

Film blowing of PHB-based systems for home compostable food packaging

P.F. Teixeira¹, J.A. Covas¹, M.J. Suarez², I. Angulo², L. Hilliou¹

¹Institute for Polymers and Composites, University of Minho, Guimarães, Portugal.

²GAIKER Technology Centre, Basque Research and Technology Alliance (BRTA), Zamudio, Spain.

[*loic@dep.uminho.pt](mailto:loic@dep.uminho.pt); Tel: +351 253510320.

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Abstract.

One of the routes to minimize the environmental impact of plastics waste is the use of bio-sourced and biodegradable alternatives, particularly for packaging applications. Although Polyhydroxyalkanoates (PHA) are attractive candidates for food packaging, they have poor processability, particularly for extrusion film blowing. Thus, one relatively successful alternative has been blending PHA with a biodegradable polymer. This work proposes film blowing of a co-extruded Poly(hydroxybutyrate) (PHB) layer with a poly butylene adipate-co-terephthalate (PBAT) layer to enhance bubble stability,

mechanical and barrier properties. Co-extrusion is detailed, together with the different strategies followed to improve adhesion between film layers and the PHB content in the films. Films with thicknesses below 50 micron and elongation at break beyond 500% were consistently produced.

Keywords: film blowing, co-extrusion, polyhydroxybutyrate, biodegradable packaging.

1. Introduction

Approximately 37% of food packaging are made of plastics (Halonen et al., 2020), which demonstrates the positive contribution of these materials to food safety and consumers wellbeing. Simultaneously, food packages represent a significant share of plastics waste. For instance, 40% of the European plastics production is dedicated to packaging applications (PlasticsEurope, 2019). The resulting environmental impact triggered research and innovation efforts for the development of bio-sourced and biodegradable alternatives. Reports on new bio-based and biodegradable film packaging are abundant (Rhim et al. 2013; Muthuraj et al., 2018; Karan et al., 2019; Scaffaro et al., 2019; Narancic et al., 2020; Sharma et al. 2020), but few films actually made their way up to the market (Peelman et al., 2013; Niaounakis 2015).

Among the bio-based and biodegradable polymers available, polyhydroxyalkanoates (PHA) are attractive candidates for food packaging (Bugnicourt et al., 2014), since degradation of these microbial polyesters does not require industrial composting facilities. However, this benefit is offset by poor processability and mechanical resistance of thin films. Poly(hydroxybutyrate) (PHB) is reported to be inappropriate for film blowing (Haäangi U. J., 2013; Niaounakis, 2015). Film blowing of a commercial polyhydroxy(butyrate-co-valerate) (PHBV) was attempted (Cunha et al., 2015), but the process was unstable and 100 micron thick films showed poor tear resistance.

Melt blending PHA with other biodegradable polymers and melt compounding with additives have been attempted to improve film-blowing performance. Film blowing of PHB/poly(lactic acid) (PLA) blends using maleic anhydride as reactive compatibilizer was accomplished, but the films contained 40% or less of PHB (Jandas et al., 2013).

Using a commercial PHBV/poly butylene adipate-co-terephthalate (PBAT) blend yielded 35 micron thick films with 30 wt.% PHBV content (Russo et al., 2013). PHBV melt compounded with 70 wt.% of an experimental Mater-Bi® compound was processed into blown films with thickness ranging from 80 to 100 micron, but the bubbles were relatively unstable (Cunha et al., 2016). Relatively thick films (between 180 and 230 microns) were produced using a thermoplastic starch/poly(3-hydroxybutyrate-co-4-hydroxybutyrate) blend containing 36 wt.% of the latter (Sun et al., 2017).

Co-extrusion is an alternative route to convert biodegradable plastics into films for food packaging (Scaffaro et al., 2018). A reported commercial application of PHBV for food packaging is an 87 micron thick multilayered film with PBAT (Peelman et al., 2013). Film blowing of a co-extruded PHA layer with a PBAT or biodegradable composite layer displayed enhanced bubble stability when compared to film blowing of the corresponding blends (Cunha et al., 2016). However, films containing more than 50% PHBV could not be produced, and delamination between the two layers occurred at strains as low as 10 %.

Based upon previous results (Cunha et al., 2016), the present study explores co-extrusion film blowing to produce bi-layered PHB/PBAT films for food packaging applications. The research was carried out within the framework of EU funded YPACK project (High performance polyhydroxyalkanoates based packaging to minimise food waste). The main objectives are to maximize the PHB content in the bi-layered films and to enhance adhesion between layers. The first objective involves optimization of processing parameters. The second objective is pursued through two routes: the addition at-line of a reactive crosslinking agent to PHB, and the co-extrusion of a compatibilized PHB/PBAT blend containing 10 wt.% PBAT with PBAT. Dicumyl peroxide (DCP) was chosen as crosslinker, since it has long been established that its reactive extrusion with PHBV promotes chain branching (D'Haene et al., 1999), which is a critical chain conformational

attribute for enhancing film blowing of bio-based polymers such as PLA (Nouri et al., 2015).

