

Film blowing of PHBV blends and PHBV-based multilayers for the production of biodegradable packages

Mara Cunha,¹ Bruno Fernandes,² José A. Covas,¹ António A. Vicente,² Loïc Hilliou¹

¹IPC/I3N, Institute for Polymers and Composites, Department of Polymer Engineering, University of Minho, Campus de Azurém 4800-058 Guimarães, Portugal

²CEB - Centre of Biological Engineering, Department of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

Correspondence to: L. Hilliou (E-mail: loic@dep.uminho.pt)

ABSTRACT: Poly(hydroxy butyrate-*co*-valerate) (PHBV) is a biodegradable polymer that is difficult to melt process into films. Such difficulty is mirrored in the lack of literature on film blowing of PHBV- or PHBV-based materials. To circumvent this problem, 70/30 wt % blends of PHBV with a biodegradable compound (PBSebT), or with poly(butylene adipate-*co*-terephthalate) (PBAT), were prepared and tested for extrusion film blowing. Both blends showed a similar rheological pattern at 175°C, which is the maximum processing temperature with tolerable thermal degradation. Blending stabilized the film bubbles, thus widening the processing window. However, film properties such as tensile modulus, strain at break and tear resistance remained isotropic and crystallinity characteristics in the machine and transverse directions were generally similar. To bypass the thermal degradation associated with polymer blending, PHBV/PBAT films were coextruded. These showed enhanced functional properties when compared with films blown from blends. The mechanical properties of bilayered films matched those of films blown from commercial PBAT designed for food packaging. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42165.

KEYWORDS: biodegradable; films; packaging; rheology

Received 7 January 2015; accepted 5 March 2015

DOI: 10.1002/app.42165

INTRODUCTION

The societal push to improve food safety and to reduce the impact of plastic packaging on the environment has triggered research efforts to develop new bio-sourced polymers (i.e., from renewable, non-fossil resources) with domestic compostability features. These features allow for the plastics decomposition in the same waste stream of food. In parallel, the package should augment the shelf life of the food, thus improving safety and further contributing to the reduction in food waste. The biodegradable package should also match the performance of the existing nonbiodegradable solutions and should be ideally produced at an equivalent cost. Despite the whelm of studies attempting to improve such properties as barrier, antioxidant, antimicrobial, biodegradability, or stretchability by developing new bio-sourced materials or processing strategies,^{1–6} a food package meeting all the requirements has not yet reached the market.⁷

Polyhydroxyalkanoates (PHA) are particularly good candidates for a new generation of bio-based packaging materials. PHA are biopolyesters synthesized by microorganisms and naturally compostable at ambient temperature⁸; they can be efficiently produced from mixed microbial cultures fed with wastes of the food industry,⁹ or with sludge or wastewater,¹⁰ thus adding an

even higher eco-friendly attribute to the biodegradability and bio-sourced characteristics. However, PHA also display significant drawbacks that currently limit their widespread use as packaging materials, both for food or non-food applications.¹¹ First, commercially available PHA are still significantly costlier than conventional polymers for packaging. Second, they are very difficult to convert into marketable packages using conventional melt processing routes. PHA degrade rapidly upon melting, the melt has a too low shear viscosity and melt elastic strength is insufficient to sustain stretching or blowing. Finally, a slow crystallization rate adds difficulties to the post processing, resulting in brittle products, e.g., films or trays with elongation at break of the order of 1%.

Recently, part of these difficulties have been surpassed by compounding poly(hydroxy butyrate-*co*-valerate) (PHBV) with beer spent grain fibers to lower costs, improve the rheological response and tailor barrier properties, followed by conventional extrusion film blowing,¹² one of the most popular industrial film producing techniques. PHBV was selected given its lower melting temperature and higher thermal stability when compared to polyhydroxybutyrate (PHB), together with a less brittle mechanical behavior. However, the processing window showed

to be very narrow due to the propensity for bubble instability and the mechanical properties were somewhat disappointing.

Blending of PHBV with other biodegradable polymers is an alternative approach to improve properties, the topic having received considerable attention.^{7,11,13–15} However, in the recent reviews on the use of PHBV in biodegradable packaging,^{11,13,14} film extrusion or film blowing of PHBV-based materials are generally absent. These two melt processes are industrially relevant for the large scale production of packaging films. In particular, film extrusion of PHBV is nearly not documented in the open literature, as most studies use compression molding or injection molding of blends to produce sheets or test specimens for characterization and property measurement.^{14,15} For example, a single recent paper was found that reported the successful extrusion film blowing of a commercial blend of 70 wt % poly (butylene adipate-co-terephthalate) (PBAT) with 30 wt % PHBV.¹⁶ A bench top blowing line¹⁶ was used to convert the blend into films, but the processability window was not reported nor were the film properties relevant for food packaging applications. Manufacture of multilayered films by co-extrusion is another common route to tune the barrier properties of film packages. Here again, the literature on coextruded multilayers of PHBV- or PHBV-based materials is scarce. In a recent review on the use of biodegradable plastics for food packaging applications, Peelman *et al.*⁷ reported the mechanical and barrier properties of commercial multilayered films of PHBV and PBAT. However, no details on how the films were produced were presented, as films samples were simply provided to the authors for characterization.

This study focuses on extrusion film blowing of PHBV blended with two different biodegradable commercial plastics suitable for this technique. The main objective is to fill the existing knowledge gap on the melt processing of PHBV-based biodegradable plastics into packaging films, using a scalable and thus industrially relevant converting technology. The large PHBV content in the blend (70 wt %) contrasts with earlier studies. The strategy used to address the film blowing ability of these new compounded biodegradable plastics encompasses their rheological characterization and the systematic study of the impact of processing parameters on the films' properties that are relevant to food package application. Moreover, coextrusion film blowing of bilayered films consisting of PHBV and PBAT is also reported. The benefits of the coextrusion of bilayered films is demonstrated by a systematic comparison of the bilayered films properties with those of films blown from blends.

EXPERIMENTAL

Materials

A commercial PHBV (ENMAT™ Y1000P, produced by Tianan Biologic Materials Company, with a density of 1.25 g/cm³, glass transition temperature $T_g = 8^\circ\text{C}$ and melting temperature $T_m = 165^\circ\text{C}$) containing 3 mol % HV, a commercial aliphatic-aromatic copolyester-based polymer (Ecoflex® F blend C1200, a film blowing grade produced and donated by BASF, labeled here as PBAT, with melt flow index (MFI) of 2.5–4 g/10 min (measured at 190°C, with a load of 2.16 kg, following ISO1133) and a biodegradable compound (Mater-Bi® P.T.C.S, an experi-

mental film blowing grade with proprietary formulation produced and donated by Novamont, hereafter labeled as PBSebT, with MFI of 2 g/10 min measured at 190°C with a 2.16 kg load (as specified by Novamont), were used. All materials were dried during 24 h at 60°C before processing.

Compounding and Characterization of Blends

PHBV/PBAT and PHBV/PBSebT 70 /30 wt % blends (denoted as PHBV+PBAT and PHBV+ PBSebT, respectively) were melt compounded in a Coperion ZSK26 corotating intermeshing twin screw extruder, followed by cooling, drying, and pelletization. Both the screw profile and operating conditions (barrel and die set to 179°C, screw speed of 250 rpm, feed rate of 12 kg/h) were optimized for minimizing thermal degradation of the blends components. The compounds were dried at 60°C for 24 h prior to processing.

