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Compatibilization, processing and characterization of poly(butylene adipate terephthalate)/polylactide (PBAT/PLA) blends

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Abstract

A blend of poly(butylene adipate terephthalate) (PBAT) and polylactide (PLA) is a combination of biodegradable materials. This study aims to prepare compatibilized PBAT/PLA in a cost-effective and timesaving way and to process the material into blown films by fine-tuning the processing parameters. First, a catalyst masterbatch is prepared by transesterification of PBAT and PLA in the presence of tetrabutyl titanate (TBT) as a catalyst. This is followed by the compounding of the two polymer types in combination with the catalyst masterbatch. Third, the compounds are processed into blown films and panels. The processing parameters for film blowing are set to reduce the anisotropy. Finally, the material properties are evaluated such as mechanical tests. The fine-tuning of parameter settings including the blow-up ratio and draw-down ratio results in a higher degree of isotropy of the blown film. By adding the catalyst masterbatch (2 wt%, which corresponds to TBT of approximately 0.002 wt% with copolymers formed) in combination with the fine-tuning of parameter settings, the samples achieved a significant improvement on the material properties. The morphology of the cryogenically fractured panel samples shows a decrease in the diameter of the dispersed phase. In the cross and machine directions, the elongation at break increased by 85 and 93%, and the trouser tear propagation resistance increased by 2.4 and 10 N mm $^{-1}$, respectively. Furthermore, both the elongation at break and the trouser tear propagation of the blown films achieved a higher degree of isotropy.

1. Introduction

Packaging materials and mulch films are usually made of fossil-based plastics such as polyethylene that can accumulate in the environment after usage as solid wastes [1, 2]. Due to the UN Sustainable Development Goals [3], EU Bioeconomy Strategy [4] and China’s plastic waste import ban [5], the research and development of biodegradable materials have been promoted. Biodegradable films have been intensively studied based on renewable raw materials [6], biodegradable polymers [7], and combinations of both [8, 9]. In 2021, poly(butylene adipate terephthalate) (PBAT), polylactide (PLA), poly(butylene succinate) (PBS) and starch blends accounted for 58 percent of the global bioplastics production capacities [10]. Among them, PBAT and PLA belong to the main drivers of the bioplastic market.

PBAT is a linear aliphatic-aromatic random copolyester, which is petroleum-based or partly bio-based but biodegradable, highly flexible and designed for film extrusion [11]. PLA is a biobased polyester with a high modulus of elasticity but low toughness [7]. Blending the flexible PBAT with stiff PLA can potentially generate material with complementary properties without losing biodegradability. Polymer blends have generally the problem that the components are insufficiently miscible with each other and tend to separate at lower temperatures. Unmodified blends of PBAT and PLA are no exception. The reason for the incompatibility is that the intermolecular interactions are so different from each other that the interfacial adhesion between the
individual components is very weak [12], leading to separated phases and separated glass transition temperatures of the components [13–16].

For applications like mulch films, not only biodegradability but also mechanical properties are required. Therefore, it is important to increase the compatibility of the polymer blend. Different approaches were applied to overcome the problem with the low interfacial adhesion between PBAT and PLA [17, 18]. For example, it is possible to compatibilize PBAT/PLA blend by creating new chemical bonds, in particular covalent bonds, e.g. using dibenzoyl peroxide (BPO), glycidyl methacrylate (GMA) [19] or polypropylene glycol diglycidyl ether [20]. In this way, molecular chains of both polymer types are connected by newly formed covalent bonds (crosslinking) or chain extensions are formed, preventing macroscopic phase separation. However, crosslinking may block the enzymatic degradation of the blend [21]. Furthermore, it is also possible to use pre-made block copolymers by polymerization from monomers for blend compatibilization. Sun et al [22] synthesized firstly \( HO-\text{PBAT-OH} \) and then linear triblock copolymers \( \text{PLA}–b–\text{PBAT}–b–\text{PLA} \). Ding et al [23] used a similar synthesis route to obtain such triblock copolymers. However, the synthesis of hydroxyl-terminated PBAT and the block copolymers requires a long reaction time (>24 h) and vacuum. The long duration and the high-energy cost are disadvantageous for industrial-scale applications. A further approach is producing copolymers through transesterification reactions. An adequate catalyst enables and accelerates the exchange of segments between the polyesters of the incompatible blend at an elevated temperature so that block or random copolymers can form by transesterification reactions [24]. Coltelli et al [25] and Lin et al [26] used tetrabutyl titanate (TBT) as a catalyst to improve the mechanical properties of PBAT/PLA blends. This approach is timesaving, however, a weight ratio for catalyst/polymers blend of about 0.07–0.5 wt% is required to compatibilize the blends. Due to the cost of the catalyst, this approach is not particularly competitive for industrial applications.

