second elastomeric phase.

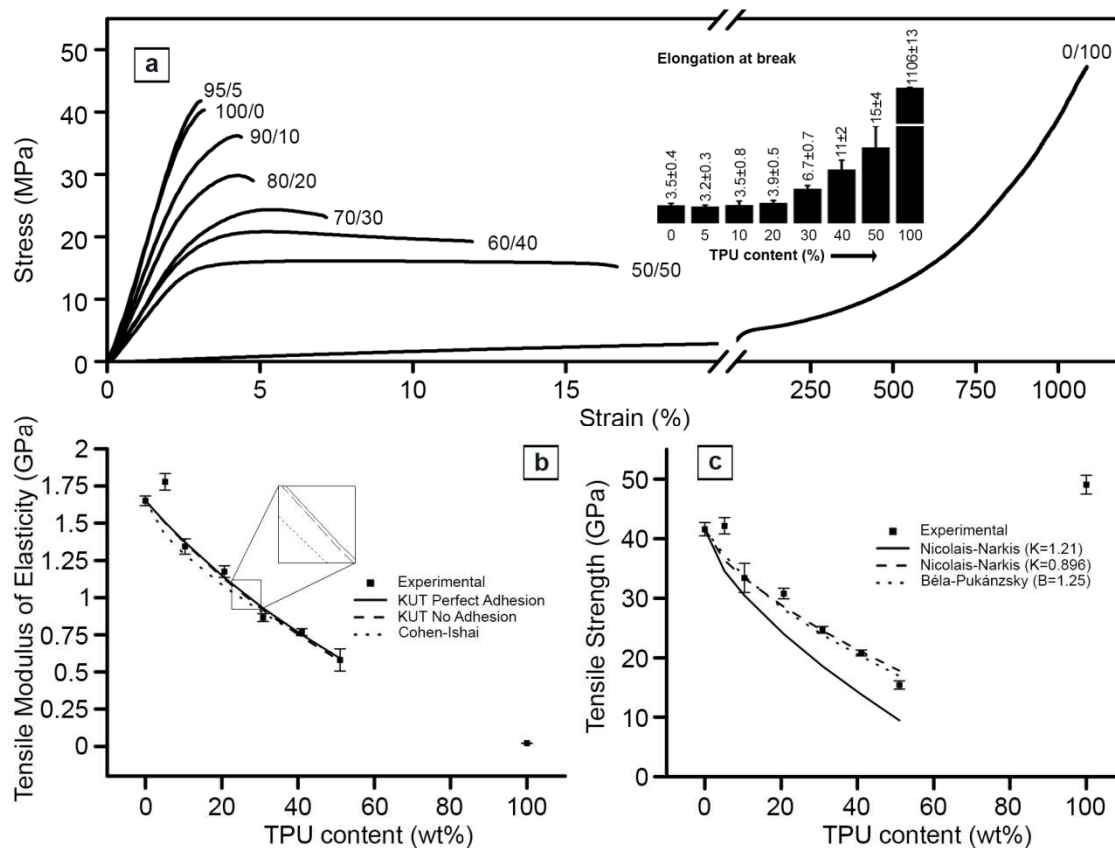


Figure 4. Tensile stress curves of the PHBV/TPU blends. Inset displays the tendency in elongation at break of blends with increasing TPU content (a). Variation of the tensile modulus of elasticity (b) and tensile strength (c) with the incorporation of TPU and fitting to the respective predictive models.

Figure 4a shows the strain-stress curves of the pure PHBV and TPU, as well as of all the studied blends. As expected, the addition of the TPU to the PHBV resulted in a decrease in the rigidity and resistance of the blend, but an increase in the elongation at break and tensile toughness. Thus, the tensile modulus of elasticity decreased from ca. 1.7 GPa for the pristine PHBV to below 1 GPa for the high TPU content blends, the decrease being dependent on the TPU content. The variation on the elastic modulus with the addition of the elastomer was compared with the theoretical values derived from two different models: Kerner–Uemura–Takayanagi (KUT) and Cohen–Ishai. Figure 4b shows the experimental values of the modulus of elasticity of the PHBV/TPU blends as a function of the TPU content as well as the plots obtained from the predictive models. In both models, PHBV and TPU have been considered the

continuous and dispersed phase respectively, and only the compositions in which the PHBV is the major phase have been represented.

