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Monolayer films from poly(lactic acid) PLA/poly(3-hydroxybutyrate-*co*-hydroxyvalerate) PHBV blends for food packaging applications

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Abstract. Four out of twelve different formulations consisting of poly(lactic acid) (PLA), poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV), triethyl citrate (TC), and epoxy-functionalized styrene acrylate (ESA) components were selected based on their superior elongation at break, rheological properties, and composition range from other batches. Each batch was made into a monolayer thin film via a blown film extrusion process. The films' mechanical, oxygen gas, and moisture barrier and aesthetic properties were measured. The findings paved the understanding for developing biodegradable packaging to extend the shelf life of oxygen and moisture-sensitive food products. The results proved the significance of systematic analysis of the interacting effects of components' mixing ratios on different properties of the blend. The produced films' oxygen gas and moisture barrier properties showed significant improvement compared to neat PLA; however, still more than neat PHBV.

1. Introduction

The packaging sector is the biggest global consumer of petroleum-based plastics and the largest contributor to global plastic waste [1]. It is determined that about 45% of the plastic packaging waste is used for food packaging [2]. This has led to a surge in research in the past decade in bio-based and biodegradable polymers to substitute petroleum-based plastics and offers a more sustainable production and waste solution for food packaging [1, 3]. The shelf life of plastic-packaged food products is specifically short due to the short shelf life of food products. Oxygen gas and moisture are particularly the two key factors influencing the shelf life of food. Curbing the diffusion of oxygen and moisture in packaging is essential to limit the initiation of biochemical spoilage reactions and microbial growth in packaged food. In

order to achieve this goal, the factors affecting the solubility coefficient and diffusion of the packaging must be carefully considered. These factors include the processing method, chain orientation, degree of crystallinity of the polymers, and the size and shape of the penetrant. However, most of these factors are not in favor of bio-polymers; for instance, the slow crystallization rate and narrow processing window; hence most bio-polymers suffer from poor barrier properties [1].

Poly(lactic acid) (PLA) and poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) are two of the most produced bio-based and biodegradable polymers recently being employed in food packaging. PLA is an aliphatic polyester that can be derived via fermentation and chemical reactions from sustainable resources such as corn starch, cassava, potato starch,

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rice, or sugar [4]. PLA is widely used in packaging as film and coating [5]. Similar to most biopolymers, PLA has its shortcomings. Slow crystallization rates, high brittleness, and poor barrier properties to gases such as oxygen, water vapor, and different aromas urge PLA to be blended with other polymers and additives to amend its properties to be more suitable for food packaging applications [6]. PHBV is a subset of polyhydroxyalkanoates (PHAs) and the copolymer of polyhydroxy butyrate (PHB)-hydroxyvalerate (HV) with significant ductility improvement over PHB polymer. PHAs are produced mostly from batch fermentation of bacteria and algae [7–9].

Many studies have been conducted on blends of PLA with PHAs at different mixing ratios, processing conditions, and for different applications. This is due to the synergistic effect as well as complementary properties [10–16] of these two polymers in the final blend. Table 1 summarises the properties of PLA and PHBV that are most important for food packaging applications.

Employing PLA and PHAs in flexible food packaging is specifically challenging due to the processing difficulties such as narrow processing windows and the brittleness of final products. Researchers employed different manufacturing methods to utilize PLA-PHAs combination in films. Some of the most notable works include solvent casting [26], compression molding [27, 28], and cast extrusion [29]. Guinault *et al.* [30] manufactured a multi-layer sheet composite via a coextrusion process with a total PLA:PHBV ratio of 90:10. The films' ductility was improved compared with neat PLA. The gas barrier properties of the films were also improved due to an increase in the crystallinity of the blend, which was corroborated by the observance of 'numerous long,

thin crystallized lamellae' of PHBV in the layered composite. However, for comparison, the cooling time of final products in sheet extrusion (about 4 min) is significantly longer than for the blown film extrusion (about 10 s). This influences the molecular arrangement and degree of crystallinity, leading to higher barrier properties in sheet extrusion compared to blown film extrusion.

Hernández-García *et al.* [28] manufactured 75:25 ratio PLA-PHBV monolayer blends consisting of 15 wt% polyethylene glycol (PEG)/polymer mass and antimicrobial compounds via extrusion blending and compression molding. This study focused mostly on end-of-life options and active biodegradation of the blends, assuming the mixing ratio of the polymers and additives is suitable for food packaging applications. However, it was found earlier that the component contents can significantly affect the mechanical properties of the final blends. The closest research to the present study is the study done by Pietrosanto *et al.* [31] where monolayer blown-extruded films were manufactured from a melt-blended mixture of PLA:PHB ranging from 60:40 to 80:20 wt% without employing plasticizers. The resulting films showed an increase in ductility of the films and the degree of crystallization of PLA, hence, an improvement in barrier properties of the final films.

The significance of the present study is due that many papers reported a synergistic elongation at break increase from 250 to 5750% for PLA:PHBV blends with the ratio of 70:30 to 90:10 wt% [32–35], however, no studies have systematically investigated the interactive effect of each mixing component on the properties of the blend. We systematically explored this synergistic elongation effect region for the first time by defining a Mixture Design and identifying

Table 1. Summary of the most important properties of PLA and PHA for food packaging applications, adapted from [1, 3, 17–25].