This study aims at developing compatible biodegradable PBAT/PLA blends through a cost-effective and time-saving approach. To achieve this, the work was carried out in three steps. First, catalyst masterbatches were prepared by transesterification of PBAT and PLA in the presence of a catalyst laboratory scale. Second, compounds containing PBAT, PLA and the catalyst masterbatches with different weight ratios were produced. Third, the compounds were processed into panels and blown films using optimized processing parameters for film blowing. For the evaluation of the effect of this procedure on the final products, the material properties of panel and film samples were determined. The relationship between the processing conditions and properties was elaborated and will be discussed in this paper.

The novelty of this work is firstly the PBAT/PLA blend compatibilization using a self-developed catalyst masterbatch. Secondly, the influence of the processing parameters on the blown film properties was investigated, and the parameters were optimized.

2. Materials and methods

2.1. Materials
PBAT (Ecolflex\textsuperscript{®} F Blend C1200, BASF SE, Ludwigshafen, Germany) possesses a density of 1.26 g cm\(^{-3}\), a number-average molecular weight \((M_n)\) of 52.1 kg mol\(^{-1}\) and a polydispersity index of 2.0. PLA (Ingeo\textsuperscript{TM} Biopolymer 2003D, NatureWorks LLC, Minnetonka, MN, USA) has a density of 1.24 g cm\(^{-3}\), \(M_n\) of 127.0 kg mol\(^{-1}\), a polydispersity index of 1.6 and a D-isomer content of 4.4%.

A biodegradable fatty acid ester (Loxiol\textsuperscript{®} P728, Emery Oleochemicals GmbH, Düsseldorf, Germany) was used as an internal lubricant.

Titanium(IV) butoxide a.k.a. tetrabutyl titanate (TBT) (CAS: 5593–70–4, purity of >98%, density of 0.99 g cm\(^{-3}\) at 20 °C, Merck KGaA, Darmstadt, Germany) and n–heptane (purity > 99%, boiling temperature at 98 °C, CARL Roth GmbH, Karlsruhe, Germany) were used as received.

2.2. Preparation methods
The fabrication of PBAT/PLA blends proceeded in three steps:

1. Preparation of catalyst masterbatches
2. Formulation development and compounding
3. Blown film production / panel production

Panels pressed from PBAT/PLA blends were investigated regarding morphological, mechanical and thermal properties. Blown film samples were evaluated using mechanical and thermal characterization.
### 2.2.1. Preparation of catalyst masterbatches

In step (1), a measuring kneader (Messknetz 350 E, Brabender Technologie, Duisburg, Germany) was used to prepare catalyst masterbatches. The total volume of the mixing chamber is 370 ml. It was found that the kneader worked well at a filling degree of 70% of the mixing chamber, which corresponds to a volume of 259 ml. The density of PBAT and PLA is around 1.25 g cm$^{-3}$.

The amount of the liquid catalyst TBT was based in relation to the total mass of the polymers (320 g). A concentration of 0.1 phr corresponds to the catalyst amount of 0.32 g and a volume of 0.32 ml since the density of liquid TBT is about 1 g cm$^{-3}$. TBT was premixed with the solvent n-heptane (approx. 5 ml) at room temperature. This dilute solution of the catalyst enables uniform distribution of the catalyst into the polymer blends in the mixing process resulting in a proper reaction conversion with a small amount of TBT.