2. Experimental

2.1. Materials and compounding

An experimental PHB grade (Biomer® P309) was supplied by BIOMER (Krailling, Germany). The batch was expressly produced for the YPACK project, being essentially designed for injection molding and being processed at a maximum temperature of 185 °C. This grade has a melt flow index (MFI) of 10 g/10 min at 180 °C for a load of 2.16 kgs. A film blowing grade of PBAT (Ecoflex® F blend C1200) was purchased from BASF (Ludwigshafen am Rhein, Germany). This grade has a MFI of 2.7-4.5 g/10 min at 190 °C for a load of 2.16 kgs. BASF kindly offered a multifunctional epoxide styrene-acrylic oligomeric chain extender (CE). This family of chain extenders has been extensively used to modify PLA or PBAT, or to compatibilize their blends, for improving extrusion film blowing (Al-Itry, 2015; Arruda et al., 2015; Li et al., 2018; Mallet et al. 2014; Schneider et al., 2016). Dicumyl peroxide (DCP) was purchased from Sigma-Aldrich (CAS Number 80-43-3). All materials were dried overnight at 60 °C before processing.

PHB modification with DCP was performed in an intermeshing co-rotating twin screw extruder Collin ZK 25. Premixes of PHB and DCP fed the extruder at a rate of 3.5 kg/h. The temperature profile was set to 180 °C / 180 °C / 170 °C / 170 °C / 170 °C / 160 °C / 160 °C from hopper to die, and the screws rotated at 100 rpm. Premixes of PHB (90 wt.%), PBAT (10 wt.%) and CE were prepared in the same extruder, with identical processing parameters.

2.2. Rheological characterization

Materials and compounds were characterized using an ARG2 rotational rheometer (TA instruments), equipped with a parallel-plate geometry (25 mm diameter). In order to avoid additional thermal degradation associated with compression molding to produce circular discs, pellets (dried overnight at 60 °C beforehand) were directly loaded in the shearing geometry pre-heated to 180 °C. The same amount of material was used for all measurements. A circular metallic ring maintained the pellets on the bottom plate and allowed material compaction during gap setting. After reaching the required gap (0.9 mm), the ring was removed and the excess of material trimmed. Time was given for thermal equilibrium and for relaxation of the sample normal force. Mechanical spectra were determined with small amplitude oscillatory (sinusoidal) shear frequency sweeps from 100 Hz to 0.1 Hz, at 180°C under a constant strain amplitude of 5 % (within the linear viscoelasticity regimen, as evidenced from the sinusoidal stress responses). To assess the thermal stability of the samples, time sweep measurements were performed (with fresh samples) at 1 Hz and 180 °C, during approximately 6 min, again with a sinusoidal deformation of 5%. Steady viscosity flow curves were measured at 180 °C with fresh samples, by logarithmically ramping the steady shear rate from 0.1 s⁻¹ to 20 s⁻¹, and allowing a maximum of 30 seconds at each shear rate step to read the viscosity value.

2.3. Film blowing

Films were produced using a laboratorial prototype extrusion blown-film line (Periplast, Portugal) detailed at length elsewhere (Carneiro et al., 2008). The equipment was configured for conventional extrusion film blowing (it can also make biaxially oriented film), with one or two extruders and extrusion/co-extrusion dies, for the production of mono-layered or bi-layered films, respectively. The set temperature profile for extruder

A (3 heating zones) was 180 °C / 160 °C / 155 °C from hopper to screw tip, and for extruder B (4 zones) was 180 °C / 160 °C / 155 °C / 170 °C. Extruder A was fed with PHB, PHB/DCP and PHB/PBAT blends to produce the internal layer of bi-layered films, as well as monolayer film of modified PHB. Extruder B was fed with PBAT to create the external layer of bi-layered films and the corresponding PBAT monolayer. The extrusion/co-extrusion head (with a die lip gap of 0.5 mm) was kept at 175 °C / 165 °C / 160 °C from extruder outlet to die exit, except for the modified PHB monolayer (175 °C / 170 °C / 160 °C). External bubble cooling conditions were maintained constant, whereas operating conditions were varied in order to generate a range of blow up (BUR) and take up (TUR) ratios. Table 1 identifies and presents data for the 10 films produced. When performing extrusion trials aiming at maximizing the PHB content in the films while minimizing their thicknesses (films 1 to 5), the screw speeds were adjusted and TUR and BUR were also maximized. The film blowing parameters used to produce film 1 were employed to test the modified PHB (film 6) and the PHB/PBAT blend (films 7 and 8) as adhesive second layer. An extrusion run with PHB/PBAT blend aimed at maximizing the PHB content by increasing the screw speed of the corresponding extruder.

Table 1: Films produced in the extrusion trials.

Film label	Internal layer	External layer	BUR	TUR	Extruder A (rpm)	Extruder B (rpm)
PHB	PHB+DCP	-	1.9	6.4	30	-
PBAT	-	PBAT	2.2	12.1	-	20
Maximizing PHB content and film thickness						

1	PHB	PBAT	1.8	10.1	15	15
2	PHB	PBAT	2.0	9.2	15	15
3	PHB	PBAT	2.1	9.0	20	20
4	PHB	PBAT	1.9	13.9	18	15
5	PHB	PBAT	2.1	12.5	20	15
Optimizing adhesion between layers						
6	PHB+DCP	PBAT	1.9	10.1	15	15
7	PHB+PBAT+CE	PBAT	1.9	7.9	15	15
8	PHB+PBAT+CE	PBAT	2.0	7.1	30	15

2.3. Films characterization

The average lay flat width of the films was measured at 30 cm lengthwise steps over a total length of 6 m. At the same lengthwise intervals, films thicknesses were measured at 5 cm steps along the transverse direction (TD).