Property/Polymer		PHAs	PLA
Elongation at break	[%]	1.4 to 5.5	0.5 to 9.2
Tensile strength	[MPa]	20 to 40	37 to 66
Glass transition temperature	[°C]	−9 to 9	55
Chemical resistance		Poor	Poor
Transparency		Medium	High
Water absorbance	[%]	0.7	3.1
Oxygen gas permeation (OP)	[cc·mil/(m^2·day·atm)]	8 (23 °C, 85%) 85 (23 °C, 0%) 230 (25 °C, 80%)	132–590 (23 °C, 0% or 50%)
Water vapor permeation (WVP)	[g·mil/(m^2·day·kPa)]	106 (23 °C, 50%) 30 (25 °C, 100%) 26 (37.8 °C, 100%)	63–342 (23 °C, 85%)

the most effective responses [36]. Four mixing compositions out of twelve were chosen to be processed into monolayer thin films based on their better exhibiting mechanical properties, rheological properties, and composition differences. The present paper studies the mechanical, barrier, and aesthetic properties of these films to understand and develop biodegradable flexible packaging based on PLA/PHBV blends for application in food products.

2. Materials and methodology

2.1. Materials

The PHBV and PLA polymer grades with the minimum difference in melting temperature were selected to minimize the chance of immiscibility of the blend. For PHBV, the polymer grade of ENMAT thermoplastic resin was supplied by TianAn Biopolymer (Ningbo, China) with $T_m = 180\,°C$ and MFI = 8–15 g/10 min, 180 °C, 2.16 kg). For PLA, Ingeo Biopolymer 2003D was supplied by NatureWorks (Minnesota, USA) with $T_m = 160\,°C$, MFR = 6 g/10 min, 210 °C, 2.16 kg), and D-lactide content of 4.3%. This grade is suggested by the manufacturer as a grade used as part of a formulated blend. Triethyl citrate ($C_{12}H_{20}O_7$) (CAS-No 77-93-0), liquid state at room temperature, was used as a plasticizer with a molecular weight of 276.28 g/mol and supplied by Sigma Aldrich (Milwaukee, USA). An epoxy-functionalized styrene acrylate chain extender (Joncryl ADR 4468) was supplied by BASF, Singapore. Based on the supplier's claim, this polymeric chain extender reacts specifically with polycondensation polymers such as PLA and is used specifically for food contact applications. All materials were used as received without any treatment or modification.

2.2. Methodology

High values of melt strength and elongational viscosity of a polymer blend at molten state are the prerequisites for maintaining a stable bubble during the blown film extrusion process [37]. On the other hand, flexible packaging made via blown extrusion normally has high elongation at break values (>500%). Hence, a chain extender was added to the blend to improve the melt strength of the blend. Plasticiser was added to the blend to improve the elongation at break and boost the synergistic elongational effect of the blends. Mixture Design statistical analysis was employed to consider the synergistic elongation effect between the PLA/PHBV blend components
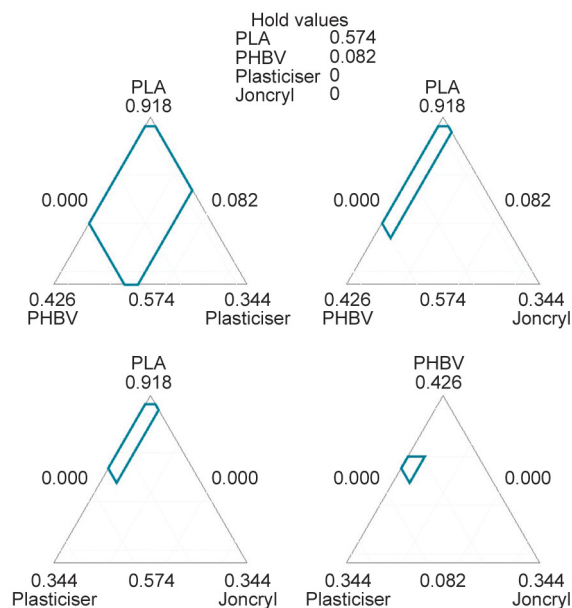

Figure 1. The material components simplex design plots [36].

within the 70/30 to 90/10 mixing ratios. PLA, PHBV, TC, and ESA were chosen as mixing components. Elongation at break and elongational viscosity were chosen as response surfaces to be maximized. A more thorough description of the statistical analysis could be found in our earlier work [36]. Figure 1 shows the simplex design plots of the mixing component. The extreme vertices design in a quadratic model with linear constraints of 0.82 < PLA + PHBV < 0.95 was considered.

Rheological results and trial tests showed that all twelve blends could be processed into blown films. However, the mechanical properties tests showed that batches 2, 3, 9, 10, 11, and 12 have the highest elongational strain values (near 200%). These blends all contained the highest plasticizer contents. Among these six candidate batches, batches 2, 3, 10, and 12 were chosen for blown film extrusion. This is because these batches contain a range of high and low PLA, PHBV, and ESA contents which would provide sufficient data for understanding the effect of component ratios on the properties of the final films. The material contents of selected batches for the blown film extrusion process are shown in Table 2.