The KUT model is commonly used to assess the interfacial adherence in immiscible polymer blends. [47-50] This model assumes the blend has spherical inclusions of a polymer (*disperse*, d), having an elastic modulus (E_d), in a continuous matrix of polymer (*matrix*, m), having an elastic modulus (E_m) and a Poisson's ratio (ν_m) taken to be 0.5. The KUT model has two equations: one for a perfect adhesion in the interface (Equation 4) and the other assumes no adhesion (Equation 5).

$$E_b = E_m \left(\frac{(7-5\nu_m)x E_m + (8-10\nu_m)x E_d - (7-5\nu_m)x (E_m - E_d)x \phi_d}{(7-5\nu_m)x E_m + (8-10\nu_m)x E_d + (8-10\nu_m)x (E_m - E_d)x \phi_d} \right) \quad (4)$$

$$E_b = E_m \left(\frac{(7-5\nu_m)x E_m - (7-5\nu_m)x E_m x \phi_d}{(7-5\nu_m)x E_m + (8-10\nu_m)x E_m x \phi_d} \right) \quad (5)$$

Where E_b is the elastic modulus of the blend and ϕ_d is the volume fraction of the dispersed phase.

As can be seen in Figure 4b, the difference between the perfect adhesion and the no-adhesion curve is minimal for our system, as it is also from the experimental results for both of them (see Figure 4b). This can be attributed to a very low elastic modulus of the dispersed phase when compared to that of the matrix. Hence, the contribution of the TPU to the elastic modulus of the blend is negligible. This can be confirmed when fitting the experimental results to the Cohen–Ishai model (Equation 6), in which no interaction between the phases is considered, with the dispersed phase considered as voids.

$$E_b = E_m (1 - \phi_d^{2/3}) \quad (6)$$

Figure 4c shows the experimental values of the tensile strength as a function of the TPU content. The tensile strength of the blends also decreases gradually when the TPU is incorporated to the PHBV. It can be pointed out that, although the pure TPU has a tensile strength close to that of the PHBV, the strength corresponding to the elongation at which rupture takes place is still very low. The interaction between the two polymers at the interface was assessed by fitting the experimental values to two different models: the Nicolais–Narkis model (NN) and the Béla Pukánszky model (BP). These two models allow for quantifying the adherence between two immiscible polymer blends. [47, 48, 50, 51] The NN model (Equation 7) defines an interface interaction constant (K) which is a function of the blend structure. For spherical inclusions, $K = 1.21$ stands for the extreme case of poor adhesion, while a lower K value denotes better interfacial interaction. By fitting the experimental results to that model, a K value of 0.896 has been determined (see Figure 4c), indicating a degree of interaction.

$$\sigma_b = \sigma_m (1 - K \phi_d^{2/3}) \quad (7)$$

On the other hand, the BP model (Equation 8) establishes parameter B that is related to the load-bearing capacity of the dispersed phase. This value depends on the size of the contact surface between the matrix and the dispersed phase and on the properties of the interface that is formed. For lower interactions of the interface, the B value decreases. A value of the B parameter of 1.25 is found when fitting the experimental data to the BP model. This also indicates some degree of interaction at the interface, thus in accordance with the NN value.

$$\sigma_b = \sigma_m \left(\frac{1-\phi_d}{1+2.5\phi_d} \right) e^{B\phi_d} \quad (8)$$

With respect to the elongation at break, the addition of small quantities of TPU to the PHBV does not seem to affect the yielding capacity of the PHBV (being below 4% for all the samples below 20 wt% TPU). However, when the TPU content surpasses 20 wt%, a clear increase in the elongation at break has been detected. Thus, the 70/30 samples exhibit a value for the elongation at break, double that of the pure PHBV and a clear yielding effect is detected. Therefore, the addition of a TPU above 20 wt% would result in a change in the mechanical behaviour of the blend, thus decreasing the inherent fragility of the PHBV.

Overall, the mechanical results show that incorporating TPU promotes the potential applications of these materials, with higher ductility and similar tensile strength as polylactides, these being the natural competitors in the field of biodegradable polyesters.