The PHB volumetric content was assessed from scanning electron microscopy (SEM) observations of the surface normal to the extrusion direction, performed with a NanoSEM - FEI Nova 200 using an acceleration voltage of 15kV. Prior to SEM examination, the bilayered films were fractured in liquid nitrogen. The fractured surface was sputtered (Scancoat Six Edwards, Crawley, UK), with a thin layer of gold under argon atmosphere, to avoid electrostatic charging under the electron beam.

The tensile properties of the films were determined both in the machine (MD) and transverse (TD) directions using a Zwick/Rowell Z005 (Ulm, Germany) universal testing machine, following the ASTM Standard Method D 882-02, with a 5 KN load cell, a strain rate of 50 mm/min and a gauge length of 50 mm. Rectangular test specimens (80 mm × 10 mm) were cut from films previously stored for 24 hours at room temperature (approximately 22 °C) and 60% relative humidity. Each specimen thickness was measured at 5 points. The mechanical properties of welded films joints were evaluated following the same protocol. Welding of PHB on PHB and of PHB on PBAT were performed with an Impulse Heat Sealer F-200 for sealing plastic bags. The sealer sends an electric impulse to heat the wire for 0.2 - 1.5 seconds. For welding the films, two consecutive impulses of 1.5 s were defined. Films tear resistance were measured by drop weight impact tests according to ASTM D2582-03, using a ROSAND IFW IT 5 impact testing machine, equipped with a dart weighing 113.5 g, dropped from a height of 74 cm. For the bi-layered films, tests were performed with the PHB and PBAT side facing the load.

Optical properties were determined with a XL-211 Hazegard system, following ASTM D1003-61. This test method covers the evaluation of specific light-transmitting and wide-angle-light-scattering properties of planar sections of films.

Comparative water vapor transmission rate (WVTR) through the various films was measured according to ASTM E398:03, using a Permatran W398 apparatus. Tests were carried out in duplicates at 30 °C and 90% relative humidity, with film samples of 5 cm², at a pressure of 760 mm Hg. For bi-layered films, PBAT side was facing the nitrogen flushing chamber.

3. Results and Discussion

3.1. Film blowing of monolayers and co-extruded layers

Figure 1 illustrates film blowing trials with PHB and modified PHB, during the preliminary campaign conducted to screen the processability of PHB under different processing conditions. As expected for an injection molding grade, blowing a stable bubble was unfeasible. The PHB melt is too viscous at low extrusion temperature (160°C), whilst it lacks melt strength at higher temperatures (170 to 175 °C) and shows significant degradation.



Figure 1. Preliminary film blowing trials with PHB (left) and PHB modified by DCP (middle and right).

The rheological characterization of PHB displayed in Figure 2 shows the impact of PHB degradation on shear viscosity during the compounding stage. PHB was melt mixed with 0.2 wt.% dicumyl peroxide (DCP), since this radical initiator promotes PHB chain branching and thus improves extensional viscosity (D’Haene et al. 1999; Kolachi and Kontopoulou, 2015). However, mixing PHB with DCP yielded a material with slightly improved thermal stability (see inset to Figure 2a), but a depressed melt shear viscosity. Conversely, DCP impacted positively on melt strength, as film blowing of modified PHB

seemed possible (Figure 1). This is explained by the Van Gorp-Palmen plot (see Figure 2b), which indicates that DCP modified the distribution of relaxation times of PHB chains when compared with the virgin or degraded materials, possibly because of chain branching (Kolachi and Kontopoulou, 2015). However, film blowing lacked stability (as illustrated in Figure 1), with the bubble exhibiting a certain degree of draw resonance that could not be solved by tuning process parameters. Nonetheless, films approximately 80 micron thick were produced, thus confirming the benefits of using DCP for improving PHB extensional viscosity (D'Haene et al. 1999; Kolachi and Kontopoulou, 2015). Blending PHB with PBAT (10 wt.%), which is thermally stable (see inset to Figure 2a), and with chain extender (2 phr), does a better job than DCP, at least in terms of shear viscosity, since the zero shear viscosity is nearly doubled. In addition, the blend is more elastic than the modified PHB (see inset to Figure 2b). As such, more stable bubbles are expected to be blown with the blend (Fang et al., 2003).

