



# Faba bean lignocellulosic sidestream as a filler for the development of biodegradable packaging

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## ABSTRACT

In this work, bio-composites were produced using faba bean sidestream (stems, pods and mixed stems and pods) as a filler to a bio-based and biodegradable polymer blend of Poly(butylene succinate-co-adipate)/Poly(hydroxy butyrate-co-valerate) (PBSA/PHBV, ratio 85/15). The faba bean sidestream was added at 10, 20, and 30 % wt. to the PBSA/PHBV matrix. The bio-composite pellets were compounded by a twin-screw extruder and the pellets were further processed into tensile rods by injection moulding and into bio-composite films by film extrusion. The mechanical, barrier, thermal and morphological properties of the bio-composite films and injection moulded specimens were evaluated. The tensile stress at maximum force and Young's modulus of the injection moulded specimens increased with an increase in fibre loading, with the bio-composite containing 30% fibres showing the largest increase in relation to the neat blend. The increase in tensile stress suggests good interfacial adhesion between the polymer matrix and the fibres as evidenced by scanning electron microscope. However, a decrease in tensile strain and impact strength was observed with an increase in fibre loading. With the addition of 20 and 30% of fibres, the oxygen transmission rate decreased by 29 and 52% respectively in relation with the neat blend, while there was no statistical significance in the water vapour transmission rate of the bio-composite containing 20 and 30% fibres in relation to the neat blend. The study demonstrated that PBSA/PHBV composited with faba bean sidestream are processible by both injection moulding and film extrusion with balanced mechanical and barrier properties for potential application in food packaging as flexible films or for rigid packaging.

## 1. Introduction

Packaging accounts for approximately 40–42% of total plastic consumption, which is predominantly made up of polypropylene, polyethylene, and polyethylene terephthalate that are not biodegradable and can accumulate in natural environments as pollutants [1,2]. According to the latest statistics from Organization of Economic co-operation and development (OECD, 2022), it is estimated that as of 2019, of all total plastic waste generated, about 9% was recycled, 19% incinerated and 72% was improperly managed, leading to its accumulation in landfills and natural environments. The accumulation of plastic waste is expected to grow as the population grows, especially in Sub-Saharan Africa, where there is inadequate infrastructure for plastic waste management

[3]. To curb plastic waste pollution, about 25 African countries have partially or completely banned the production and use of plastic bags, with some countries imposing a levy on retailers for selling plastic bags. For example, Kenya, Rwanda, Mali have banned the production, import, sale and use of non-biodegradable plastic bags, while countries like South Africa banned plastic bags that are less than 30 µm thick and placed levy on retailers for thicker ones [4]. This demonstrates the need for locally driven alternative sustainable packaging solutions.

Bio-packaging materials from agricultural lignocellulosic sidestream, not only reduce agricultural waste, but add value to the agricultural sidestream that would otherwise be considered as waste. Agricultural biomass waste, such as wheat straws, soy stalks, corn stalks [5], olive pomace [2] have previously been used to prepare

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bio-composites. However, agricultural biomass waste from African crops, such as faba bean have not been previously demonstrated as potential filler to produce bio-composites.

Faba bean (*Vicia faba* L.) is one of the oldest crop in the world, produced in more than 58 different countries, and is the third most important grain legume [6]. Sub-Saharan Africa is the second biggest producer of faba beans, accounting for 21% of global production with a significant portion being produced in Ethiopia [7]. Currently, faba bean sidestream is not traded as a commodity in Africa and as such has no commercial value. The faba bean sidestream amounts are estimated to be about 21 600 tons per area for Ethiopia and 7600 tons per area for Kenya using the data from Food and Agriculture Organization of the United Nations (FAOSTAT, 2022). Therefore, the use of faba bean sidestream as a filler to develop bio-composite packaging materials would increase the use of locally available raw materials, while providing new sustainable packaging materials.

Biopolymers such as Poly (hydroxy butyrate-co-valerate) (PHBV) and Poly (butylene succinate-co-adipate) (PBSA) are attractive matrix in producing bio-composite packaging solutions because they are biodegradable in various environments, such as soil, home and industrial compost conditions compared to other biodegradable polymers [8]. PHBV belongs to a group of microbiologically synthesised polyesters polyhydroxyalkanoates (PHA), whereas PBSA is synthesised from copolymerization of 1,4-butanediol, succinic acid and adipic acid monomers. Both these biopolymers can be totally or partially bio-sourced therefore lowering carbon footprint compared to their petrochemically derived counterparts, such as poly( $\epsilon$ -caprolactone) (PCL) [9]. PBSA has excellent thermoplastic processibility compared to other biodegradable polymers via a broad range of techniques, such as blow moulding, foaming, injection moulding and sheet extrusion [9,10]. However, PBSA has relatively poor barrier properties compared to other biodegradable polymers, such as PHBV. On the other hand, PHBV has good stiffness, fast biodegradation rate and has relatively good barrier properties making it suitable for food packaging compared to other biodegradable polymers. In addition, it is also biodegradable in marine environments [11]. PHBV has several drawbacks, such as, brittleness, and insufficient melt strength. Therefore, compositing of PBSA and PHBV can combine the desirable properties of both biopolymers.