The MFI of PHBV and all blends was measured with a Davenport LPF-002, using a 2.16 kg load and at a temperature of 180°C as to limit the thermal degradation of the PHBV in all compounds (see below).

PHBV and blends were molded into 25 mm disks by compression molding (20 tons during 5 minutes) at 175°C for later rheological characterization. This was carried out in a rotational stress-controlled rheometer (ARG2, TA Instruments) equipped with 25 mm diameter parallel plates. Each disk was loaded at 180°C to ensure full melting and the temperature was then set to 175°C while thermal and rheological equilibrium was monitored during 5 min by recording storage and loss moduli (G' and G'' , respectively) using a strain of 1% and a frequency of 1 Hz. This equilibration step was followed by recording the mechanical spectrum obtained by performing a frequency sweep from 10² Hz down to 10⁻¹ Hz with a strain of 1% to ensure a linear stress response. PHBV and blends were also characterized by capillary rheometry to access the rheological behavior at large strain rates, typically between 10² s⁻¹ and 10⁴ s⁻¹. In this case, pellets were fed and compacted into the reservoirs of a dual bore (equipped with 2 capillary dies of diameter 1 mm and different lengths of 2 and 8 mm, to allow on-line Bagley corrections) Rosand RH10 capillary rheometer preheated to 180°C. The temperature was then set to 175°C and a 10 min thermal equilibrium step was completed prior to the ramp in piston velocities (from small to large) and the recording of steady pressure drop readings.

The thermal properties of PHBV, PBAT, PBSebT, and blends were measured with a Differential Scanning Calorimeter (DSC) from Netzsch, using ~5 mg pellet samples heated at 10°C/min from 5°C to 190°C, then cooled down to 5°C at -10°C/min and finally reheated to 190°C at 10°C/min. This final heating run was used to detect transition temperatures and melting enthalpies.

Film Blowing of Blends and Coextrusion of Bilayered Films

A laboratory blown film extrusion line (Periplast, Portugal)¹⁷ configured with one or two extruders (with screw geometries typical for polyolefins processing) and extrusion/coextrusion head and die was used for the production of mono-layered films from blends and bi-layered films from combined grades.

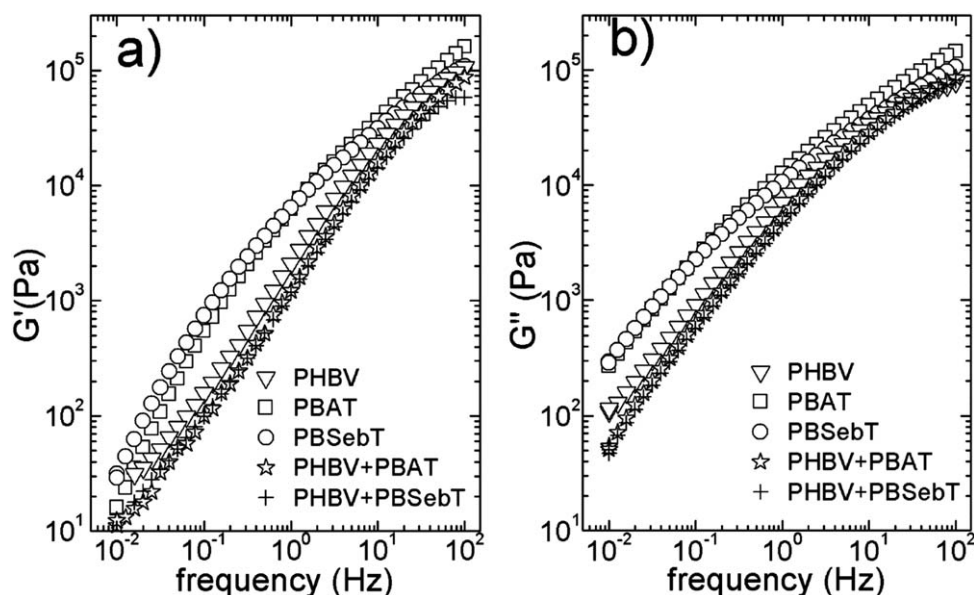


Figure 1. Mechanical spectra (a, storage modulus, G' ; b, loss modulus, G'') of neat polymers and blends measured at 175°C.

The set temperature profile in each extruder was 150°C/155°C/155°C from hopper to screw tip and the head and die were kept at 155°C/155°C/160°C. The screw speed was maintained at 46 rpm, which corresponded to outputs of roughly 3 kg/h.

In the case of the film blowing of blends, external bubble cooling was varied by tuning the fan speed and the air ring aperture at three levels (each denoted as min, med or max, thus defining nine possible air cooling intensities), whereas the blow up ratio (BUR) was kept to 2.5 and the take up ratio (TUR) around 5 (but variations between 4.3 and 5.3 were allowed). BUR is the ratio between the final bubble diameter and the diameter of the die lips, whereas TUR is given by the take-up speed divided by the extrusion speed. BUR is controlled by tuning the air pressure used to inflate the bubble. TUR is controlled by tuning the rotational speed of the pulling rolls. The extrusion speed is controlled by tuning the screw speed of the extruder(s). Full detail on controlling operating parameters and on the monitored variables of the laboratorial line is given elsewhere.¹⁷ Under such processing conditions, films with thicknesses ranging from 70 to 100 μm were produced.

During coextrusion both fan speed and air ring aperture were kept constant (to maintain similar cooling conditions), while both BUR and TUR were varied to produce films with thicknesses ranging roughly from 70 to 150 μm .

Films Characterization

Wide Angle X-ray Diffraction (WAXD) spectra of film samples were captured with a Bruker D8 Discover diffractometer (lambda source of 0.154 nm). The scanning range was $2\theta = 5^\circ$ to 35° , with 0.04° steps. A FEI field emission Scanning Electron Microscope (SEM) (Nova NanoSEM 200) with an acceleration voltage of 5 kV was used to measure the thickness of coextruded layers.

The tensile properties of the films were determined both in the machine (MD) and transverse directions (TD), with an Instron

Universal testing machine (model 4505), according to EN ISO 527, at a strain rate of 5 mm/min (for PBAT and PBSebT films, additional tests were conducted at 50 mm/min to reach break-up) and using a gauge length of 90 mm. Rectangular specimens (150 mm \times 10 mm) were directly cut from films stored for 24 h at room temperature and 60% relative humidity. The mechanical properties of joints of welded films (made with an Impulse F200 sealer, thermostat 6 during 2 min) were assessed using the same protocol. Drop weight impact tests (dart weight 113.5 g, height 100 cm) were performed using a ROSAND IFW IT 5 impact testing machine, according to ASTM D2582-03, in order to determine tear resistance. In the case of the bilayered film, the PBAT side was facing the load.

Optical properties were assessed with a XL-211 Hazegard system, as set by ASTM D1003-61.