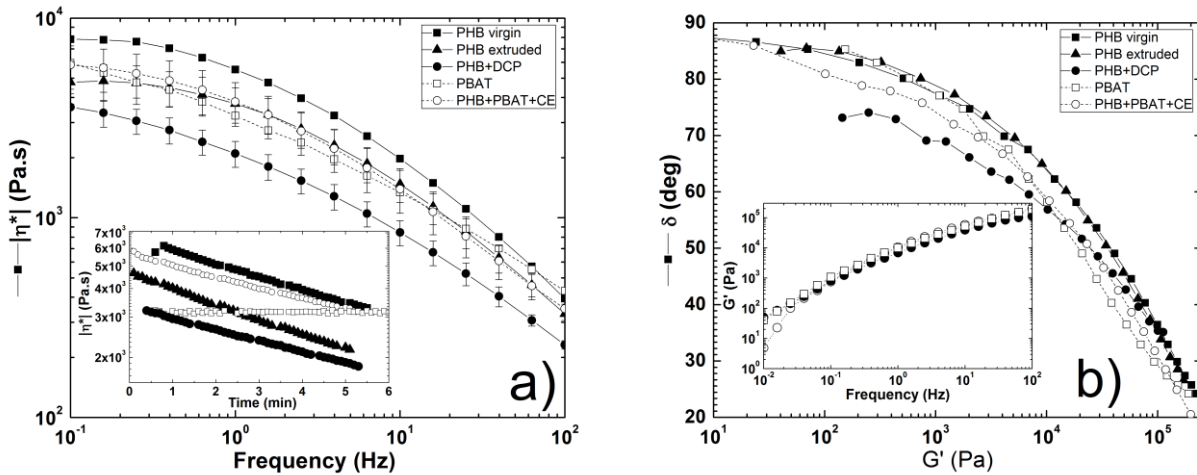


Figure 2. Dynamic shear viscosities (a) and Van Gorp-Palmen plots (b) measured at 180 °C with all tested materials (PHB: poly(hydroxybutyrate); DCP: dicumyl peroxide; PBAT: poly(butylene adipate-co-terephthalate); CE: chain extender. Inset in a: time sweeps performed in dynamic rotational rheometry right after loading samples in the shearing geometry. Inset in b: frequency dependence of storage modulus G' .

The advantages of adopting a co-extrusion strategy for improving process stability are illustrated in Figure 3. The figure shows a bubble of co-extruded PHB and PBAT and a bubble of neat PBAT. PHB is the internal layer of the bi-layered film, since previous research demonstrated that this film construction had enhanced stability (Cunha et al., 2016). Film blowing was much more stable than for monolayer film with modified PHB.

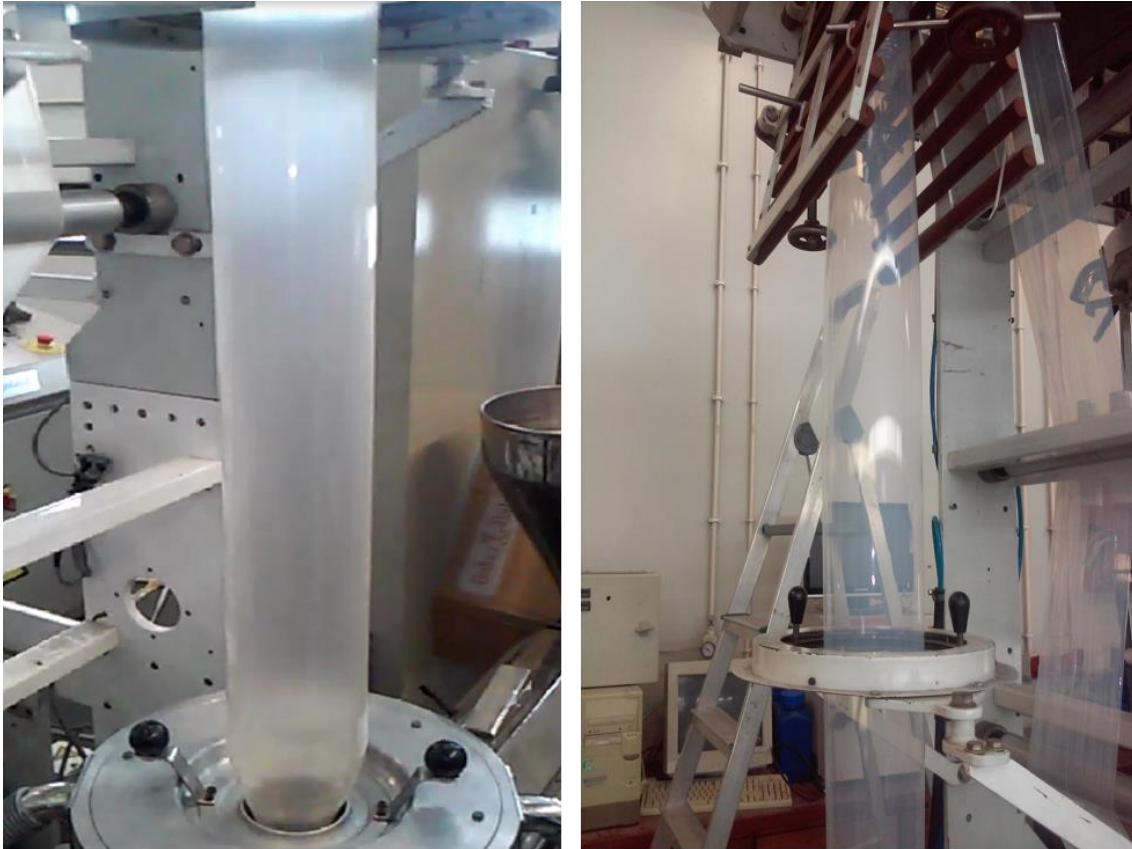


Figure 3: Bubbles of co-extruded PHB and PBAT (left) and of a PBAT monolayer (right).