Previously, PHBV based bio-composites containing agro-residue crops, such as corn straws, soy stalk, wheat straws have been produced by extrusion followed by injection moulding [5]. Similarly, PBSA based bio-composites containing short hemp fibres have been produced by extrusion followed by injection moulding [12]. These studies focused on injection moulded bio-composites containing either PBSA or PHBV alone as a matrix, and not film extrusion or using PBSA/PHBV blend as a matrix. Therefore, film extrusion should be studied to demonstrate the potential of bio-composites based on PHBV, PBSA and agro-residues. Previous studies have reported immiscible PHB/Bio-PBS and PHBV/Bio-PBS blends [13]. However, in our previous studies it was demonstrated that PBSA/PHB polymer blend with balanced processibility, sufficient mechanical and barrier properties can be produced for use in packaging applications. Notably the addition of PHB at low amounts (10–20%) was found to increase the Young's modulus, oxygen and water vapour transmission rate of the PBSA/PHB blend [14].

The objective of the study is to investigate whether the faba bean sidestream could be used as a new filler in a PBSA/PHBV (85/15) blend matrix and processed via existing polymer processing machinery, such as film extrusion and injection moulding. Herein, the effect of faba bean sidestream at different loading to a biopolymer blend matrix will be investigated on the mechanical and barrier properties of the bio-composites, with the aim of developing environmentally friendly rigid and flexible packaging materials with balanced mechanical and barrier properties. This will potentially result in novel bio-packaging material and, reduce agricultural sidestream waste from faba bean by value addition.

## 2. Materials and methods

### 2.1. Materials

PHBV ENMAT Y1000P was procured from Helian Polymers (Belfeld, Netherlands). This polymer contains nucleating agents to induce crystallinity and is suitable for injection moulding and extrusion. According to manufacturer, this grade has a density of 1.25 g/cm<sup>3</sup>, melting point of 170–176 °C, modulus of 2.8–3.5 GPa, yield strength of 31–36 MPa and elongation at break of 2%. PBSA BioPBS FD92PM was procured from PTT MCC biochem Co.,Ltd (Bangkok, Thailand). According to manufacturer, it has a density of 1.24 g/cm<sup>3</sup>, melting point of 84 °C, yield strength of 17 MPa and elongation at break of 380%. Acetone, acetic acid, sulfuric acid, and sodium chlorite (80%) were procured from Merck (Johannesburg, South Africa).

The faba bean seeds used were of acid and Al<sup>3+</sup> tolerant Ethiopian genotype that were initially planted in Ethiopia. Faba beans of Ethiopian origin were grown at the University of Helsinki, Finland. After harvest, the unsorted faba bean sidestream that consisted of mixed stems and pods were received from the University of Helsinki, Finland. The faba bean sidestream (mixed stems and pods) were dried at 80 °C for 10 h and some were manually separated into faba bean pods and stems to see the effect of each part in the end-product. The holocellulose, cellulose and hemicellulose content of the faba bean stems and pods were determined according to the method described by Ref. [15]. Lignin content was determined according to LAP-003 method [16]. The cellulose, hemicellulose, and lignin contents of the faba bean pods were 31%, 21% and 16% while the faba bean stems had 39%, 32% and 16% respectively.

### 2.2. Preparation of the bio-composites

Faba bean sidestreams were manually separated into stems and pods, then milled with the industrial Rivakka suction blower mill (1.8 mm sieve) in a first step and with the Polymix knife-mill (2 mm sieve) in a second step for refining the retained particles. The obtained lignocellulosic fibres were dried at 50 °C overnight. The PBSA and PHBV were bag mixed (85:15 ratio) and dried overnight at 80 °C. The materials were compounded with the corotating twin-screw extruder (Berstorff ZE 25 × 33 D, Berstorff GmbH, Hanover, Germany) with a temperature profile 165/170/175/175/175/175/175/170 °C (zone 1 to die), screw speed of 70, 75 or 100 rpm depending on samples and output of 2.4–3 kg/h according to Table 1. The PBSA/PHBV blend was used as a control/reference. Stems or pods were added at 10 and 20%; mixed pods and