Table 2. The weight percent materials of testing batches based on extreme vertices design in a quadratic model Mixture Design.

Batch	PLA	PHBV	Triethyl citrate	Joncryl
2	76.8	8.2	15	0
3	73.8	8.2	15	3
10	57.4	27.6	15	0
12	57.4	24.6	15	3

2.2.1. Sample manufacturing

The virgin PLA and PHBV pellets were subjected to a drying process at a temperature of 90 °C for 3 hours, which resulted in a moisture content of less than 0.025% (250 ppm). The PLA, PHBV, and ESA were premixed and then fed to the extruder through the hopper at a constant feeding speed. The TC was added to the extruder through a tube that was connected to a multi-syringe liquid pump (Cole-Parmer, IL, USA) equipped with a 60 ml syringe. Chain extenders are compounds with low molecular weight and bifunctional groups which have been reported to increase the molecular weight of biopolymers such as PLA and PHBV by engaging in a rapid reaction such as reacting with terminal alcohol groups in polyesters [38, 39]. The extrusion process was carried out using a co-rotating twin screw extruder (Labtech, Samut Prakan, Thailand) with an *L/D* ratio of 40:1, screw diameter of 25 mm, rpm of 75 and temperature profile of 160–180–185–190–185–180 °C for the different extrusion zones. The extruded filaments were then cooled down using an air-powered conveyer and wound onto filament spools. Some of the filaments were separated and used as a test sample for further mechanical tests. The remaining filaments were pelletized using an automatic pelletizer (Labtech, Samut Prakan, Thailand) to produce samples for rheological studies.

To manufacture monolayer film, the collected pelletized polymer blends were fed to a single screw blown film extrusion machine (Friend Machinery, Zhangjiagang, China) with an *L/D* ratio of 25, screw diameter of 25 mm and annular die diameter of 42 mm at rpm of 19 and heating profile of 170 °C for all zones. The blown film made from each batch was collected at the end of the machine via a mechanized thin film roller.

A set of compression molded films were manufactured to draw a comparison with blown film extruded samples. These samples were extruded, blended, and pelletized, similar to the rest. The blends were compression molded in the following sequence: The blend pellets (nearly 10 grams) were placed in the center of an aluminum frame with a thickness of 0.1 mm. Using a hydraulic press (Labtech, Samut Prakan, Thailand), the pellets were preheated to 180 °C at the point of contact of upper and lower heating plates for 4 min so that all pellets were molten and evenly spread across and within the frame. The molten materials were compressed for 1 min at 160 bar and then cooled to room temperature. The cooling time was set to 4 min. The compression molded samples were used only in oxygen transmission rate due to test limitations involved with water vapor permeability and mechanical properties.

2.2.2. Mechanical properties characterization

Tensile strength and elongation at break
Tensile strength, Young's modulus, and elongation at break of blown film samples were tested in both machine directions (MD), complying with ASTM D882-18 standard. The tests were conducted via a universal tensile testing machine (Instron 5567, Instron, Massachusetts, USA). A set of rubber-lined grips were used to hold the thin films in place. Strips of uniform thickness with a width of 15 mm were cut as test samples. An initial grip separation of 250 mm and a grip separation speed of 25 mm/min were used to determine the modulus of elasticity. To determine tensile strength, the initial grip separation was changed to 50 mm and crosshead speed to 500 mm/min.

Tear resistance
Tear-propagation resistance of the blown films was measured via the single-tear or trouser tear method based on ASTM D1938-19 standard via a universal tensile testing machine (Instron 5567, Instron, Massachusetts, USA). Sets consisting of at least five samples of 25×75 mm with the same thickness (varied between batches) were tested in both machine and transverse directions. The grip-separation speed was set to 250 mm/min. The test was continued until the tear was propagated through the entire unseparated part. A load [N] *vs.* time [s] graph was produced for each test. An average tear propagation force was calculated based on the films' performances. The initial force and maximum load point were used for highly extensible samples. For the non-extensible samples, the load was averaged over a 25.4 mm interval, disregarding the final and initial parts of the graph.

2.2.3. Barrier properties

Oxygen gas transmission rate
The oxygen gas transmission rate (O_2GTR) of the blown extruded films was measured by MOCON OX-TRAN® 2/10 (MN, USA) according to the ASTM F1927 standard. The tests were conducted at a recommended 10 sccm steady-state flow for oxygen gas (test gas), 0% relative humidity level for both the test gas and the carrier gas, and at a testing temperature

of 23 °C. In this test, the oxygen molecules permeate through the film, transporting them via a mixture of 98%-nitrogen/2%-hydrogen gases (carrier gas) to the coulometric device. The coulometric device generates a linear output as predicted by Faraday's law. In principle, four electrons are produced by the detector for each molecule of oxygen that passes through it. The amount of permeated oxygen was determined proportionately to the generated electric current. All test samples were cut via a 13 cm diameter annular cutting die to minimize the possible error due to variations of the area between the unmasked section of the samples. Each result was obtained from an average value from at least three samples. Samples were conditioned for 3 hrs before the tests. Conditioning in this test denotes the following sequence:

1. Before a measurement is taken, the samples are placed in the testing cell.
2. Test gas flows into the test cell, and oxygen molecules permeate the testing sample so that the sample reaches an equilibrium state with the testing condition.