3.4. Barrier performance

Water vapour permeability by weight loss or gain measurements (ASTM E96) are common methods to determine the water barrier properties of materials, while D-limonene is a commonly used standard compound to test mass transport of volatile compounds, such as aromas. Figure 5 shows the vapour permeability (VP) values of both compounds and all PHBV-TPU blends with increasing TPU fraction. Values for both water and D-limonene vapour permeability of blends with up to 30 wt% TPU are not significantly affected, as compared to neat PHBV. Indeed, permeability values are relatively low (close to the detection limit of the technique), especially for limonene permeability. The values are in agreement with previous studies on neat PHBV and reinforce the excellent water and aroma barrier properties of these bacterial polyesters. [6, 10, 52, 53] A detrimental interaction between the PHBV and TPU phase would cause preferential diffusion pathways to drastically affect the permeability values even at low TPU load. However, increased permeability only occurs at very high TPU contents. In fact, increased permeability is mostly a result of the increased sorption of the volatile compounds, while actual diffusion coefficients do not contribute as drastically to the decreasing barrier properties at very high TPU loads (Table S1). This suggests a degree of interaction between both phases, which supports the discussion elaborated in the morphology and mechanical properties section. This decrease may therefore be attributed to the considerable increase in free volume in the absence of PHBV from the combination. These results point out that the incorporation of high

quantities of the TPU does not affect the excellent barrier properties of the materials against water or aroma compounds.

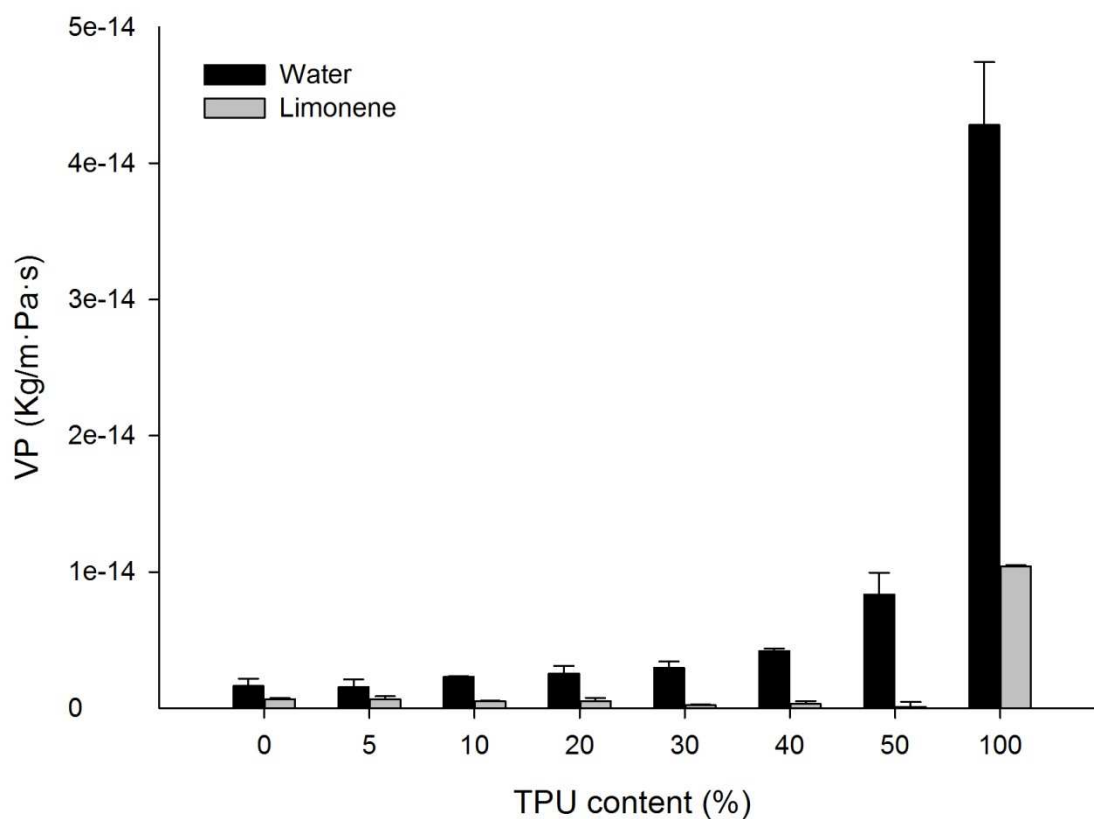


Figure 5. Vapour permeability of the neat materials and their tested blends to water and limonene.