Water vapor permeability (WVP) was determined gravimetrically, based on ASTM E96-92 with modifications reported elsewhere.^{18,19}

RESULTS AND DISCUSSION

Thermal and Rheological Characteristics of Individual Materials and Blends

Figure 1 presents the isothermal (at 175°C) rheological spectra of PHBV and its blends with PBAT or PBSebT. PBAT and PBSebT showed virtually the same viscoelastic behavior. Both storage and loss moduli, G' and G'' , respectively, of PHBV were smaller than those of PBAT and PBSebT in the whole range of frequencies tested. Assuming a simple linear mixing rule, it would be expected that the moduli for both blends would stand somewhere between those of PHBV and PBAT. This was not the case, as the moduli of the blends were lower than those of each component. Also, at low frequency, the storage modulus of the blends did not show the classical terminal regime of a melt. In this regime, polymer melts are expected to show a Newtonian behavior characterized by the following power law behaviors for

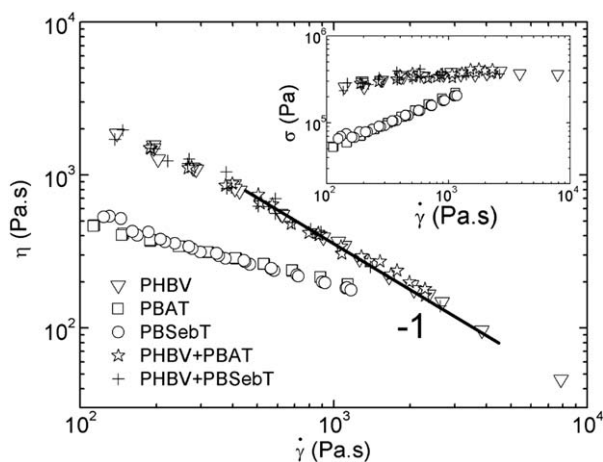


Figure 2. Shear rate dependence of the steady shear viscosity, η , measured at 175°C with capillary rheometry, for neat polymers and blends. Inset: shear rate dependence of the steady shear stress, σ , measured under similar conditions.

both storage and loss moduli: $G' \sim \omega^2$ and $G'' \sim \omega$, where ω denotes the oscillating frequency. In contrast to neat PBSebT and PBAT, which showed a Newtonian behavior at lower frequencies, the storage modulus of the blends departed from a quadratic dependence with frequency. This behavior was probably caused by thermal degradation of PHBV occurring during compounding, where an average residence time of 180 s was measured. Chain scission resulting in depressed viscosity was recently reported for a similar PHBV and for residence time as short as 100 s.²⁰ Indeed, G' and G'' of PHBV almost overlap the shear moduli of the blends, thus confirming that thermal degradation of the blends originates from PHBV.

The capillary rheometry data at 175°C presented in Figure 2 suggests that for large shear rates PHBV and its blends were more viscoelastic than PBAT and PBSebT. More importantly, the slope of the steady shear viscosity of PHBV-based materials as a function of the shear rate approached the critical value of -1 , which is indicative of a stress plateau (see inset in Figure 2) occurring at large enough shear rates. In turn, this plateau was associated with the onset of elastic instabilities, or with the development of wall-slip flow conditions.²¹ Since the extrudates collected during the tests did not present sharkskin or melt fracture anomalies, elastic instabilities can be ruled out and the stress plateau could be assigned to slip. Anyway, the thermal degradation of PHBV evidenced in Figure 1 might also significantly contribute to the shear thinning exponent approaching the value of -1 . The effect of thermal degradation was clearly evidenced in the MFI values measured at 180°C and gathered in Table I: the MFIs of the blends were significantly higher than those of its components, due to the viscosity drop related to PHBV chain scission during compounding.

As such, the rheological characterization suggests that blending brings thermal degradation of PHBV into play, which might negatively impact on both processability and final film properties. Therefore, apart from film blowing of PHBV-based melts, it might be interesting to by-pass compounding by blowing bilayered films.

The thermal characteristics of the blends summarized in Table I are indicative of phase separated morphologies. Two peaks corresponding to melting of PHBV and of PBAT or PBSebT crystals were observed in the DSC curves measured during the second heating run. The melting temperatures did coincide with those measured for neat PBAT and PBSebT and to a less extent (a 5°C shift) with that for as-received PHBV, thus confirming the thermal degradation of the latter during compounding. The phase separated morphology suggested by DSC results for the PHBV + PBAT blend has been confirmed elsewhere in terms of an emulsion-like structure.²²

Films Blown from Blends

Although blending of PHBV with PBAT (PHBV+PBAT) or with PBSebT (PHBV+ PBSebT) has a positive impact on film blowing ability, propensity for bubble instabilities at various processing conditions was observed. Especially for neat PHBV, draw resonance (pulsating film diameter) developed at the upper TUR values, while a relatively slow helical instability (periodic undulations) that is usually assigned to insufficient melt resistance was normally present. Conversely, stable bubbles were produced for nearly all processing conditions tested for the PHBV+PBAT blend (see Figure 3, center). As a result, the effect of bubble cooling on film properties could be studied for the blends, but not for PHBV (only two films were blown with different TUR and BUR).

Bubble stability was reflected in the variations of the films' lay flat widths (corresponding to a flattened bubble); overall, data in Figure 4 show smaller differences for PHBV+PBAT films measured at 10 different circumferential locations along 2 m of film relative to PHBV+ PBSebT films. Deviations in film thickness in the transverse (along the lay flat width) and machine direction (along the film length) are also displayed in Figure 4. Again, PHBV+PBAT films showed less sensitivity to changes in the cooling parameters; taking moderate cooling (med-med) as a basis of comparison, these films also exhibited the smallest variation in film thickness.

Figure 5 shows the WAXD spectra of representative films blown from the blends and their components, using matching cooling conditions (max-max) and nearly identical BUR and TUR. No differences between spectra recorded along the machine direction (MD) and along the transverse direction (TD) could be noticed. Additionally, no significant dependences of peaks intensity, half-width and location on TUR, BUR, and bubble cooling conditions were found, which confirms analogous results of an

Table I. Melt Flow Index, MFI, Measured at 180°C and Thermal Properties (Lower, T_{m1} and Higher, T_{m2} Melting Temperatures) for Neat Polymers and Blends

Samples	MFI (g/10 min)	T_{m1} (°C)	T_{m2} (°C)
PHBV	5.2 ± 0.4	–	176 ± 1
PBAT	3.6 ± 0.1	119 ± 7	–
PBSebT	2.0 ± 0.1	141 ± 3	–
PHBV+ PBSebT	8.5 ± 0.4	142 ± 6	171 ± 1
PHBV+PBAT	7.2 ± 0.3	127 ± 6	171 ± 1