The procedure for preparing catalyst masterbatches is described as follows with the specification of compositions and operating parameters (table 1): first, the mixing chamber is heated to the desired temperature. Second, pre-dried and pre-mixed PBAT and PLA granules are filled into the mixing chamber quickly. This is followed by the addition of the liquid mixture containing TBT into the system, which is counted as the starting point. Due to the low boiling point, n-heptane evaporates rapidly from the hot mixing chamber. The rotational speed of the mixer was pre-set to achieve the target temperature after 5–6 min. The temperature afterward remained constant until the end of the experiment by reducing the rotational speed appropriately. Thereafter, the material was taken out from the mixing chamber. After cooling in liquid nitrogen, the material was then cut using a cutting mill (SM 2000, Retsch GmbH, Haan, Germany).

The weight ratio of PBAT/PLA was fixed at 80/20. Mass fractions of TBT between 0 and 0.5 phr were added. The processing temperature of the control sample was set to 180 °C, due to the melting temperature of PBAT (about 120 °C) and PLA (approx. 150 °C) [11]. Transesterification was found as a dominant degradation mechanism of PLA. This reaction is promoted by increasing temperature on one hand. On the other hand, temperatures above 200 °C lead to the formation of cyclic oligomers [27]. Thus, the kneading temperature for masterbatch preparation was set to 200 °C. The processing duration was 10 min. Longer processing times (e.g. 30 or 60 min) led to color changes of the material implying significant oxidation, which was observed in additional experiments.

### 2.2.2. Formulation development and compounding

In step (2), the materials obtained from step (1) were used as a catalyst masterbatch in the compounding process. Three formulations containing different amounts of the catalyst masterbatch M1 (0, 2 and 4 wt%) were developed (table 2). The formulation without a catalyst is the control sample, namely C0, which was compounded at a relatively low temperature (180 °C) so that almost no transesterification takes place during compounding. Two formulations containing catalyst masterbatch in different concentrations, namely C1 and C2, were compounded at a higher temperature. Thus, it was expected that the blends generate more copolymers by transesterification reactions.

The procedure of the compounding is described as follows: the polymers, catalyst masterbatch and lubricant are pre-dried. PBAT/PLA with a weight ratio of 80/20 is pre-mixed with further components and then melt-blended according to the list of formulations and processing parameters. A gravimetric dosing unit (DDW-H31-FW33/2–17, Brabender Technologie, Duisburg, Germany) is used for dosing the formulations with the prescribed throughput into a co-rotating twin-screw compounding extruder (EMP 26–40, diameter: 26 mm, L/D ratio: 40, TSA Industriale S.r.l., Luisago, Italy). The screw rotation speed was set as indicated for each formulation. Two different temperature profiles were set from the feed zone to the die (150 °C–200 °C and 150 °C–220 °C). Each strand was quenched in a water bath and then pelletized. The compounds obtained in this way were dried before further processing.

| Table 1. Recipes of the catalyst masterbatches, control sample and main setting parameters. |
| Catalyst masterbatch | PBAT (wt%) | PLA (wt%) | TBT (phr) | Target temperature (°C) | Duration (min) | Rotational speed (rpm) |
|----------------------|------------|------------|-----------|-------------------------|----------------|------------------------|
| M0 (control)         | 80         | 20         | 0         | 180                     | 10             | 40–50                  |
| M1                   | 80         | 20         | 0.1       | 200                     | 10             | 40–50                  |
| M2                   | 80         | 20         | 0.5       | 200                     | 10             | 40–50                  |

Legend: wt%: weight percentage; M: catalyst masterbatch; phr: parts per hundred resin; rpm: rounds per minute.
Table 2. Formulation ID and processing parameters on the compounding extruder.

| Formulation ID (extruder) | PBAT (wt%) | PLA (wt%) | M1 (wt%) | Lub. (wt%) | TP (kg h⁻¹) | R_{speed} (rpm) | Heating zones (°C) | T_{die} (°C) |
|---------------------------|-----------|-----------|----------|------------|-------------|-----------------|--------------------|-------------|
| C0                        | 79.6      | 19.9      | 0        | 0.5        | 10          | 200             | 150/160/170/180/180/180/180/180 | 180         |
| C1                        | 78        | 19.5      | 2        | 0.5        | 10          | 200             | 150/160/170/180/200/220/220/220 | 220         |
| C2                        | 76.4      | 19.1      | 4        | 0.5        | 10          | 200             | 150/160/170/180/200/220/220/220 | 220         |

Legend: C: compound; M1: catalyst masterbatch refers to table 1; Lub.: lubricant; TP: throughput; R_{speed}: rotational speed; T_{die}: temperature of the die.
2.2.3. Blown film production

In step (3), blown films were produced using a single-screw extruder in combination with a blown film line (Extruder: LE 25–30/C, diameter: 25 mm, L/D ratio: 30; film blowing line: LF–400, die gap: 1 mm, die diameter: 50 mm, LabTech Engineering company Ltd, Samutprakarn, Thailand) (figure 1).