The testing area of each film was 50 cm². Each film took 10 testing cycles, each cycle being 30 min, and the final permeation value was measured when the oxygen transmission rate (OTR) reached a constant level. To ensure that the coulometric sensor indicates the correct value for each specimen, the sensor was calibrated via the National Institute of Standards and Technology (NIST) certified calibration film with the O_2GTR of 0.198700 cc·mil/(pkg·day). The O_2GTR and permeance (PO_2) were determined as Equations (1) and (2):

$$O_2GTR = \frac{E_e - E_0}{A} \tag{1}$$

$$PO_2 = \frac{O_2GTR}{P} \tag{2}$$

where E_e is the steady state O_2GTR level [cc·mil/(m²·day·atm)], E_0 is zero O_2GTR level [cc·mil/(m²·day·atm)], A is specimen area [m²] and P is the partial pressure of oxygen [atm], the mol fraction of oxygen multiplied by the total pressure (nominally, one atmosphere) in the test gas side. The partial pressure of O_2 on the carrier side is zero.

Water vapor transmission rate

The water vapor transmission rate (*WVTR*) test was carried out based on ASTM E96/E96M-16 standard.

All the samples were cut via a 70 mm diameter annular cutting die to minimize the possible measurement error by keeping the exposed section of all samples equal, hence normalizing the passage of water vapor from outside the mouth section of the test vessels for all test specimens. Distilled water was poured into the light test vessels to a level of 20 mm from the specimen. Test dishes were placed in a controlled environment chamber with relative humidity maintained at 50% and temperature at 23 °C for a period of two months. The test assemblies were weighed once a day during this period to determine the rate of water vapor movement through the test films. To cancel out the possible adverse effect of the environment on the test dishes, an aluminum-foil-covered dish and an empty dish (a dummy unit) were also periodically weighed. The aluminum-foil-covered dish indicated the water that escaped through the water-repelling-grease used as a sealant for each test assembly. The empty dish indicated the weight changes of the test dish due to atmospheric conditions. An analytical balance sensitive to 0.0001 g was used for weighing. Water vapor transmission and permeance were calculated as Equation (3):

$$WVT = \frac{G}{t \cdot A} \tag{3}$$

where G is a weight change [g], t is time [h], G/t is the slope of the straight line [g/h], A is the test area or the cup mouth area [m²] and *WVT* is the rate of water vapor transmission rate [g/(h·m²)] (Equation (4)):

$$\text{Permeance} = \frac{WVT}{\Delta p} = \frac{WVT}{S(R_1 - R_2)} \tag{4}$$

where Δp is a vapor pressure difference [mmHg, $1.333 \cdot 10^2$ Pa], S is saturation vapor pressure at test temperature [mmHg, $1.333 \cdot 10^2$ Pa], R_1 is relative humidity at the source expressed as a fraction in the dish, and R_2 is relative humidity at the vapor sink expressed as a fraction. Average permeability was calculated as Equation (5):

$$\text{Average permeability} = \text{Permeance} \cdot \text{Thickness} \tag{5}$$

The Equation (6) is used to correct the excess *WVT* due to edge masking:

$$\text{Percent excess } WVT = \frac{400t}{\pi S_1} \ln \frac{2}{1 + e^{-\frac{2\pi b}{t}}} \tag{6}$$

where t is specimen thickness [m], b is the width of masked edge [m], and S_1 is four times the test area divided by the perimeter [m].

3. Results and discussion
3.1. Mechanical properties

Four batches out of twelve were chosen to be processed into thin films. Although more than four blends had the capability to be filmed, however batches 2, 3, 10, and 12 were selected to provide the widest diversity of compositional content. For instance, the material contents in batch 9, which was also capable of being blown filmed, are close to batch 10. Hence batch 9 was omitted. This method was chosen to minimize the number of tests and identify the major differences in properties for the selected samples. If one sample is identified as best performing, the batches with close material contents would subsequently be investigated.

It is known that the mechanical properties of PLA/PHBV blend near 70:30 to 90:10 mixing ratio undergo a significant decrease within a month [32]. To consider this behavior, the manufactured films were stored in a freezer overnight, and the mechanical properties characterization was completed within 24 hrs of the processing time. Figure 2 shows the average tear propagation force obtained by the trouser tear resistance test for the four chosen blown film extruded samples. Upon initial inspection, it is observed that the tear propagation force is higher for the samples in the transverse direction compared with the sample where the slit is in the machine direction. It is commonly known that due to the existing shear forces in the extrusion barrel, polymer molecules tend to align along the length of the barrel to die direction,

also known as the machine direction. Hence the polymer molecules are more intertwined in the machine direction than in the transverse direction. This means propagating the tear from a slit created in the structure of the processed film; it requires more force when the slit direction is perpendicular to the machine direction than when it is parallel to it.