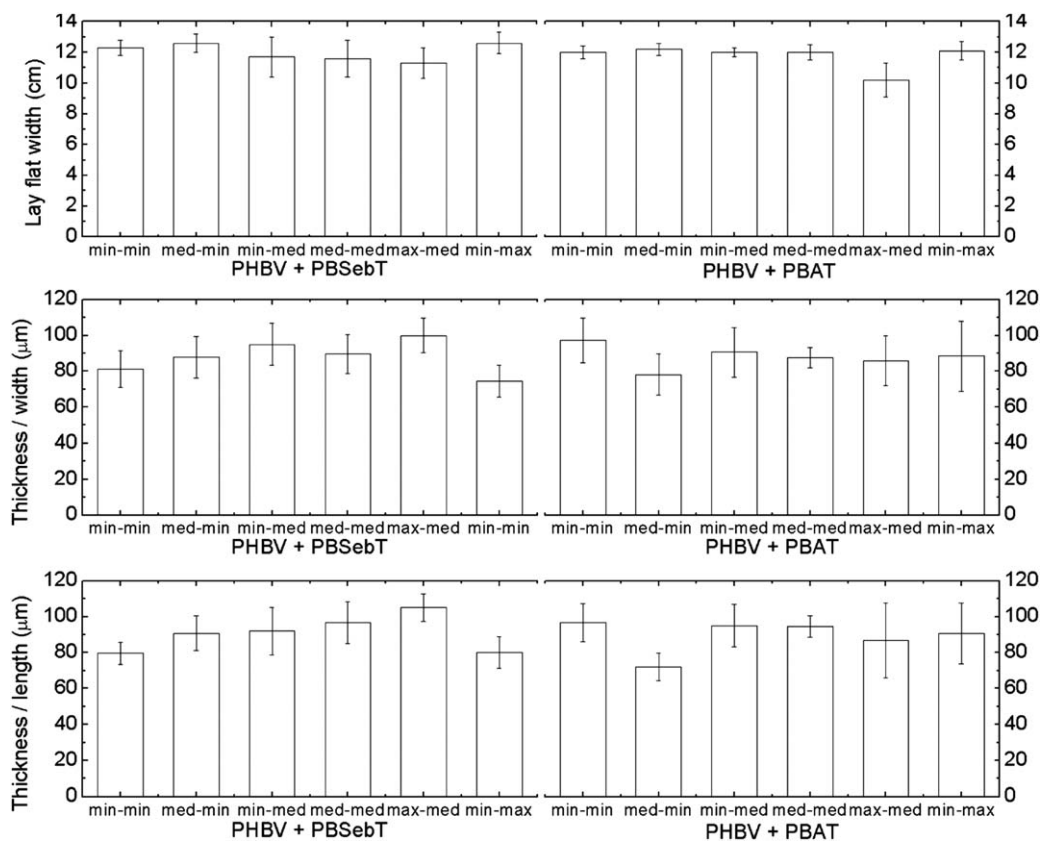


Figure 3. Bubbles lay flat widths (top) and thickness variations along the film width (middle) and length (bottom) for films blown from blends using the cooling parameters (fan and ring apertures) summarized in the horizontal axis. Error bars indicate the standard deviation computed from the statistical analysis of 40 measurements at equally spaced locations along the film length (at the middle of width and the edge of film), or along the lay flat width (at 50 cm intervals along film length).

earlier study carried out with PHBV composites.¹² Given the poor PHBV film blowing ability, the operating window for the blends remained narrow, i.e., only small changes in BUR, TUR and cooling were admissible and they did not generate quantifiable differences in crystals sizes and orientations.¹² The addition of PBAT or PBSebT did not alter the semicrystalline features of PHBV, no shift in the position or change in the half-width of

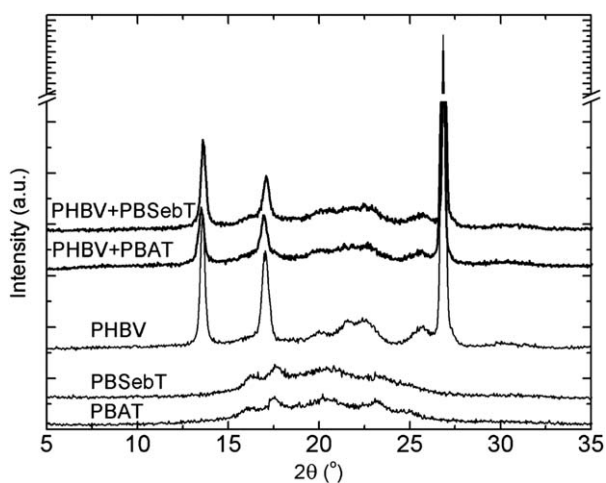


Figure 4. WAXD spectra of films blown using maximum cooling.

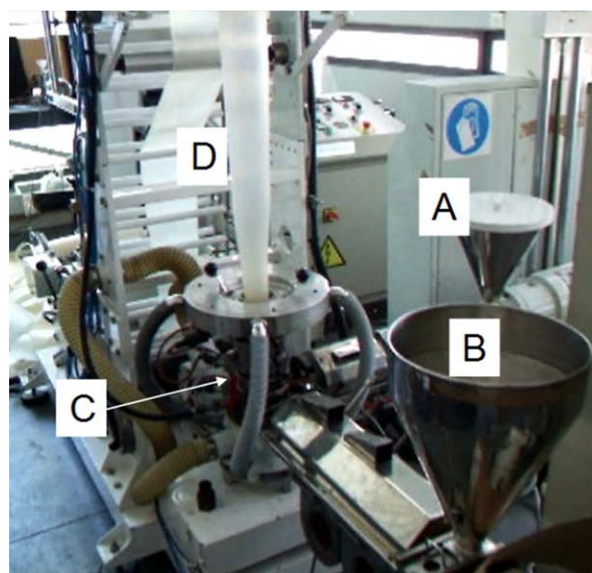


Figure 5. Film blowing of coextruded layers of PHBV and PBAT. A: extruder feeding the coextrusion tubular die (C) with the external layer. B: extruder feeding the die (C) with the internal layer. D: bilayered bubble. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Mechanical Properties (E : Young's Modulus, ϵ_B : Strain at Break) Measured in the Machine Direction (MD) and in the Transverse Direction (TD) for Films Blown from Blends, Using the indicated Cooling Conditions (Fan Aperture-Ring Aperture), BUR, and TUR

PHBV +	COOLING Fan - Ring	BUR	TUR	E (MD) (GPa)	E (TD) (GPa)	ϵ^B (MD) (%)	ϵ^B (TD) (%)
PBAT	min - min	2.4	4.3	2.0 ± 0.4	1.9 ± 0.2	7.3 ± 1.9	1.7 ± 0.1
PBAT	min - med	2.4	4.6	1.6 ± 0.2	1.8 ± 0.1	11.5 ± 3.5	2.4 ± 0.2
PBAT	min - max	2.4	4.7	1.9 ± 0.1	1.6 ± 0.1	8 ± 2.8	1.7 ± 0.1
PBAT	med - min	2.4	5.3	2.2 ± 0.2	1.6 ± 0.2	16.1 ± 8.1	1.4 ± 0.2
PBAT	med - med	2.4	4.7	2.3 ± 0.2	1.9 ± 0.2	5.2 ± 1.2	2.7 ± 0.3
PBAT	med - max	2.4	5	2.5 ± 0.3	1.7 ± 0.2	4.5 ± 1	2.2 ± 0.2
PBAT	max - min	2.5	5.3	2.7 ± 0.3	2.0 ± 0.2	7.2 ± 2.8	1.3 ± 0.1
PBAT	max - med	2.4	5.8	2.2 ± 0.2	1.6 ± 0.2	9.9 ± 2.3	1.7 ± 0.2
PBSebT	min - min	2.5	4.9	2.2 ± 0.1	1.7 ± 0.1	1.7 ± 0.1	1.1 ± 0.1
PBSebT	min - med	2.3	4.6	2.2 ± 0.1	1.9 ± 0.1	2.3 ± 0.2	1.8 ± 0.1
PBSebT	min - max	2.5	5.4	2.1 ± 0.1	1.9 ± 0.1	2.7 ± 0.2	1.9 ± 0.2
PBSebT	med - min	2.5	4.6	2.0 ± 0.2	1.7 ± 0.1	2.8 ± 0.3	2.1 ± 0.1
PBSebT	med - med	2.3	4.9	2.2 ± 0.2	1.7 ± 0.1	1.5 ± 0.1	1.3 ± 0.1
PBSebT	med - max	2.3	4.3	2.2 ± 0.2	1.9 ± 0.1	1.5 ± 0.1	0.9 ± 0.1

peaks assigned to PHBV having been inferred from the spectra displayed in Figure 5. All films exhibited crystallinities ranging from 40 to 42% for all operating conditions tested. This is not surprising, as the blends exhibited similar rheology and phase separated morphology. Films blown from PBAT or PBSebT under similar conditions showed 10% and 8% crystallinity, respectively, whereas PHBV films had crystallinities varying between 55 and 61%. Consequently, WAXD data demonstrates that the addition of PBAT or PBSebT to PHBV does increase the amorphous portion of the films while maintaining the crystalline form of PHBV, which is consistent with the blends phase separation. Phase separation in blends of PHBV with PBAT has indeed been established elsewhere by thermomechanical characterization, which showed the existence of two distinct glass transition temperatures corresponding to the transition of each component.^{22,23} Similar characterization would help here supporting the phase separation suggested by WAXD data and DSC for blends of PHBV with PBSebT.