In this process, the pre-dried compounds were filled into a hopper of the extruder. The screw speed determined the throughput. The heating zones and the die were set to a temperature range between 165 and 170 °C which was suitable for processing the blown films. It was found that the melt temperature measured was 3 °C–4 °C lower than the nozzle temperature set. After pumping the melt through an annular die, the melt was blown with injecting air through the center of the die mandrel. While the air supply controlled the cross direction of the blown films, the draw-down speed and the winding speed affected the machine direction of the blown films.

For simplicity, each blown film ID consists of a letter ‘C’ with a number and a letter ‘B’ with a number. C0, C1 and C2 refer to the formulation ID (table 2). B1 and B2 refer to the processing conditions in the blown film production (table 3). For example, C0B1 is a blown film made of the formulation C0 and processed at the B1 condition.

2.2.4. Panel production

In addition to blown films, panel samples were produced. Two samples were pressed using the formulations M0 and M2. The other two samples were made by adding M0 and M2 to fresh PBAT and PLA using a measuring kneader, respectively, and then pressing to panels. The recipes and setting parameters are listed (table 4).

The procedure for producing material with M-samples is similar to that of preparing catalyst masterbatches. First, the mixing chamber was heated to the desired temperature. Second, pre-dried and pre-mixed fresh PBAT and PLA granules and the catalyst masterbatch (or control sample) were added to the mixing chamber. The rotational speed was set to achieve the target temperature after 5–6 min. The temperature remained constant to the end of the experiment by adjusting the rotational speed. Afterward, the material was taken out from the mixing chamber. The material was cooled in liquid nitrogen and then cut into small pieces.

A laboratory press (LP–S–20, Labtech Engineering Company Ltd, Samutprakarn, Thailand) was used for pressing panels. The pre-dried materials were placed in a metal frame (thickness: 0.8 mm) and covered from the top and bottom with silicone-coated papers (90 g m⁻², Neptun Technologies GmbH, Kruenkel, Germany), offering an easy removal of the paper from the panel. The top and bottom layers were covered with a metal plate, respectively. After placing this into the press, preheating was started (180 °C, 2 min), which was followed by venting (10 s) and fully pressing (180 °C, 5 MPa, 4 min). Finally, plate cooling was implemented (2 min). The resulting panels had a dimension of approx. 0.8 × 150 × 150 mm³.
Table 3. Parameter settings for blown film production.

| Blown film ID | $R_{\text{speed}}$ (rpm) | Heating zones (°C) | $T_{\text{die}}$ (°C) | Draw-down speed (m min$^{-1}$) | Winding speed (m min$^{-1}$) | LF width (mm) |
|---------------|---------------------------|--------------------|----------------------|-------------------------------|-------------------------------|--------------|
| C0B1          | 45                        | 150/155/160/165/165| 165                  | 4.7                           | 3.2                           | 180          |
| C1B1          | 45                        | 150/155/160/165/165| 165                  | 4.7                           | 3.2                           | 180          |
| C2B1          | 45                        | 150/155/160/165/165| 165                  | 4.7                           | 3.2                           | 180          |
| C1B2          | 45                        | 150/155/160/165/165| 165                  | 3.7                           | 2.4                           | 210          |
| C2B2          | 45                        | 150/155/160/165/165| 165                  | 3.7                           | 2.4                           | 210          |
2.3. Characterization

Film ductility and tear propagation resistance are important mechanical properties for blown films [28]. The film ductility can be determined by specifying the elongation at break in a tensile test. The tear resistance of a plastic film has two properties: (1) the initiation of tear and (2) tear propagation resistance. Compared with the initiation of tear, the tear propagation is expected to be much lower [1], since it describes the tearing behavior of a film following any kind of initial localized failure because of initial tearing, puncturing, etc [29]. Therefore, tear propagation resistance is considered a more important property for applications of blown films. Su et al [11] observed a good trend correlation between the film ductility and the tear propagation resistance. Furthermore, it was found that the method of trouser tear method (according to DIN EN ISO 6383–1:2016) is more applicable to differentiate highly extensible blown films than the Elmendorf tear method.