Although in the blown film extrusion process, the bubble stretches the polymer in a transverse direction hence providing molecular orientation in the transverse direction, however, the polymer orientation would depend on both the blow-up ratio (BUR) and draw-down ratio (DDR). The BUR is the ratio of the final diameter of the tube to the diameter of the die, and the DDR is the ratio of the thickness of the extrudates exiting the die, *i.e.*, the die gap to the final film thickness. Table 3 presents the BUR and DDR of the processed films.

The significant tear propagation force difference between Samples 2 and 3 could be attributed to the presence of a joncryl chain extender in Sample 3. The formation of longer PLA and PHBV polymer chains due to chain extension could be associated with the increase of the chance of molecular intertwining, hence increasing the force required to break the intermolecular van der Waals forces via tearing. This effect is also visible in comparison of Samples 10 and 12, where it takes more force to tear Sample 12 (containing a 3% chain extender) in the transverse direction than to tear Sample 10 (containing no chain extender). It also can be seen that all blends have tear propagation force values at least 4.4 and 5.0 times the virgin PLA in the machine direction and transverse direction, respectively. This is a significant improvement to PLA, providing value to the produced films regarding packaging products that require tear propagation forces higher than virgin PLA. The addition of PHBV and plasticizer, specifically, adds to the ductility of PLA, rendering it more tear resistant. Figure 3 presents the obtained yield strength, ultimate tensile strength, and modulus of the films from the uniaxial tensile strength test. It is observed that Sample 2 has a significantly higher (3.6 times higher) modulus than Sample 3, and similarly, Sample 10
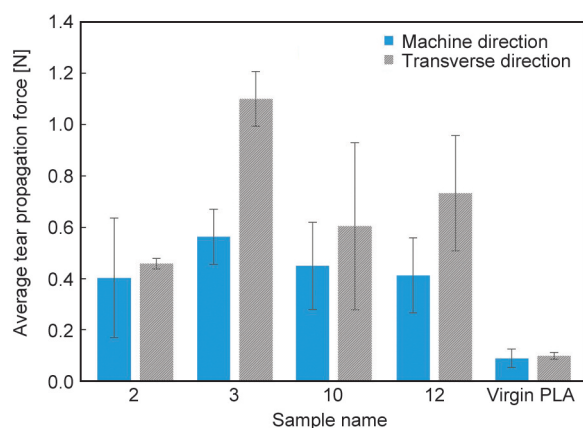

Figure 2. The average tear propagation force obtained by the trouser tear resistance test of blown film extruded samples.

Table 3. Properties of the samples related to the blown extrusion process.

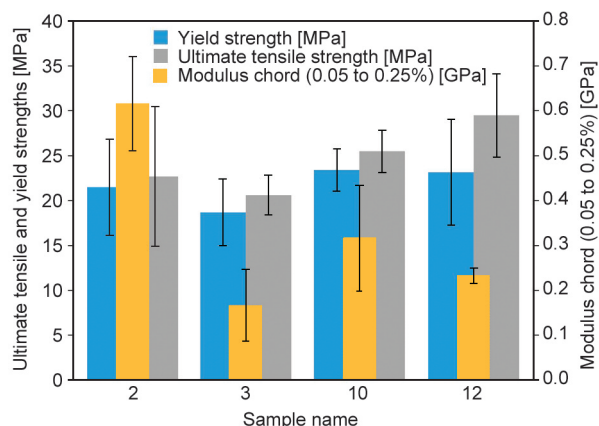| Sample name	2	3	10	12
Blow-up ratio (BUR)	2.00	1.50	1.50	1.50
Draw down ratio (DDR)	19.64	10.36	16.83	19.64

Figure 3. Comparison of the yield strength, ultimate tensile strength, and Young's modulus of the blown extruded film samples.

has a 26% higher modulus than Sample 12. The prominent compositional difference here is that Samples 2 and 10, although at similar PLA:PHBV ratio with Samples 3 and 12, both lack joncryl content in their composition compared to Samples 3 and 12. As established earlier [36], joncryl in addition to extending the chain lengths in most polyesters, when used in a dosage similar to the one used in this research, has a plasticizing effect in the blend as well. This effect increases the ductility of the blends containing joncryl, hence lowering their modulus. The same trend can be identified in the comparison of Sample 2 and Sample 10. In this case, both the triethyl citrate and joncryl content are equal between the two samples, but Sample 10 contains higher PHBV contents than Sample 2. Although both PLA and PHBV are considered brittle polymers, when blended, the addition of PHBV adds ductility. Hence Sample 10, with higher PHBV content, would be more ductile than Sample 2, having a modulus of only 316 MPa. The ultimate tensile strength from Samples 2 to 3 and Samples 10 to 12 decreases, however, this change is not significant, and it could be concluded that all samples have a tensile strength in the range of 20 to 25 MPa, considering the standard deviation range. Sample 12 stands out from all samples, presenting a different set of tensile properties. Although it follows the trend of other samples in modulus, as explained earlier, it has an ultimate tensile strength higher than Sample 10, although it contains triethyl citrate contents. This could be associated either with the synergistic effect between the components or the presence of the chain extender that when the formulation enters the plastic deformation region, it can withstand higher tensile forces compared to Sample 10,

which contains no chain extender. The increase in chain length could also be associated with the increase in ultimate tensile strength.