The mechanical properties of films blown from blends are compiled in Table II. A small mechanical anisotropy (compare Young's moduli, E , and strain at break, ϵ_B , in MD and TD) was achieved for larger values of BUR and TUR, with the strain at break of PHBV+PBAT films showing the largest difference. This is due to the fact that a PBAT film blown under similar conditions had a Young's modulus of 0.1 and 0.095 GPa in MD and TD, respectively, whereas the strain at break reached 741 and 945 in the MD and TD, respectively. Conversely, PBSebT films were almost isotropic (modulus of 0.108 GPa and 0.112 GPa, strain at break of 934% to 988% in the MD and TD, respectively). All films from blends showed comparable mechanical properties, which are essentially ruled by the PHBV matrix. Indeed, PHBV films blown with similar BUR, TUR, and bubble cooling conditions showed isotropic Young's modulus of 2.7–3.2 GPa and strain at break of 1.2–1.6%. It is interesting to note that the MD strain at break of films made from

PHBV+PBAT are higher than those of all other films, thus either suggesting that PBAT acts as a plasticizer that allows for more intense stress-induced orientation, or that interfacial

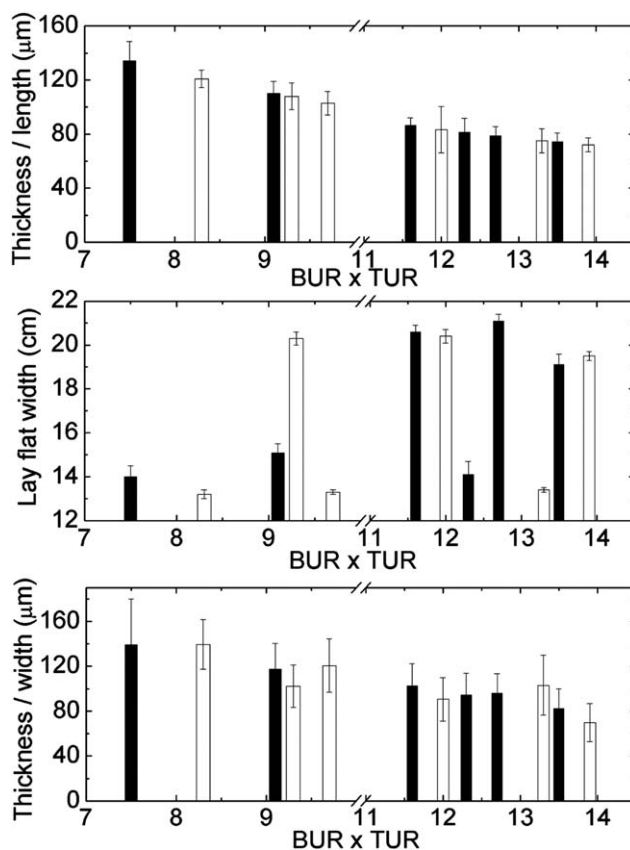


Figure 6. Thickness variations along the film width (bottom) and length (top) and bubbles lay flat width (middle) for coextruded blown films. Black columns: PHBV is the external layer. White columns: PBAT is the external layer. Error bars have the same meaning as in Figure 3.

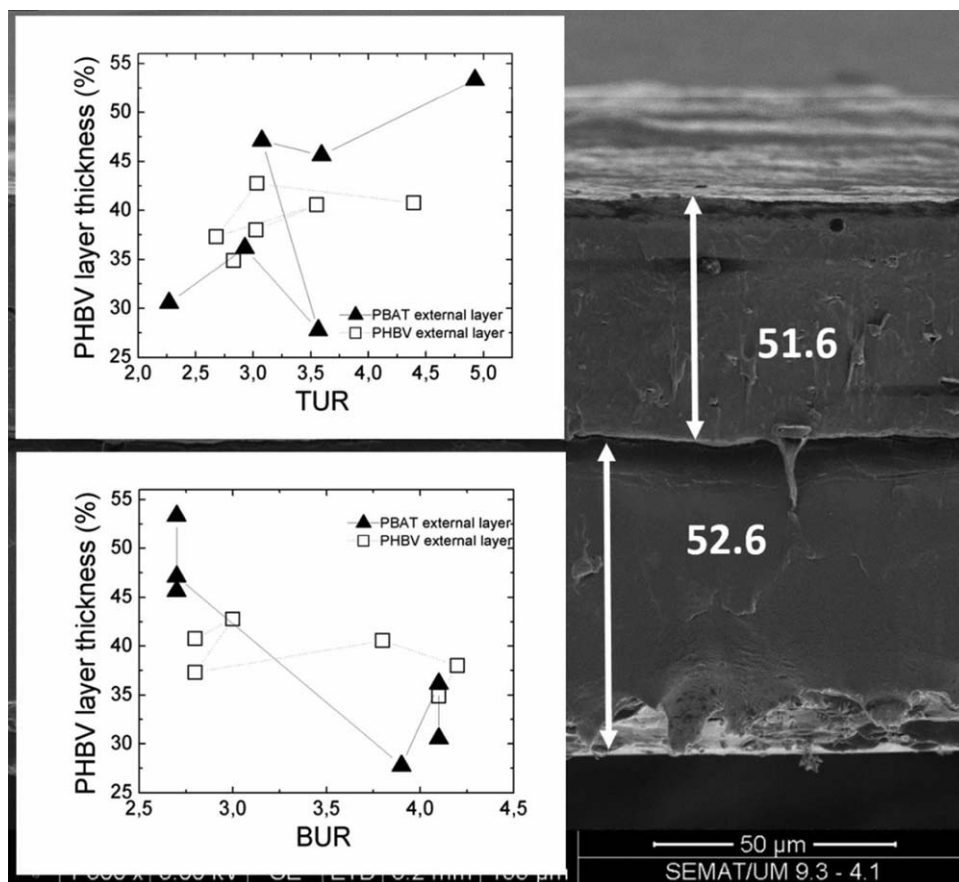


Figure 7. SEM micrograph of a bi-layered film blown with $TUR = 4.1$ and $BUR = 2.3$ with PBAT as external layer. Numbers indicate the respective layer thickness in microns (PHBV layer is the thicker one). Insets: BUR and TUR dependences of PHBV relative layer thickness for films using PBAT (solid symbols) or PHBV (open symbols) as external layer.

phenomena are at play and that a simple mixing rule cannot explain the mechanical data of the films blown from blends. The plasticizing effect of PBSeBT was less evident as the Young's moduli of corresponding films were only slightly smaller than those of the PHBV films mentioned above, while strain at break remained essentially unaffected.