### Table 4. Recipe ID with M-samples and setting parameters on the measuring kneader.

| Recipe ID (kneader) | PBAT (wt%) | PLA (wt%) | M-sample type | M-sample (wt%) | Target temperature (°C) | Duration (min) |
|---------------------|------------|-----------|---------------|---------------|-------------------------|----------------|
| M0M0                | 79.2       | 19.8      | M0            | 1             | 180                     | 10             |
| M2M0                | 79.2       | 19.8      | M2            | 1             | 200                     | 10             |

### Figure 2. SEM micrograph of cryogenically fractured PBAT/PLA (80/20) blend panels: (a) M0 (control sample), (b) M0M0 (control sample compounded with the same control sample of 1 wt%), (c) M2 (sample compounded with the catalyst TBT of 0.5 phr) and (d) M2M0 (sample compounded with the catalyst masterbatch M2 of 1 wt%).
To examine the tensile properties of blown films and panel samples, a material testing machine with a 500 N load cell (ZwickiLine 1.0TH, ZwickRoell GmbH & Co. KG, Ulm, Germany) was used. The test specimens used in the tensile test were standard specimen type 2 according to DIN EN ISO 527–3: 2019. The width of each sample was 10 mm. The thickness of blown films was approximately 25 μm. The thickness of the panels was about 0.8 mm. The tensile properties of blown films were investigated in both cross and machine directions. A crosshead speed of 1 mm min\(^{-1}\) was set to determine the modulus of elasticity. Subsequently, an increased cross speed (50 mm min\(^{-1}\) for panels and 200 mm min\(^{-1}\) for blown films) was set to measure the tensile strength and elongation at break.

To examine the tear propagation resistance, the same machine applied for the tensile test was used. The trouser tear test was applied according to DIN EN ISO 6383–1: 2016. The blown film samples had a thickness of about 25 μm, a width of 50 mm and a length of 150 mm. The length of the incision in the center of the specimen was 75 mm. The trouser tear test applied a constant speed of 200 mm min\(^{-1}\).

The following applied to both the tensile test and the tear propagation test: The exact thickness of each sample was measured. Before testing, all test specimens were conditioned at 23 °C and 50% relative humidity for at least two days. At least six specimens of blown films were tested in each direction. Each panels sample was also tested with six specimens at least.

The thermal properties of PBAT/PLA blown films were determined using a DSC (DSC 204 F1 Phoenix, Netzsch-Gerätebau GmbH, Selb, Germany). The DSC cell was constantly purged with nitrogen at a flow rate of 10 ml min\(^{-1}\). Each PBAT/PLA blown film sample (approx. 10 mg) was sealed in an aluminum pan. The temperature program was set as follows: at the beginning, the sample was cooled from room temperature to −60 °C with a cooling rate of 10 °C min\(^{-1}\). After holding this temperature (−60 °C, 15 min), the first heating program started (from −60 to 200 °C, heating rate 10 °C min\(^{-1}\)). After holding this temperature (3 min), the first cooling step was carried out (from 200 to −60 °C, 10 °C min\(^{-1}\)). Subsequently, this temperature was kept (−60 °C, 15 min). Next, the second heating step (from −60 to 190 °C, heating rate: 10 °C min\(^{-1}\)) was performed.

The morphological properties of PBAT/PLA blend panels were examined using a scanning electron microscope (SEM) (Vega 3, TESCAN ORSAY HOLDING a.s., Brno, Czech Republic) with secondary electron (SE) detectors. Panels were fractured under the cryogenic condition in liquid nitrogen. The fractured surfaces were sputter-coated with gold (120 s) to enable electron flow. For scanning the fractured surfaces, an accelerating voltage of 20 kV was used.