Table S1. Mass transfer parameters through PHBV/TPU blends.

PHBV/TPU (%)	Water			Limonene		
	Sorption (vol.%)	Diffusion coefficient (m^2/s)· 10^{-14}	Permeability ($\text{kg}/\text{m}\cdot\text{Pa}\cdot\text{s}$)· 10^{-15}	Sorption (vol.%)	Diffusion coefficient (m^2/s)· 10^{-14}	Permeability ($\text{kg}/\text{m}\cdot\text{Pa}\cdot\text{s}$)· 10^{-15}
100/0	2.5±0.2	6.6±0.2	1.6±0.5	0.4±0.1	17.5±0.5	0.7±0.1
95/5	2.1±0.1	7.2±0.1	1.5±0.6	0.4±0.1	15.3±1.2	0.6±0.2
90/10	2.6±0.4	8.8±0.4	2.3±0.1	0.4±0.0	12.4±0.1	0.5±0.1
80/20	3.2±0.8	7.8±0.3	2.5±0.6	0.3±0.0	16.0±0.2	0.5±0.3
70/30	3.7±0.0	7.9±0.0	2.9±0.5	0.3±0.0	7.3±0.1	0.2±0.6
60/40	4.2±0.6	9.8±0.1	4.2±0.2	0.5±0.0	6.3±0.3	0.3±0.3

50/50	5.6±1.0	14.9±0.5	8.3±1.6	1.2±0.1	1.7±0.2	0.1±0.1
0/100	7.6±0.9	56.5±0.7	42.8±4.6	3.2±0.1	32.3±0.1	10.4±0.1

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3.5. Biodisintegration

Disintegration under composting conditions was evaluated by measuring the weight loss of PHBV and PHBV/TPU composite samples according to the ISO 20200 standard. [37] Figure 6 shows the evolution of the disintegration (%) over time for neat PHBV, neat TPU and PHBV/TPU blends in lab-scale composting conditions.