3.2. Barrier properties
3.2.1. Oxygen gas permeability
Permeation of a gas or vapor through a polymer material occurs by the following sequence: absorption of permeant molecules into the surface of the polymer, solubility, and diffusion of the permeant molecules through polymer chains, and desorption from the opposite polymer surface. The difficulty involved in this process is measured and referred to as gas transmission rate, permeation, and permeability by the researchers and the industry. Permeation accounts for the time involved, the effective surface area of the polymer, the pressure the experiment was conducted under, and the volume of permeant passed through the thin film. Permeation is independent of the thickness of the test sample because it is obtained by multiplying the testing film thickness by the gas transmission rate. Hence permeability can be used to compare the barrier performance of different materials given that the testing conditions, such as pressure, relative humidity, and temperature, remain the same. The measured oxygen gas permeability of all samples is presented in Figure 4. The permeability of blown extruded samples was compared with compression molded samples to broaden the comparison. In the sample names, 'A' denotes PLA, 'B' denotes PHBV, and 'J' denotes a joncryl chain extender. For example, the A60-B40 sample has a PLA:PHBV ratio of 60:40 percent, and 49.5A-49.5B-J1 has 49.5% PLA, 49.5% PHBV and 1% joncryl chain extender (hence 0% plasticizer). Pure PHBV could not be blown to film due to its low melt strength; hence it was only compression molded. On the blown film extruded samples, Samples 3 and 12 show higher permeation values compared to Samples 2 and 10, denoting the adverse effect of the joncryl chain extender on oxygen gas permeation through the blend formulation compared to samples without chain extender contents. This effect is seen once again in comparison of Sample A50-B50 with A49.5-B49.5-J1, where the latter has 2.6 times an inferior barrier. One reason to explain this effect could be that the amount of joncryl that was not reacted with terminal hydroxyl groups in polymer (excess joncryl content), which act as a plasticizer, facilitate the passage of oxygen molecules through the created spaces between the
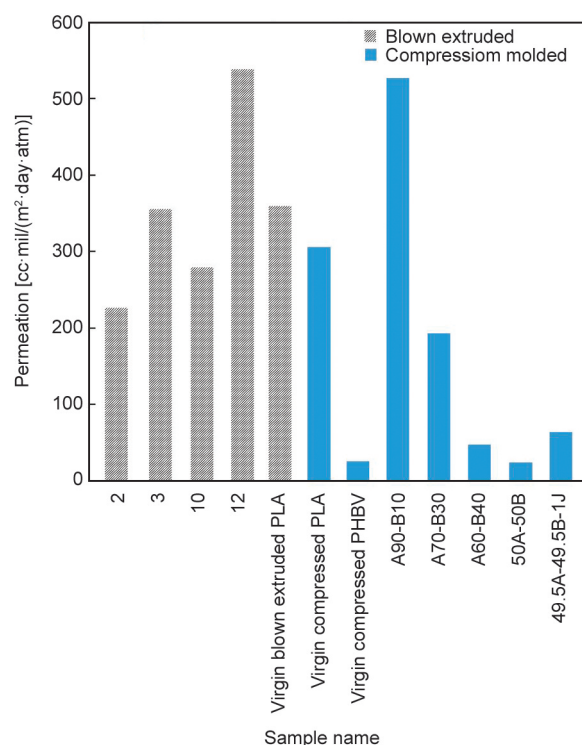
Figure 4. Oxygen gas permeability of blown film extruded samples in comparison with compression molded samples.

polymer chain. Some studies pointed out the deterioration of oxygen barrier performance by incorporating joncryl due to a possible less perfect arrangement of new crystal structures from branching or crosslinking chain structures and hence a lower crystallinity of the compound [40].

The oxygen permeation of blown extruded pure PLA (395.6 cc·mil/(m²·day)) is higher than but relatively close to the compression molded pure PLA (305.7 cc·mil/(m²·day)). This is expected as PLA polymer molecules in compression molding experience a longer (roughly 4 min compared to 8 s) cooling time to arrange and form crystals compared to almost instant cooling in blown film extrusion. This takes to account that PLA is a semi-crystalline polymer. It also provides a good basis for comparing the permeability of different samples. For instance, in blown extruded samples, although it was expected to observe a permeability decrease from Sample 2 to Sample 10 because Sample 10 has a higher PHBV content, the permeability increases. But in compression molded samples, oxygen permeability decreases with the increase of PHBV. For example, permeation in Samples A70-B30, A60-B40, and A50-B50 is 192.7, 47.4, and 24.3 cc·mil/(m²·day), respectively.

One comparison that comes as a key to resolving the contrasting results from the effect of the increase of PHBV content on the permeability of the blend is the comparison of the A90-B10 sample vs the compression molded pure PLA. Here, with the addition of 10% PHBV with a measured oxygen permeability equal to 8% of PLA (25.4 cc·mil/(m²·day)) with PLA, the oxygen permeability of PLA increases by 72%. This comes hand in hand with the premise of this study which was based on the synergistic effect of PLA/PHBV blend when the PHBV content is at around 10 to 30%. This synergistic effect is identified in the elongation at break in other studies [32, 40].