3. Results

3.1. Morphological, mechanical and thermal properties of panels

Four samples were pressed into panels, including the control sample M0, M0M0 (without catalyst), M2 (with catalyst) and M2M0 (with catalyst masterbatch). These samples were investigated regarding their morphological and tensile properties, respectively. The SEM micrographs of cryogenically fractured panels are shown (figure 2).

Picture (a) for the control sample M0 shows phase separation with large dispersed phases and holes. A similar morphology can be seen in picture (b), which was made of fresh PBAT/PLA (80/20) blends (99 wt%) with the control sample (1 wt%). However, picture (c) shows much more particles and holes with reduced
diameters, due to adding the catalyst TBT (0.5 wt%) to the polymer blends. Picture (d) shows that the sample M2M0 made of PBAT/PLA (80/20) (99 wt%) with the catalyst masterbatch M2 (1 wt%) had many small particles and holes distributed on the surfaces. These SEM micrographs indicate that both the catalyst and catalyst masterbatch contributed to the increase in particle numbers and the decrease in particle sizes.

In addition to the morphological investigation, the tensile properties of the panels were analyzed. The ductility can be determined by specifying the elongation at break in the tensile test (figure 3). The Origin’s normality test confirmed at the 0.05 level that the data used in the evaluation were significantly drawn from a normally distributed population.

From the column plot, it is observable that the control sample M0 and the sample M0M0 have lower mean values of the elongation at break than the samples M2 and M2M0. According to the ANOVA one-way test (Turkey) at the 0.05 level, the population means of M0 and M2 are significantly different. The population means of M0 and M2M0 are also significantly different. The elongation at break of M0M0 is also significantly different from the one for M2 and M2M0. Therefore, the catalyst TBT helped to increase the elongation at break of the PBAT/PLA blend. However, M2 and M2M0 are not significantly different regarding the population means of the elongation at break, indicating that the direct addition of the catalyst TBT (0.5 phr) had a comparable effect on the improvement of the elongation at break as the addition of the catalyst masterbatch (containing TBT of approx. 0.005 wt%) into the PBAT/PLA blend.

The glass transition temperature ($T_g$) and melting temperature ($T_m$) of neat PLA, neat PBAT and the samples M0 and M2M0 were determined using DSC from the second heating scan (table 5).

The $T_g$ (PBAT) for M0 and M2M0 are almost unchanged around $-28.5 \, ^\circ C$. Compared with the neat PLA ($T_g$ value of 61.4 °C), the two PBAT/PLA blends had slightly lowered $T_g$ values (59.7 and 59.8 °C). The $\Delta T_g$ value of the two neat polymers is 89.7 °C. The $\Delta T_g$ decreased to 88.5 °C for the control sample M0 and 88.0 °C for the modified sample M2M0. The small shift of $\Delta T_g$ values into each other indicates that the miscibility of the PBAT/PLA blend was slightly improved.

Using DSC, the blends were heated to an elevated temperature, so that the catalyst in the sample could be activated again to accelerate the transesterification reaction between both components. Thereby, copolymers with smaller chain segments or even random copolymers could be generated, likely leading to a change in the structure of the polymer blends. To differentiate the samples containing the catalyst TBT, the mechanical

**Table 5.** Thermal characteristics from the second heating curves of neat PLA, PBAT and their blends.

| Sample ID | $T_g$(PBAT) (°C) | $T_g$(PLA) (°C) | $\Delta T_g$ (°C) | $T_m$(PBAT) (°C) | $T_m$(PLA) (°C) |
|-----------|------------------|-----------------|-----------------|-----------------|-----------------|
| Neat PLA  | —                | 61.4            | 89.7            | —               | 150.2           |
| Neat PBAT | $-28.3$          | —               | —               | $120.4$         | —               |
| M0        | $-28.8$          | 59.7            | 88.5            | $117.8$         | 151.0           |
| M2M0      | $-28.2$          | 59.8            | 88.0            | n.p.            | 151.3           |

Legend: n.p.: specification not possible.

**Figure 4.** Mechanical properties of PBAT/PLA (80/20) blown films: (a) elongation at break, (b) tear propagation resistance in CD and MD.
investigations have the benefit that the chemical structure of the samples does not change during the measurements.