3.2. Optimizing PHB layer thickness and adhesion between layers

The impact of BUR, TUR, set temperature profiles and screw speed in each extruder on process stability of PHB / PBAT co-extruded films were studied. Figure 4 shows the relative variations in lay flat width and film thickness for different operating conditions (see Table 1). Films 1 to 3 involved tuning screw speed and BUR to improve bubble stability. In the case of films 4 and 5, the relative outputs of the extruders were changed

and TUR was increased to minimize film thickness. This yielded more stable bubbles and thinner films. Still, achieving film thickness below 40 microns came at the price of lower PHB content in the film (in the order of 45%).

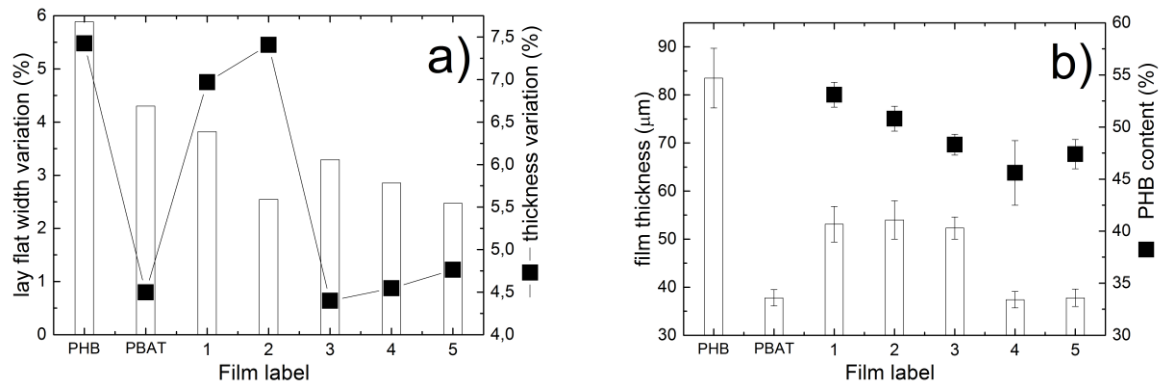


Figure 4. Bubble stability of PHB, PBAT and co-extruded films labelled 1-5 inferred from lay flat width and thickness variations (a) and resulting film thickness and PHB content (b).

To improve adhesion between the PHB and PBAT layers, two strategies were followed. First, DCP was added to PHB, to promote chemical reactions between PBAT and PHB chains. DCP powder was thus pre-mixed with PHB and fed to extruder A. This procedure avoided a compounding step that would degrade PHB, as seen in Figure 2. A film was produced (film 6 in Figure 5), but the process lacked stability. Indeed, variations in both film thickness and lay flat width were 2 to 4 times larger than corresponding deviations for films 1 to 5 (compare vertical axes in figures 4 and 5). This behavior could be due to the poor mixing ability of the single screw extruder, and the resulting non-homogeneous distribution of reacted PHB chains in the melt. Still, 50 micron thick films containing nearly 45% PHB were produced.

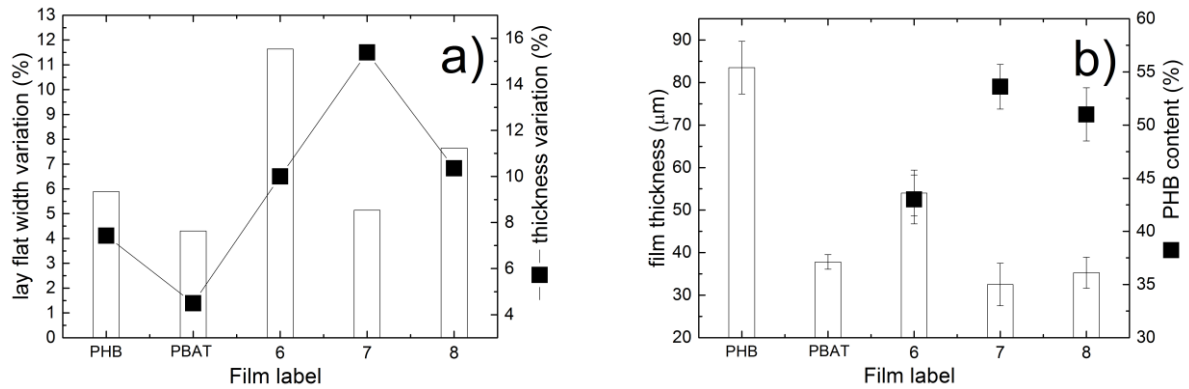


Figure 5. Bubble stability of PHB, PBAT and co-extruded films labelled 6-8 inferred from lay flat width and thickness variations (a) and resulting film thickness and PHB content (b).