3.2.2. Water vapor permeability

The water vapor permeation (*WVP*) of manufactured films is presented in Figure 5. The water permeability of PLA at 23 °C and 85% relative humidity is reported in the literature between 63–342 g·mil/(m²·day·kPa) [1, 21, 24] while we found it at 393 g·mil/(m²·day·kPa). This value is slightly higher than the highest reported value in the literature. However, there are two main differences between this and the reported values. First, this test was conducted in standard condition (*RH* at 50%, which is lower than the reported 85%). The permeability coefficients of PLA are reported to decrease with the increase in moisture content [41]. Second, the films were blown extruded rather than melt cast or calendered. It is more plausible that blown extrusion could reduce the barrier properties of the films. Alternatively, pure PLA film is very crinkly, so when the bubble is formed and the tube is narrowed down and folded by the take-up nips, many creases are made on the surface of the film. The creases could be potential failure points that may lead to increased water vapor permeation of a blown extruded brittle film compared to a non-creased melt casted film.

Samples 2 and 10 show the lowest, and Samples 3 and 12 show the highest permeability values. The presence of trace joncryl contents in Samples 3 and 12 clearly indicates that the presence of a joncryl chain extender is the only reason for the significant increase in the water vapor permeability of the films, regardless of the PLA/PHBV ratio. This behavior could be attributed to the increased molecular polarity of the blends containing chain extenders. Furthermore, joncryl is a multifunctional compound containing an epoxy functional group. This can facilitate the formation of secondary hydrogen bonding between
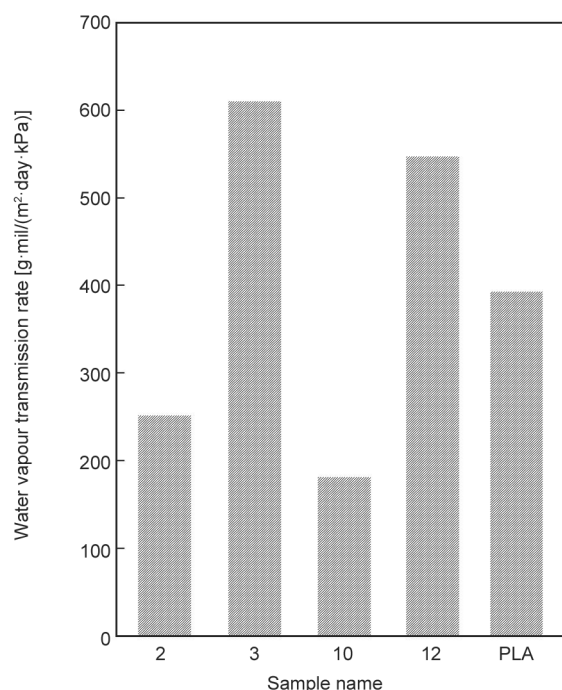
Figure 5. Water vapor transmission rate of blown film extruded samples, equilibrium over a two-month period.

the surface of the films and the water vapor molecules, leading to faster absorption of water vapor particles and an increased *WVP* value. In total, the addition of 3 wt% chain extender increased the *WVP* of Sample 2 by 142% and Sample 3 by 203%.

By comparing Sample 2 with 10 and Sample 3 with 12, it can be deduced that the increase of PHBV content improved the water vapor transmission rate of Sample 2 by 38% and Sample 3 by 11%. It can be seen again that the effect of the chain extender with the epoxy functional group is dominant compared to the effect of the increase of PHBV content in reducing the *WVP* when comparing the proportion of reduced *WVP* between Samples 2 and 10 and with Sample 3 and 12. By observing the *WVP* value of pure PLA film that was blown extruded with the very same processing condition as the other four samples, it can be concluded that the addition of PHBV can significantly improve the *WVP* of the PLA up to 55% (PHBV being added 27%). However, pure PLA would still be a higher barrier to water vapor than a PLA-PHBV blend containing an epoxy group containing a chain extender. It would, however, be interesting to see whether the same applies if a PLA-PHBV blend would have less chain extender content, for instance, up to only 0.3%.

3.3. Texture and haze

All the samples were manufactured at the same processing conditions; however, as each had a different material composition, the texture, and haze of each sample were different from one another (Figure 6). To indicate the texture and haze difference, samples were placed in front of the same background scene tion made to the background image was used as a reference to texture and haze differences between samples. It was observed in the bubble formation in the processing stage and can be seen in Samples 3 and 12 that the blends leave a pronounced track in the machine direction. This track for Samples 3 and 12 is quite wavy, especially in Sample 12, where this effect is even more pronounced. However, this effect in Sample 11 is not wavy but straight and much more subdued. The waviness of the polymer track line in the machine direction could be associated with the presence of a chain extender in the blend composition.

The presence of a chain extender in the blends containing PLA and PHBV polyesters leads to an improvement in melt strength. Although the melt strength was not measured in this study, with the respect that each batch contains a different content of PLA, PHBV, and joncryl chain extender, it is expected that each formulation has a different melt strength. This means that to provide the best texture and minimize the track line of polymers in the machine direction, each batch could be processed at slightly different processing conditions. This includes tweaking the process temperature and screw speed and adjusting the air pressure inside the bubble, and spinning the speed of take-up nips. Being said, all the films in this study were processed at the exact same processing conditions.