3.2. Mechanical properties of blown films

To control the bubble forming process, relevant processing parameters include the blow-up ratio (BUR), draw-down ratio (DDR) and the forming ratio (FR). These parameters were calculated and listed (table 6).

| Blown film ID | BUR | DDR | FR |
|--------------|-----|-----|----|
| C0B1         | 2.3 | 17.4| 7.6|
| C1B1         | 2.3 | 17.4| 7.6|
| C2B1         | 2.3 | 17.4| 7.6|
| C0B2         | 2.7 | 14.8| 5.5|
| C1B2         | 2.7 | 14.8| 5.5|
| C2B2         | 2.7 | 14.8| 5.5|

Legend: BUR is the ratio of bubble diameter (Db) to the die diameter (Dd), BUR = Db/Dd

The properties of the blown films exhibit anisotropy. Especially in the three left samples (C0B1, C1B1 and C2B1), the values differ strongly in the cross and machine directions. The values in MD are only half as high as the ones in CD. Compared with the control sample C0B1, the sample C1B1 had a significantly higher elongation at break in MD and MD according to the ANOVA one-way test (Turkey) at the 0.05 level, indicating that the catalyst masterbatch (M1, 2 wt% containing TBT of approx. 0.01 wt%) helps to compatibilize PBAT/PLA blends. However, compared with the control sample, the increase in the weight ratio of this catalyst masterbatch (to 4 wt%) did not show a further improvement of the elongation at break. The elongation at break of C2B1 was even lower than the one of C1B1. The fine-tuning in the BUR from 2.3 to 2.8 and the DDR from 17.4 to 14.8 results in less difference in the two directions for C0B2, C1B2 and C2B2. The sample C1B2 showed a significant increase in elongation at break compared with the sample C0B2, implying that the addition of the catalyst masterbatch (M1, 2 wt% containing TBT of approx. 0.002 wt%) contributed to the improvement of the film ductility. However, C2B2 showed that adding more of this catalyst masterbatch could not increase the elongation at break further. Therefore, it can be concluded that both the addition of catalyst masterbatch in the compounding process and the parameter settings on the blown film line affected the tensile properties of the blown films. A combination of the two measures led to a significant increase in elongation at break and, at the same time, a decrease in anisotropy.

Diagram (b) shows that also the tear propagation resistance of the blown films differs in CD and MD. According to the ANOVA one-way test (Turkey) at the 0.05 level, the population means of C0B1 and C1B1 are significantly different in CD and MD; however, the one of C0B1 and C2B1 is only significantly different in MD. This means that the catalyst masterbatch contributed to increasing the tear propagation resistance of the blown films under the same processing conditions. This property increased in both directions when the catalyst masterbatch (M1, 2 wt% containing TBT of approx. 0.002 wt%) was added into the formulation. By improving the BUR and DDR, the tear propagation resistance tends to be less anisotropic. Although the samples C0B2, C1B2 and C2B2 showed little change for tear propagation resistance in CD, these samples showed an upward trend of this property in MD. Among them, C1B2 achieved the largest increase in the tear propagation resistance in MD. Therefore, both adding catalyst masterbatch into the compounding process and fine-tuning the processing parameters for film blowing could affect the tear propagation resistance positively.

To describe the film properties, a parameter ‘degree of isotropy’ is introduced in this study. This is the percentage of the mean values from the two directions in the tensile or tear test (the lower/higher, in this case, MD/CD). For example, the degree of isotropy of the elongation at break MD/CD for C0B1 is calculated by 222/449 ≈ 49%.

The properties of the blown films including C0B1, C0B2 and C1B2 are summarized (table 7).

The three samples showed that the degree of isotropy for the elongation at break (from 49 over 57 to 59%) had the same tendency as the degree of isotropy for the tear propagation resistance (from 57 over 71 to 86%).
This indicates that both adding catalyst masterbatch and fine-tuning processing parameters contributed to improving the degree of isotropy of the blown films.