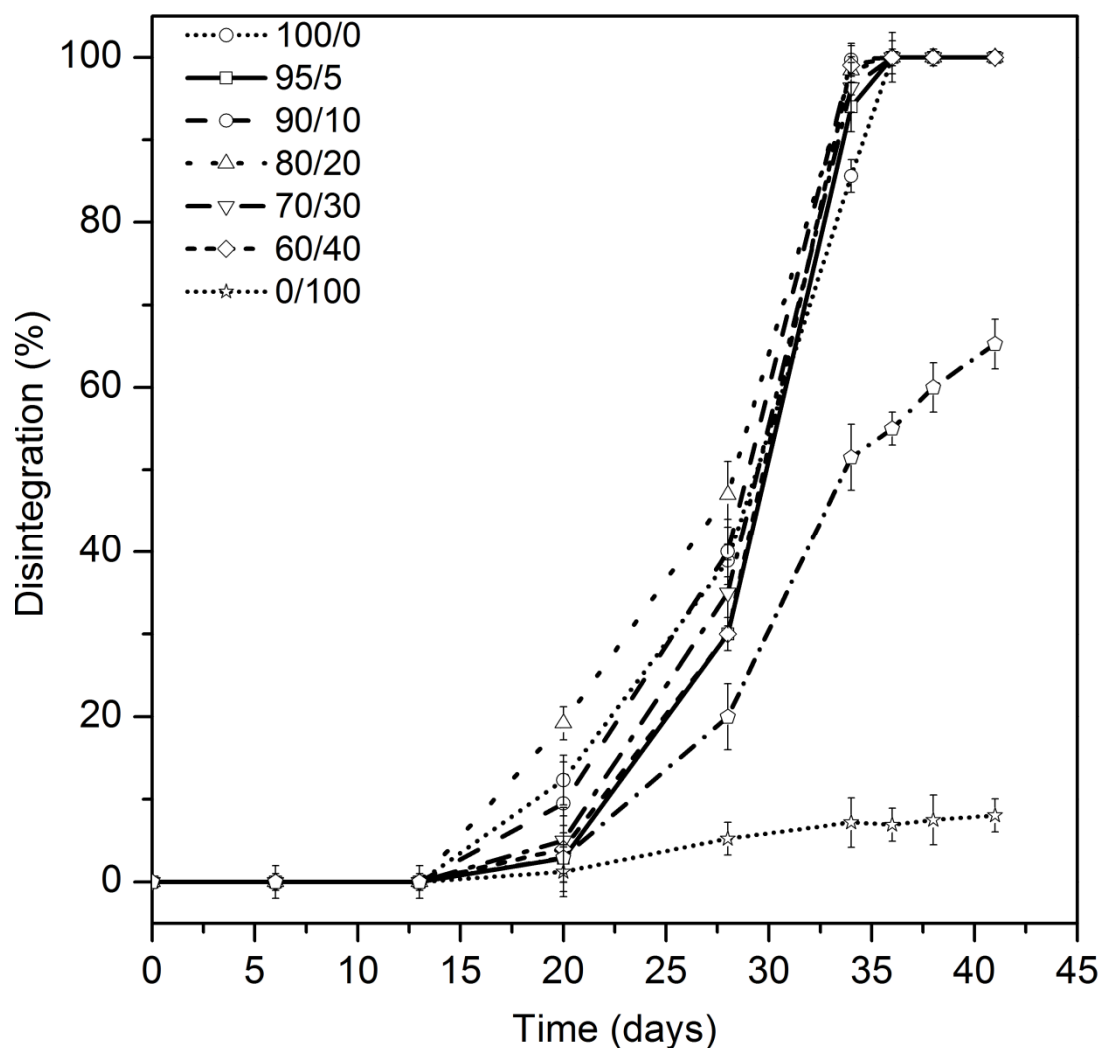


Figure 6. Disintegration of the PHBV/TPU blends over time under composting conditions.

Weight loss remains practically unchanged until the 13th day of composting. After that, weight loss increases markedly for all the blends as well as for neat PHBV. In the case of 50/50 samples, up to about 65 wt% had disintegrated at 41 days, and showed no tendency to plateau. It is estimated that the degree of disintegration would be higher if longer composting periods are considered. However, the blends with TPU content below 50 wt% reached total disintegration after 36 days of testing. No significant differences in weight loss rate were observed among samples with a content lower than 50 wt%, demonstrating that this relatively high load of TPU does not affect the disintegration of the PHBV/TPU blends. As can be observed, thermoplastic

polyurethane is only partially disintegrated after 41 days (8 wt% disintegration). This rate of disintegration is in agreement with previous reports. [29]