As a second strategy, a blend of PBAT (10 wt.%) and PHB replaced PHB in the bi-layer. This option entails the minimization of the relative thickness of the PBAT layer, in order to maintain a high PHB content in the film. As depicted in Figure 5, this had a somewhat negative impact on film dimensions stability: film 7 exhibited a large thickness variation, while the variation in lay flat width of film 8 is three times larger than that for films reported in Figure 4. The significant drop in melt viscosity of the blend relative to that of virgin PHB (see Figure 2a), together with the need to unbalance the extruders outputs, explain this loss in process stability. Anyway, co-extrusion of the PHB/PBAT blend and PBAT results in the thinnest films (of the order of 30 microns) with the highest PHB content (above 50%) achieved in this study. To the best of the authors' knowledge, these are also the thinnest and richest PHB films produced by a process suited for industrial scale up (Jandas, 2013; Peelman et al., 2013; Niaounakis, 2015; Sun et al., 2017; Jost, 2018).

3.3. Films properties

The tensile properties of all films are presented in Figure 6. Most films delaminate in the machine direction during testing. The at-line addition of DCP to PHB did not hamper delamination (film 6 in Figure 6a). In contrast, the use of a blend is effective for improving adhesion between the two layers, as seen for film 7, which only shows delamination during mechanical testing performed along the transverse direction, while no delamination was observed with film 8. As a result of this improved adhesion, film 7 nearly matches the tensile properties of the PBAT film, while it is the thinnest bi-layered film with the largest PHB content within this study.

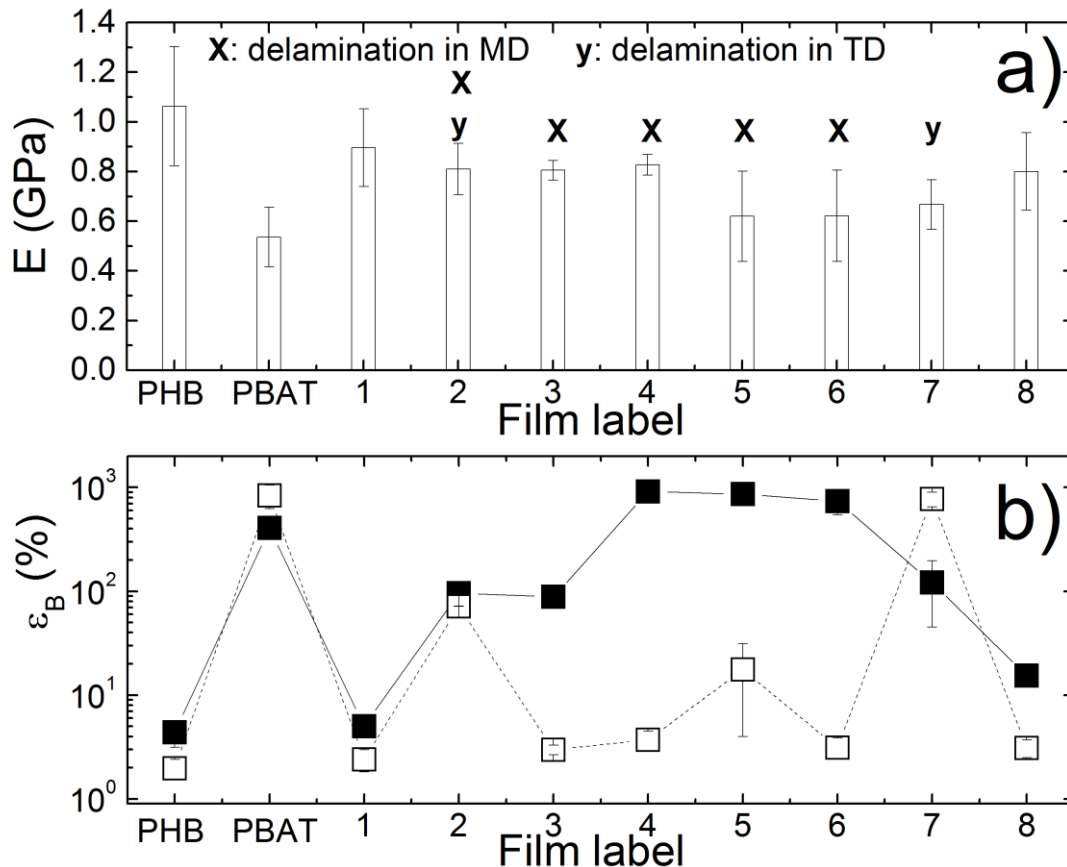


Figure 6. Young's modulus (a) and elongation at break ϵ_B (b) along the machine direction (MD: solid symbols) and transverse direction (TD: empty symbols) of co-extruded bi-layers of PHB and PBAT (films 1 to 8) and of PHB and PBAT monolayers.

All bi-layered films in Figure 6 show superior elongation at break along the machine direction than films documented in the literature and blown from non-compatible blends containing up to 40% PHA (Jandas et al., 2013; Sun et al., 2017). However, films 6 to 8 do not match the 500% elongation at break reported for a compatibilized blend of PHB with 70 wt.% PLA (Jandas et al., 2013).

Figure 7 shows the tear resistance measured on both sides of the films, normalized by the film thickness. As expected from the tensile testing results, films with optimized adhesion between layers show better balanced tear resistance. Conversely, using DCP is inefficient in improving this property, since the corresponding film (film 6) presents the weakest tear resistance.