These two measures also result in the increase of the elongation at break and tear propagation resistance. Compared with the control sample C0B1, the sample C0B2 showed significant improvement on the elongation at break and tear propagation resistance in MD, while these properties in CD were almost on the same level. Compared with the control sample C0B1, sample C1B2 had a large increase in the elongation at break from 449 to 534% in CD and from 222 to 325% in MD. Compared with the sample C0B2, sample C1B2 also comprised of a significantly increased elongation at break, indicating that the catalyst masterbatch helped to compatibilize PBAT/PLA (80/20) blends while the processing conditions remained the same. A similar tendency was found in the tear propagation resistance. The sample C1B2 showed significantly higher tear propagation resistance than the control sample C0B1 in CD from 31.1 to 33.5 N mm⁻¹ and in MD from 17.8 to 28.8 N mm⁻¹.
4. Discussion

A transesterification reaction takes place in a binary polyester at an elevated temperature in presence of an adequate catalyst to generate block or random copolymesters. Coltelli et al.\[25\] reported that TBT accelerated the transesterification reaction between PBAT and PLA. As the transesterification proceeds, the ester interchange between PBAT and PLA takes place first in large segments, a part of one polyester chain joining with a large segment of the other polyester. Limiting the extent of ester interchange results in block copolymers. As transesterification proceeds, the large segments continue to interchange and become gradually smaller. Finally, a random copolymer consisting of the building blocks of both components occurs. The process of the transesterification of PBAT and PLA is illustrated (figure 5).

The copolymers consisting of both components A (PLA) and B (PBAT) accumulate preferentially at the interface. The interaction of copolymer segments with the blend components facilitates their diffusion to the interfacial region where chain entanglements are formed. The copolymers act as compatibilizers and result in reduced interfacial tension with decreased particle size and increased adhesion between the phases [30]. The concept of the blend compatibilization using copolymers is illustrated (figure 6).

The interfacial adhesion increases with increasing amounts of the copolymers until the interface is saturated. Only the amount necessary should be added to the polymer blend because the excess concentration will not further improve the blend properties [22].

In addition to the copolymers as an interfacial agent, the processing parameters also play an important role in the film properties. Varying the draw-down speed, winding speed and the air supply to the bubble results in the change of the processing parameters such as BUR and DDR, affecting the orientation and alignment of polymers in a blown film. The fine-tuning of parameters leads to enhanced tear propagation resistance and elongation at break in MD and reduced anisotropy.

5. Conclusion

In this work, catalyst masterbatches were successfully prepared by transesterification of PBAT and PLA using the catalyst TBT. The catalyst masterbatch with different weight ratios was added into the compounding process of PBAT/PLA blends. By using these compounds, panels and blown films were produced. The processing parameters for film blowing were set to reduce the anisotropy.

The morphological analysis showed that both, catalyst (0.05 phr) and catalyst masterbatch (containing TBT of approx. 0.005 wt% and resulting copolymers), contributed to the increase in particle numbers and the decrease in particle sizes in panel samples. By using the catalyst masterbatch, the elongation at break increased from 508 to 547%. The thermal analysis showed a slight transition shift of both components into each other. When the temperature increased during the DSC measurement, the catalyst could be activated again to accelerate transesterification reactions between the polyester components, leading to a change of polymer structures.

To produce blown films with improved properties, the catalyst masterbatch M1 was used to compatibilize PBAT and PLA in the compounding and blown film production processes. Furthermore, the processing parameters including blow-up ratio and draw-down ratio were optimized to achieve a higher degree of isotropy. The properties of blown films were determined by tensile test and trouser test in CD and MD. The results showed that the addition of the catalyst masterbatch M1 (2 wt%, corresponding to the catalyst TBT of approx. 0.002 wt% with copolymers formed) significantly increased the elongation at break and tear propagation resistance. These two mechanical properties indicated anisotropy of the blown films. The degree of isotropy was improved by fine-tuning the parameter settings in the blown film production process, including the BUR from 2.3 to 2.7 and DDR from 17.4 to 14.8. Furthermore, the combination of the two measures contributed to increasing the degree of isotropy of the blown films. It was improved from 49 to 59% for the elongation at break and from 57 to 86% for the tear propagation resistance. The resistance against external force depends on the direction with the lower value. In this study, MD is the direction with the lower values. A significant improvement of the mechanical properties was achieved in MD, indicating successful compatibilization by adding catalyst masterbatch and fine-tuning the processing parameters.

For further research, the author suggests to examine the mechanical properties at different temperatures as well as the biodegradation test of the films under soil and different microbial conditions.

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Data availability statement

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Conflicts of interest

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