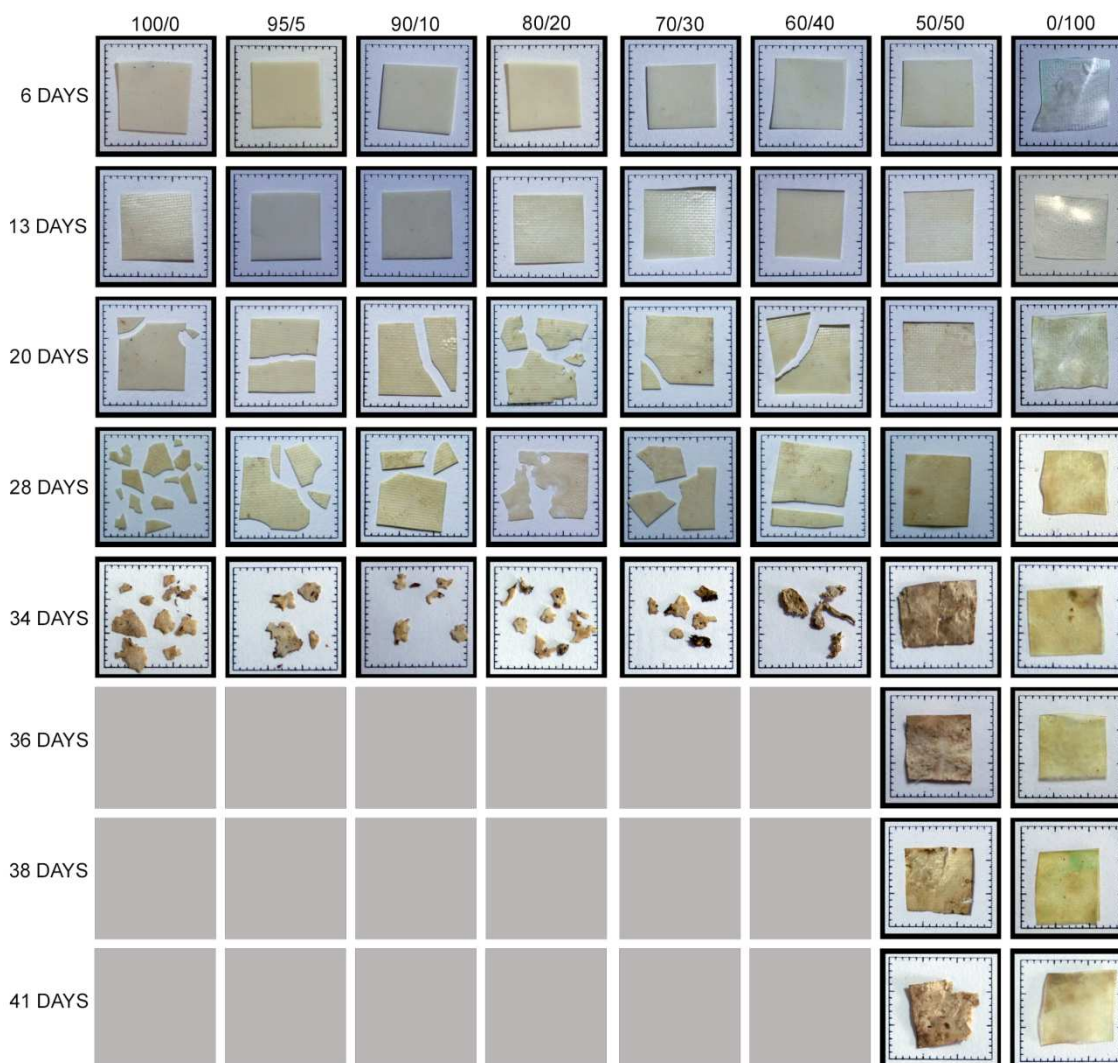


Figure 7. Visual appearance of the tested blend films (PHBV/TPU) after selected time points during the composting process.

In order to visually assess the impact over time of the composting process on the tested samples, images of the studied blends were taken at different time points (Figure 7). All the samples with a TPU content below 50 wt% exhibited considerable surface deformation and fractures started after 20 days under composting conditions. After 28 days, all these samples were broken into small pieces and showed similar roughening and physical alterations. At longer composting times, samples were found to be further disintegrated, leaving pieces smaller than 2 mm in size. Finally, after 36 days samples reached a level of disintegration where no visible fragments could be recovered.

Nevertheless, 50/50 and 0/100 samples were still present after 41 days composting. The 50/50 samples showed slight surface roughening and were visibly affected after 34 days. This surface roughening indicates the beginning of the disintegration process. In fact, as reported in the

literature, PHB and PHBV disintegration is primarily caused by microorganisms that erode the polymer surface and gradually spread into the bulk. [54-56]

On the other hand, TPU does not show this surface alteration. However, a remarkable change in colour and loss of transparency is evident after 28 days. Similar behaviour has been reported for PLA films. [57, 58] This change in the appearance of the samples was attributed to changes in the refraction index of the materials, to water absorption and/or to the presence of products formed during bacterial hydrolytic processes.

4. Conclusion

Although PHBV polymers are a promising alternative to fossil fuel derived polymers, their excessive brittleness has yet to be overcome without compromising barrier performance. In this work, for the first time an ester-based TPU, which was not stabilised against hydrolysis, has been assessed as an additive in melt blends with PHBV. The incorporation of the TPU did not alter the overall crystallinity or the thermal degradation kinetics of the blends. Elongation at break was increased without drastically compromising the tensile performance. Barrier performance against water vapour and aroma compounds was shown to be comparable to benchmark barrier polyesters when the TPU content was ≤ 30 wt% and the biodegradability was preserved for TPU loads of at least 40 wt%. Overall, the blends show a combination of mechanical and barrier performance which exceeds that of commercial PLA, the closest competitor in biodegradable food packaging applications. The study indicates the suitability of these types of elastomers to create biodegradable materials based on PHBV with high barrier properties and better performance for potential food packaging applications.

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