Coextruded Bilayered Films

Since PHBV+PBAT blends were easier to process within the range of cooling parameters studied, PBAT was chosen for the manufacture of bilayered films by coextrusion. Both AB and BA layer configuration were produced (where A and B denote the material of each layer). Figure 5 shows the laboratorial film blowing line configured for the coextrusion of PHBV fed in extruder A with PBAT fed in extruder B. In this mode, a AB bilayered film is blown resulting in an external layer of A (PHBV) and an internal layer of B (PBAT).

The effects of the operating parameters on the films lay flat width and thickness are illustrated in Figure 6. The narrow processing window of coextruded layers did not allow for the blowing of AB and BA films with exactly the same product of BUR by TUR. Overall, coextrusion film blowing was easier than equivalent extrusion film blowing of the blends, thickness variations of $\sim 5\%$ in MD having been achieved, which corresponds to half the value obtained when extruding the blend under the

same condition. While film thickness was independent of layer configuration (AB or BA), larger variations of the film lay flat width were measured when PHBV is the outer film layer (compare the error bars of the columns in the central chart). This indicates that a more stable bubble is achieved when PBAT is the outer layer, possibly due to a higher, more consistent, melt resistance. Error bars in the bottom chart of Figure 6 are larger than those in the top graph, thus meaning that films were more uniform along the MD, regardless of the layer configuration. Figure 6 also indicates that a correlation exists between the film thickness and the draw down ratio (product of BUR by TUR) used to stretch the bubble.

In most films, the PHBV layer accounted for 30–47% of the total film thickness (see Figure 7). Thicker PHBV layers were produced when using low BUR and high TUR (a PHBV layer reaching 53% of the total film thickness was produced using PBAT as external layer, minimum BUR, and maximum TUR - see SEM micrograph in Figure 7).

SEM imaging also indicates poor adhesion between PHBV and PBAT layers, since delamination frequently occurs during the cutting of film samples for testing. This poor adhesion was also responsible for the peculiar stress–strain curves recorded during tensile tests of the films, as illustrated in Figure 8. The PHBV layer broke first, at low strain (around 2%, which correlates

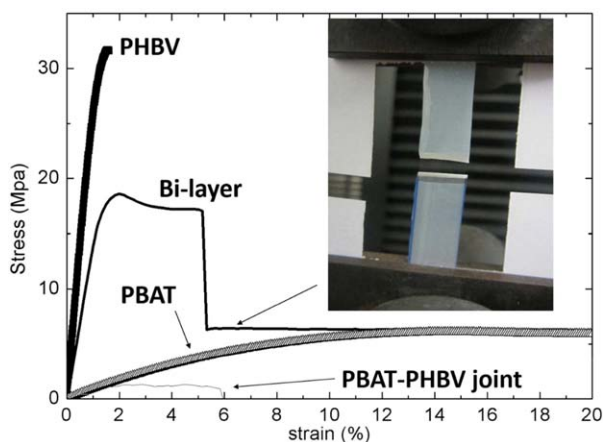


Figure 8. Stress–strain curves of a bi-layered film blown with $TUR = 4.4$ and $BUR = 2.8$ using PBAT as external layer, of a PHBV film ($TUR = 5$, $BUR = 2.5$), of a PBAT film ($TUR = 5.8$, $BUR = 2.7$) and of a PBAT film welded to a PHBV film (PBAT-PHBV joint). All films were obtained using similar cooling conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

well with the break-up of a PHBV film, see the curve with solid symbols), thus creating a local maximum in the stress, followed by a first short plateau and by a sudden drop in stress. The strain at which this drop occurred coincided with the break-up of a welded joint of a PBAT film with a PHBV film (see thin

line corresponding to the mechanical testing of the welded film). Therefore, the drop in stress of the bi-layered film can be assigned to the adhesive failure between the two materials. As the PHBV layer delaminated (see photo in Figure 8, taken during the tensile test, where the more transparent PBAT layer showed up as the delaminated yellowish PHBV layer is broken), a second stress plateau appeared. The range of strains of the latter coincided well with the drawing stage of a PBAT film being tested at the same crosshead speed (see corresponding stress–strain curve for a PBAT film in Figure 8). Eventually, the PBAT layer broke at a strain corresponding to values measured for PBAT films (see Figure 9).

Changes in operating parameters, namely BUR, TUR, and layer configuration had no tangible impact on the mechanical properties of the coextruded films (see results in Figure 9 for both Young's modulus and strain at break measured in the machine direction). A similar conclusion had already been taken for the extrusion of blends and was mostly attributable to the limited allowable range of variation of BUR and TUR.

Comparison of Films Properties

Besides requirements common to nonfood packaging applications (e.g., regarding transparency and mechanical properties), food packaging films are generally required to provide an adequate barrier to gases (mostly CO_2 , O_2 , and water vapor) and to be made from materials approved for food contact.²⁴ A selection of properties that are pertinent for food packaging

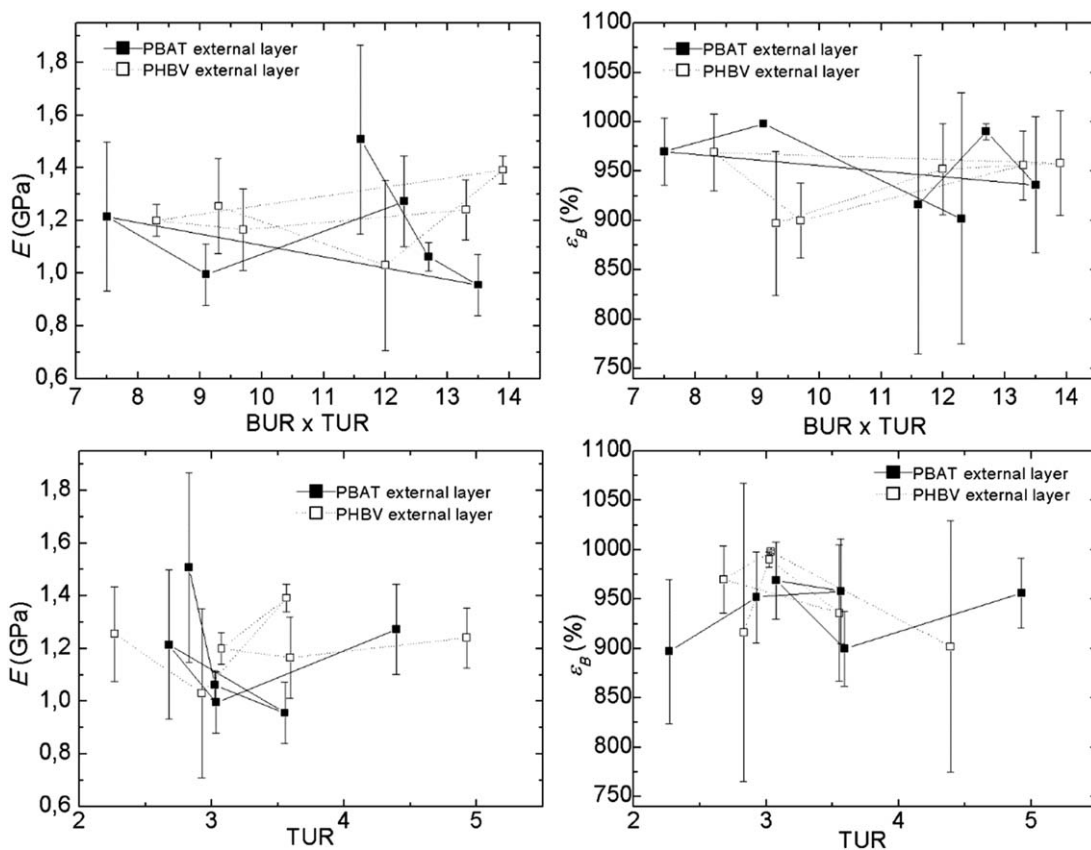


Figure 9. Mechanical properties (Young's modulus, E and strain at break, ϵ_B) of bi-layered films blown using the indicated TUR and BUR. Solid symbols: films blown using PBAT as external layer. Open symbols: films blown using PHBV as external layer.