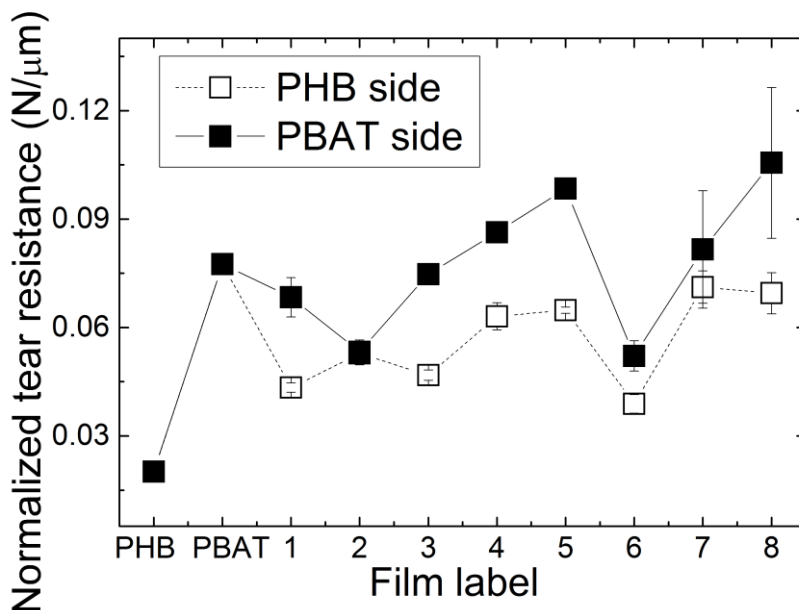


Figure 7. Normalized tear resistance of the films studied.

All films exhibit satisfactory welding performance, as demonstrated in Figure 8, which portrays the mechanical resistance of joints made by welding PHB layers on PBAT layers. Welding properties are important in food packages, but only few studies with bio based and/or biodegradable polymers are available in the literature (Tabasi and Ajji, 2017).

Most resistant weld was achieved with bi-layered film 8. This result is generally consistent with the best tear resistance and the absence of delamination during mechanical testing.

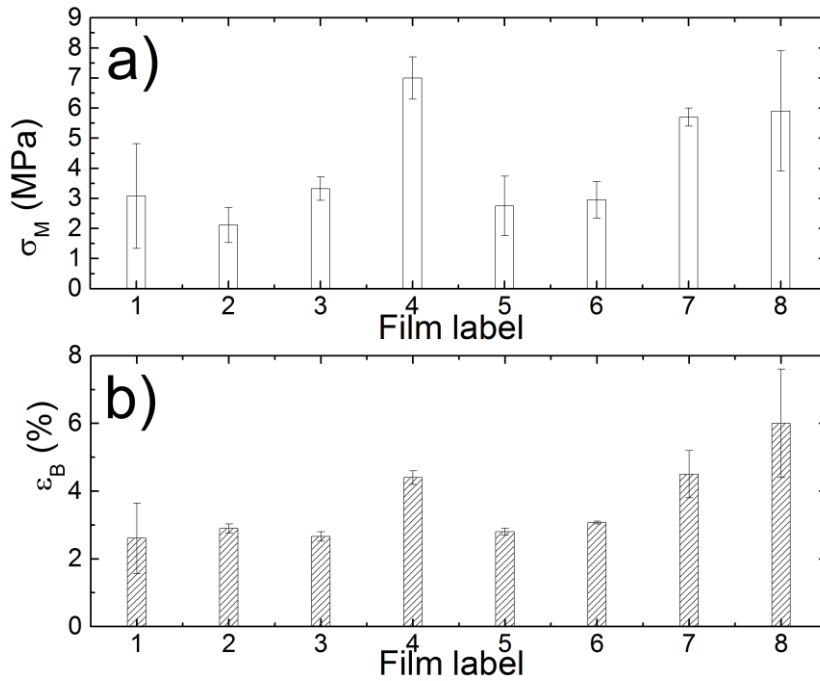


Figure 8. Maximum stress σ_M (a) and strain at break ϵ_B (b) of welded films. Welding of PHB layers on PBAT layers was performed before the tensile testing of the resulting joints.

The optical properties (in terms of haze) of all films are presented in Figure 9, together with the respective PHB contents and thicknesses, and pictures reporting the visual aspects of a PHB film and film 8. Films 7 and 8 are both as thick as films 4 and 5, but exhibit much less haze. Rather, the relative thickness of the PHB layer seems also to impact on the light scattering properties of films. Overall, films 7 and 8 are as hazy as the PBAT film at comparable thicknesses.