4. Conclusions

In conclusion, twelve different blends of PLA/PHBV with the addition of plasticizers and chain extenders were investigated. Only four blends were suitable for blown film extrusion, and these four were chosen to provide a diverse range of compositional contents for further analysis. The tear propagation force was found to be higher in the transverse direction, which was attributed to the molecular orientation of the polymers in the extrusion process. Adding PHBV and plasticizers improved the films' tear resistance
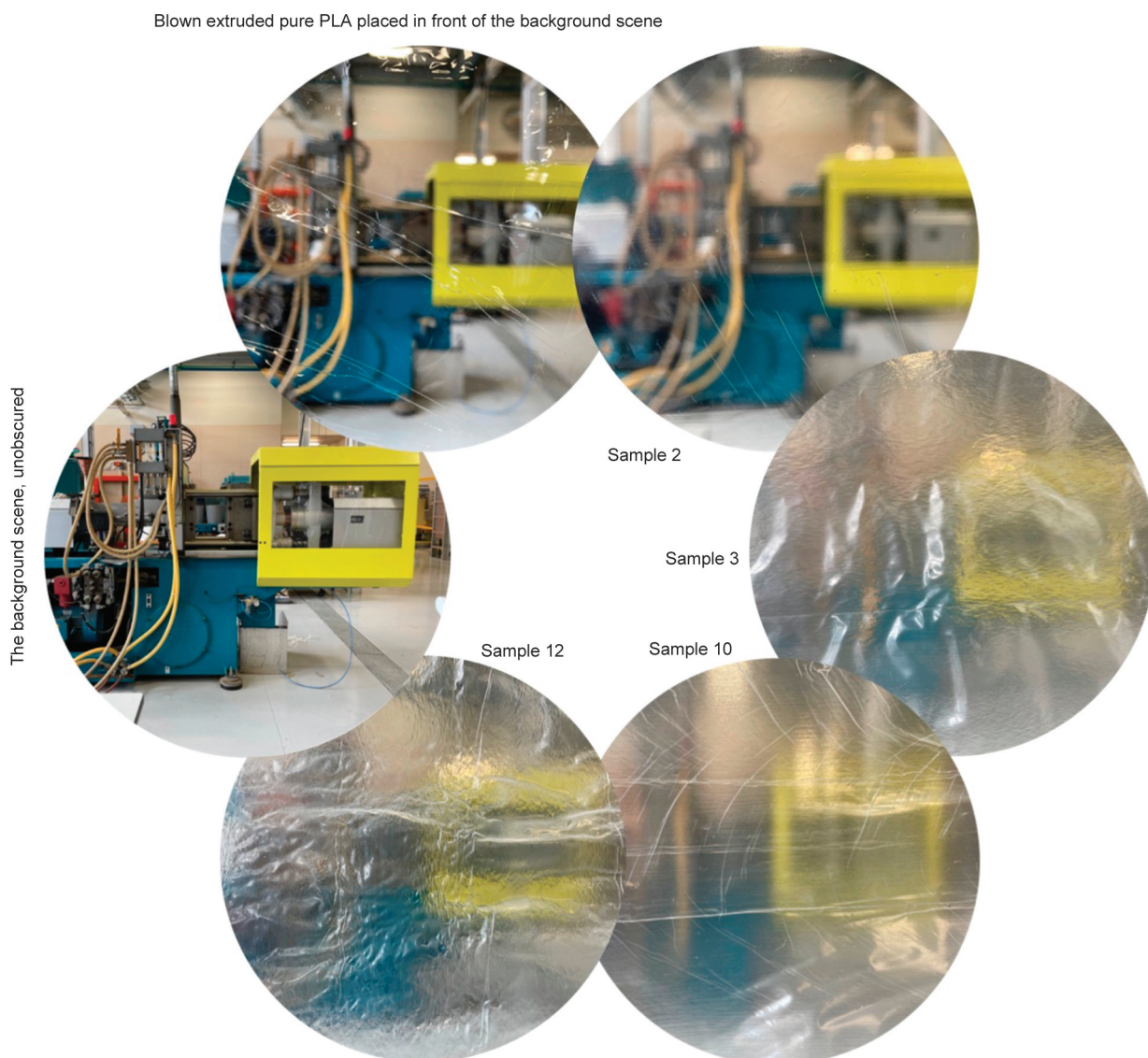
Blown extruded pure PLA placed in front of the background scene

The background scene, unobscured

Sample 2

Sample 3

Sample 12

Sample 10

Figure 6. Image of the same background taken through the samples to reflect the texture and haze of the blown extruded films. [The blur effect is due to film opacity and not lens focus. The camera remained focused on the films for all samples.]

compared to virgin PLA, making them suitable for packaging products that require higher tear propagation forces. The modulus of the films was found to be influenced by the compositional content, and the addition of a chain extender and plasticizer reduced the modulus of the films. The ultimate tensile strength of the films was found to be in the range of 20 to 25 MPa, with Sample 12 standing out for having a higher ultimate tensile strength. Overall, this study provides valuable insights into the mechanical properties of PLA/PHBV blends and their potential applications in the packaging industry.

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