Table III. Range of Properties of Films Produced with Varying BUR, TUR, and Bubble Cooling Conditions during Film Blowing of PHBV, of PHBV Blended with PBAT (PHBV+PBAT), of PHBV Blended with PBSebT (PHBV+PBSebT) and of Coextruded Layers of PHBV and PBAT (PBAT/PHBV for PBAT as External Layer and PHBV/PBAT for PHBV as External Layer)

Property	PHBV	PHBV+PBAT	PHBV+ PBSebT	PBAT/PHBV	PHBV/PBAT
Total transmittance (%)	73–77	73 – 78	75–79	73 – 80	75 – 80
Tear resistance (N)	2.0–2.2	3.0–3.4	2.7–2.9	7.4–11.6	5.2–7.3
WVP (10^{-11} g m/(m ² s Pa))	0.8–1.7	1.4–1.8	1.4–1.9	1.1–2.3	1.0–4.2
<i>E</i> (GPa)	0.5–1.1	0.9–1.1	0.6–0.7	0.35–0.7 ^a	0.3–0.54 ^b
ϵ_B (%)	1.1–1.7	8–14	7.5–8.5	11–19 ^a	358–539 ^b

WVP, water vapor permeability. The mechanical properties (*E*, Young's modulus, ϵ_B , strain at break) are those of welded layers of films (joints) measured in the machine direction.

^aPHBV welded on PHBV.

^bPBAT welded on PBAT.

applications (tear resistance, water barrier and optical transmittance) are gathered in Table III for all the films produced in this study, together with the mechanical properties of welded joints.

The latter were produced by sealing one film on the other using a thermal sealer as described in the experimental section. Overall, the table demonstrates that coextrusion of single materials brought benefits relative to the extrusion of blends. For example, the transmittance of bilayered films had a tendency to be higher than that of monolayer films produced from blends. Indeed, the total transmittance was shifted from the range 73–78% for films blown from blends to 75–80% for the bilayered films. This is probably because the extra thermal cycle involved in melt compounding was avoided. More significantly, bilayered films could be up to 4 times more resistant to tear, provided that the PBAT layer was the one exposed to tear (the value being comparable to that of a monolayer PBAT film). Welded bilayered films could attain strains up to 500%, again if PBAT is the welded material (this is roughly half the value of the strain at break of the PBAT layer in coextruded films—see Figures 8 and 9); even a welded PHBV joint made with bilayered films had a ductility 10 times larger than that done with a PHBV film (see Table III).

The water vapor permeability (WVP) results also demonstrate the advantages of coextrusion. Values found ranged from 1.0×10^{-11} to 4×10^{-11} g m/(m² s Pa), thus allowing a better tuning of this property when compared with films blown from blends, which spanned the 1.4×10^{-11} to 1.9×10^{-11} g m/(m² s Pa) range. Since the WVP of PBAT, PBSebT, and PHBV films ranged approximately from 2.1×10^{-11} to 3.0×10^{-11} g m/(m² s Pa), 1.1×10^{-11} to 2.2×10^{-11} g m/(m² s Pa) and 0.8×10^{-11} to 1.7×10^{-11} g m/(m² s Pa), respectively, the permeability of the films produced from blends essentially matched that of PHBV. Such an outcome was anticipated, since in a phase separated morphology with emulsion like droplets, PBAT or PBSebT domains do not add any significant tortuosity to the permeant, permeability depending mostly on the PHBV matrix.

It is also interesting to benchmark the properties of the films manufactured here with those of other PHBV-based biodegradable films produced and characterized in the literature. The mechanical properties displayed in Table II are comparable with

those reported for PHA, PHB, and PHBV films made by different processes,^{8,11} including cast film extrusion,^{25,26} and compression molding.^{27,28} The films blown from blends display Young's moduli and strains at break matching those of films prepared by compression molding of PHB/poly(lactic acid) (PLA)/plasticizer blends.²⁷ Binary blends of PHB with 25–50% of poly(caprolactone), poly(butylene adipate), or poly(vinyl acetate)²⁹ revealed two-phase morphologies and yielded films with mechanical properties analogous to those presented in Table II. However, in contrast to all previous reports on PHBV-based films,^{8,11,25–29} the films presented here were produced using conventional extrusion film blowing. This process is scalable to industrial production and as such is highly attractive for the future production of biodegradable films. The mechanical properties displayed in Figure 9 for the coextruded films are significantly superior to those described for a commercial multilayered film made of PHBV and PBAT (having $E \approx 150$ MPa, and $\epsilon_B \approx 700\%$),⁷ albeit no details on processing were conveyed. In contrast to this, multilayer films of PHBV and PLA reached Young's moduli of ~ 3 GPa, but the maximum strain at break was limited to 50%.³⁰ The technology employed used layer multipliers, which is currently limited to the production of narrow films in order to guarantee acceptable layer uniformity. The film was coextruded through a 200 mm \times 1 mm flat die and then stretched in the MD down to a thickness of 200 μ m. The Young's moduli of all films blown in this study are larger than the typical values reported for film blowing grades of polyethylene.¹¹ In contrast to this, only bilayered films (PBV/PBAT and PBAT/PHBV) sustain a comparison with the strain at break of polyethylene film blowing grades.¹¹ Thus, the bilayered films produced here seem to be good candidates for replacing nonbiodegradable plastics for food packaging films. Also, the range of strains at break reported here for the bilayered films surpasses the values documented in the literature for PHBV-based films,^{7,8,11,25–30} which further justifies the choice for film blowing of coextruded layers.

The WVP values for PHBV films in Table III nicely match those known for cast extruded films produced from a commercial PHBV containing 5% HV.²⁷ Corre *et al.*²⁵ found a value 60% higher than the largest permeability in Table III, but measurements followed a different protocol and were done on cast film. The unique WVP value found in the literature for a

multilayered film of PBAT and PHBV is 25 times smaller than the WVP reported here,⁷ but no details are reported on the manufacturing process. It is also worth noting that commercial PBAT and PHBV grades are formulated with a wide scope of additives, which will impact on their performance, thus adding difficulty to benchmarking. Nevertheless, data in Table III indicate that the bilayered films produced using PBAT as an external layer show WVP values matching those of the food grade PBAT material. The WVP reported for polyethylene film blowing grades (of the order of 10^{-13} gm/(cm^2Pa)¹¹) is much lower than the WVP measured here.