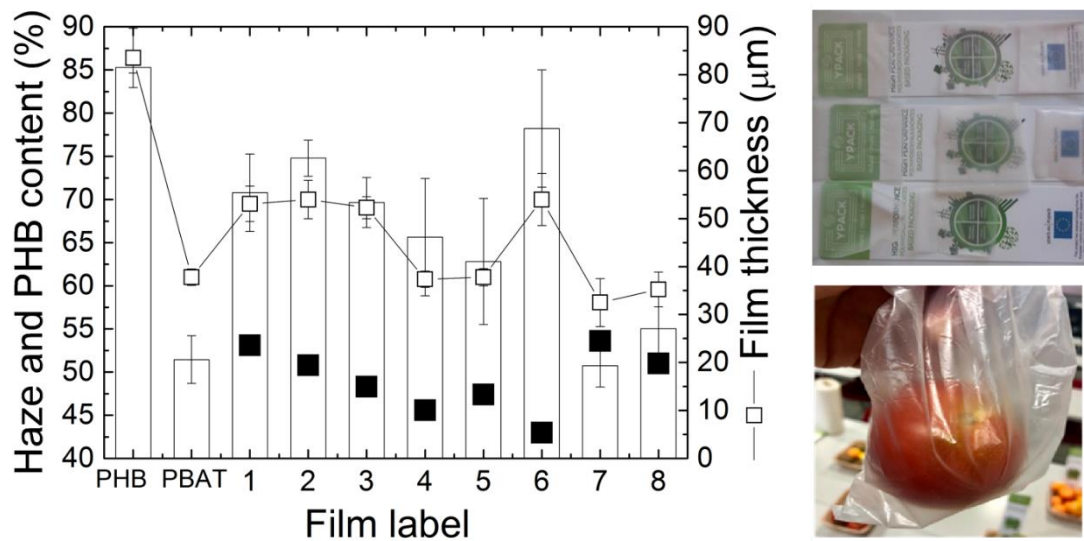


Figure 9. Haze of the films produced, together with their thickness (empty symbols) and PHB content (solid symbols). The picture on top right shows a modified PHB film (top), the PBAT side of film 8 (middle) and the PHB side of film 8 (bottom), whereas the picture on the lower right shows a bag of film 8.

The permeability of the films to water vapor is displayed in Figure 10. Co-extruding a layer of PHB improves the water vapor barrier properties of films. WVTR data for films 4 and 5 indicate that permeability is not simply related to film thickness. The inset in Figure 10, attempts to shed some light on the role of PHB content on the films barrier properties. Clearly, with the exception of one outlier (film 4), WVTR correlates well with the thickness of the PHB layer in the film. These results are in agreement with previous expectations that biodegradable plastics have poor barrier properties, PHB being the exception (Jost 2018). Therefore, Figure 10 underlines the benefits of using PHB and co-extrusion to improve the WVTR of PBAT, a result that is not achieved by blending (Cunha et al. 2015; Jost 2018).

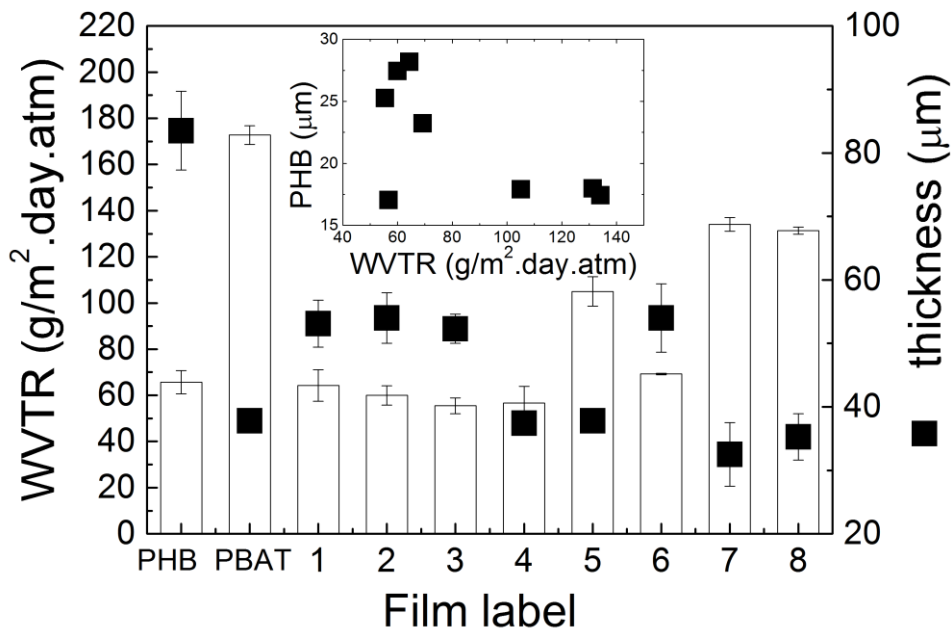


Figure 10. Water vapor transmission rates (WVTR) of blown films from PHB, PBAT and co-extruded PBAT and PHB. Inset: PHB thickness in bi-layered films plotted as a function of the water vapor transmission rates of corresponding films.

4. Conclusions

Polyhydroxyalkanoates (PHA) in general and Poly(hydroxybutyrate) (PHB) in particular are attractive candidates for food packaging applications, not only because they are suitable to home composting, but also due to the fact that they can be obtained from raw bio-based food industry by-products. However, poor processability and film performance motivated their relative successful usage as blends with other biodegradable polymers. This work explored co-extrusion film blowing of bi-layered films containing a layer rich in PHB and another rich in PBAT. 40 micron thick films containing at least 50% PHB were consistently produced. The films showed no delamination, satisfactory mechanical properties, as well as low permeability to water vapor. Moreover, good welding between

PBAT and PHB was observed. The process can be readily scaled-up to industrial production.

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