CONCLUSIONS

PHBV-based films were produced by conventional extrusion film blowing, i.e., under conditions scalable to industrial production. The effects of blending with other biodegradable polymers and changing processing conditions on the films performance were studied. Within the range of processing parameters tested, blends of PHBV with PBAT showed better processability and improved film properties when compared to films blown from a blend of PHBV and PBSebT. However, the best results in terms of film properties for food packaging, namely tear resistance, WVP and sealability, were achieved by coextruding PHBV and PBAT. The mechanical characteristics (strain at break and tear resistance) of these bi-layered films match those of films blown from commercial PBAT designed for food packaging, which reached strains at break of the order of 750%. Nevertheless, the layers show poor adhesion and delamination of PHBV may occur at strains as low as 10%.

Future work will focus on improving interfacial adhesion (for instance by appending reactive groups to PHBV or PBAT using reactive extrusion prior to film blowing,³¹ or by coextruding an intermediate third layer of material which will promote adhesion), as well as in a broader characterization of the films properties.

ACKNOWLEDGMENTS

The authors acknowledge the European Commission for the financial support of the ECOefficient BIOdegradable Composite Advanced Packaging project (EcoBioCAP) within the Seventh Framework Programme (Contract-No. FP7-265669). This work was also supported by FEDER funds through the program COMPETE (project PTDC/AGR-ALI/122741/2010), by the Portuguese Foundation for Science and Technology (PEst-C/CTM/LA0025/2013 - Projecto Estratégico - LA 25 - 2013–2014 - Strategic Project - LA 25 - 2013–2014) and by Programa Operacional Regional do Norte (ON.2) through project “Matepro – Optimizing Materials and Processes”, with reference NORTE-07-0124-FEDER-000037 FEDER COMPETE.

REFERENCES

1. Petersen, K.; Nielsen, P. V.; Bertelsen, G.; Lawther, M.; Olsen, M. B.; Nilsson, N. H.; Mortensen, G. *Trends Food Sci. Tech.* **1999**, *10*, 52.
2. Haugaard, V. K.; Udsen, A.-M.; Mortensen, G.; Hoegh, L.; Petersen, K.; Monahan, F. In *Food Biopackaging, in Biobased Packaging Materials for the Food Industry—Status and Perspectives*; Weber, C. J., Ed.; A European concerted action: Copenhagen, Denmark, 2; **2001**; 45.
3. Guilbert, S.; Guillaume, C.; Gontard, N. In *Food Engineering Interfaces*; Aguilera, J. M., Simpson, R., Welti-Chanes, J., Bermudez Aguirre, D., Barbosa-Canovas, G., Eds.; Springer: New York, **2011**; 619.
4. Tang, X. Z.; Kumar, P.; Alavi, S.; Sandeep, K. P. *Crit. Rev. Food Sci.* **2012**, *52*, 426.
5. Fabra, M. J.; Busolo, M. A.; Lopez-Rubio, A.; Lagaron, J. M. *Trends Food Sci. Tech.* **2013**, *31*, 79.
6. Song, Y. H.; Zheng, Q. *Polym. Rev.* **2014**, *54*, 514.
7. Peelman, N.; Ragaert, P.; De Meulenaer, B.; Adons, D.; Peeters, R.; Cardon, L.; Van Impe, F.; Devlieghere, F. *Trends Food Sci. Tech.* **2013**, *32*, 128.
8. Doi, Y. *Microbial Polyesters*, VCH Publishers: New York, **1990**.
9. Serafim, L. S.; Lemos, P. C.; Albuquerque, M. G. E.; Reis, M. A. M. *Appl. Microbiol. Biotechnol.* **2008**, *81*, 615.
10. Morgan-Sagastume, F.; Valentino, F.; Hjort, M.; Cirne, D.; Karabegovic, L.; Gerardin, F.; Johansson, P.; Karlsson, A.; Magnusson, P.; Alexandersson, T.; Bengtsson, S.; Majone, M.; Werker, A. *Water Sci. Technol.* **2014**, *69*, 177.
11. Plackett, D.; Siro, I. In *Multifunctional and Nanoreinforced Polymers for Food Packaging*; Lagaron, J. M., Ed.; Woodhead Publishing Limited: UK, **2011**; 498.
12. Cunha, M.; Berthet, M.-A.; Pereira, R.; Covas, J. A.; Vicente, A. A.; Hilliou, L. *Polym. Compos.* **2014**, doi: 10.1002/pc.23093.
13. Ha, C.-S.; Cho, W.-J. *Prog. Polym. Sci.* **2002**, *27*, 759.
14. Yu, L.; Dean, K.; Li, L. *Prog. Polym. Sci.* **2006**, *31*, 576.
15. Modi, S.; Koelling, K.; Vodovotz, Y. *J. Appl. Polym. Sci.* **2012**, *124*, 3074.
16. Russo, P.; Vetrano, B.; Acierno, D.; Mauro, M. *Polym. Compos.* **2013**, *34*, 1460.
17. Carneiro, O. S.; Reis, R.; Covas, J. A. *Polym. Test.* **2008**, *27*, 527.
18. McHugh, T. H.; Avena-Bustillos, R. J.; Krochta, J. M. *J. Food. Sci.* **1993**, *58*, 899.
19. Guillard, V.; Broyart, B.; Bonazzi, C.; Guilbert, S.; Gontard, N. *J. Food. Sci.* **2003**, *68*, 2267.
20. Leroy, E.; Petit, I.; Audic, J. L.; Colomines, G.; Deterre, R. *Polym. Degrad. Stab.* **2012**, *97*, 1915.
21. Hatzikiriakos, S. G., Migler, K. B., Eds. *Polymer Processing Instabilities: Control and Understanding*; Marcel Dekker: New York, **2005**.
22. Javadi, A.; Kramschuster, A. J.; Pilla, S.; Lee, J.; Gong, S.; Turng, L.-S. *Polym. Eng. Sci.* **2010**, *50*, 1440.
23. Nagarajan, V.; Misra, M.; Mohanty, A. K. *Ind. Crop. Prod.* **2013**, *42*, 461.
24. Berthet, M.-A.; Angellier-Coussy, H.; Machado, D.; Hilliou, L.; Staebler, A.; Vicente, A.; Gontard, N. *Ind. Crop. Prod.* **2015**, *69*, 110.
25. Corre, Y.-M.; Bruzaud, S.; Audic, J.-L.; Grohens, Y. *Polym. Test.* **2012**, *31*, 226.

26. Thellen, C.; Coyne, M.; Froio, D.; Auerbach, M.; Wirsen, C.; Ratto, J. A. *J. Polym. Environ.* **2008**, *16*, 1.
27. Abdelwahab, M. A.; Flynn, A.; Chiou, B.-S.; Imam, S.; Orts, W.; Chiellini, E. *Polym. Degrad. Stab.* **2012**, *97*, 1822.
28. El-Hadi, A.; Schnabel, R.; Straube, E.; Muller, G.; Henning, S. *Polym. Test.* **2002**, *21*, 665.
29. Kumagai, Y.; Doi, Y. *Polym. Degrad. Stab.* **1992**, *36*, 241.
30. Boufarguine, M.; Guinault, A.; Miquelard-Guinier, G.; Sollogoub, C. *Macromol. Mater. Eng.* **2013**, *298*, 1065.
31. Thellen, C.; Cheney, S.; Ratto, J. A. *J. Appl. Polym. Sci.* **2013**, *127*, 2314.