**Table 1**  
Composition of the PBSA/PHBV-based bio-composites reinforced with faba bean lignocellulosic fibres.

Samples	Faba bean fibre type	Fibre content (% wt)	Screw speed (rpm)	Output (kg/h)
PBSA: PHBV (85:15)	none	0	100	3.0
PBSA: PHBV- 10% mixed pods and stems	Mixed pods and stems	10	75	2.5
PBSA: PHBV- 20% mixed pods and stems	Mixed pods and stems	20	75	2.5
PBSA: PHBV- 30% mixed pods and stems	Mixed pods and stems	30	70	2.4
PBSA: PHBV- 10% stems	Stems	10	75	2.5
PBSA: PHBV- 20% stems	Stems	20	75	2.5
PBSA: PHBV- 10% pods	Pods	10	75	2.5
PBSA: PHBV- 20% pods	Pods	20	75	2.5

stems at 10, 20 and 30% were added to produce bio-composite pellets according to Table 1. The obtained pellets were further processed into tensile rods by injection moulding and into films by film extrusion.

Bio-composites pellets were injection moulded (Battenfeld Smart Power 60–210, servo hydraulic machine, 60 ton clamping unit, 25 mm screw diameter) to prepare the test specimens according to ISO 527–1:2019. For the PBSA/PHBV blend (85/15 ratio) the screw temperature was 190/190/190 °C, with a nozzle temperature of 190 °C and the mould temperature of 30 °C. For the samples containing the fibres the screw temperature was 195/195/195 °C, with a nozzle temperature of 195 °C and the mould temperature of 30 °C. Bio-composite samples required 5 °C higher processing temperatures to obtain sufficient flow properties and mould filling, since high fibre content affects the melt flow compared to the PBSA/PHBV blend without fibres.

Film extrusion was done using a laboratory scale 19 mm single-screw extruder Brabender Plasti-Corder® Lab-Station (Brabender GmbH & co KG, Duisburg, Germany). Based on injection moulding results, four samples were chosen for film extrusion, namely, PBSA/PHBV without the fibres, with 10, 20 and 30% mixed faba bean stems and pods. The compounded pellets were dried at 60 °C in a vacuum oven overnight prior further processing. The extruder was equipped with a conical screw with 3:1 compression ratio without screen pack. The temperature profile was 165/165/165/165/165/165 °C (from feed to die), with a screw speed of 50 rpm and 40 °C chill roll temperature. The recorded melt temperature was 155 °C and torque of 10.4–10.6 N m. The sheet die (Extron Mecanor Oy, Akaa, Finland) was 120 mm wide. The whole processing steps from untreated fibres to bio-composite pellets, injection moulded tensile specimens and bio-composite films is shown in Fig. 1.

## 2.3. Characterisation

### 2.3.1. Mechanical properties of the bio-composite films and injection moulding specimens

The test specimens for both tensile test and Charpy impact tests were kept in standard conditions (23 °C, 50% relative humidity) for 5 days before testing. Tensile tests of the injection moulded specimens (shown in Fig. 1) were performed according to ISO 527–1:2019 standard using an Instron 4505 Universal Tensile Tester (Instron Corp., Canton, MA, USA) and an Instron 2665 Series High Resolution Digital Automatic Extensometer (Instron Corp., Canton, MA, USA). A crosshead speed of 5 mm/min was used. A minimum of 6 specimens were tested for each treatment repetition.

The mechanical properties of the bio-composite films (shown in Fig. 1) were measured at room temperature using an Instron 5964 equipped with a 2 kN load cell and a cross head speed of 100 mm/min. The samples were prepared according to ASTM D882 – 18 in the form of strips. Films thickness was measured with a Japan Mitutoyo 500-197-20/30 200 mm/8" Digital Digimatic Vernier Caliper (0.01 mm resolution; ±0.02 mm accuracy). The test was performed on 6 samples each sample type and was analysed using the software Bluehill 3 Version 3.72 (2010–2015 Illinois Tools Works Inc.).

The Charpy impact test of the injection moulded specimens were performed in a three-point bend configuration using a Charpy Ceast Resil 5.5 Impact Strength Machine (CEAST S.p.a., Torino, Italy) according to ISO 179–1:2010 standard. A minimum of 10 specimens were tested for each treatment repetition.

### 2.3.2. Water vapour transmission rate (WVTR) and oxygen transmission rate (OTR)

The water vapour transmission rate (g H<sub>2</sub>O/(m<sup>2</sup> × day)) of the bio-composite films (shown in Fig. 1) was measured at 23 °C, 85% RH using

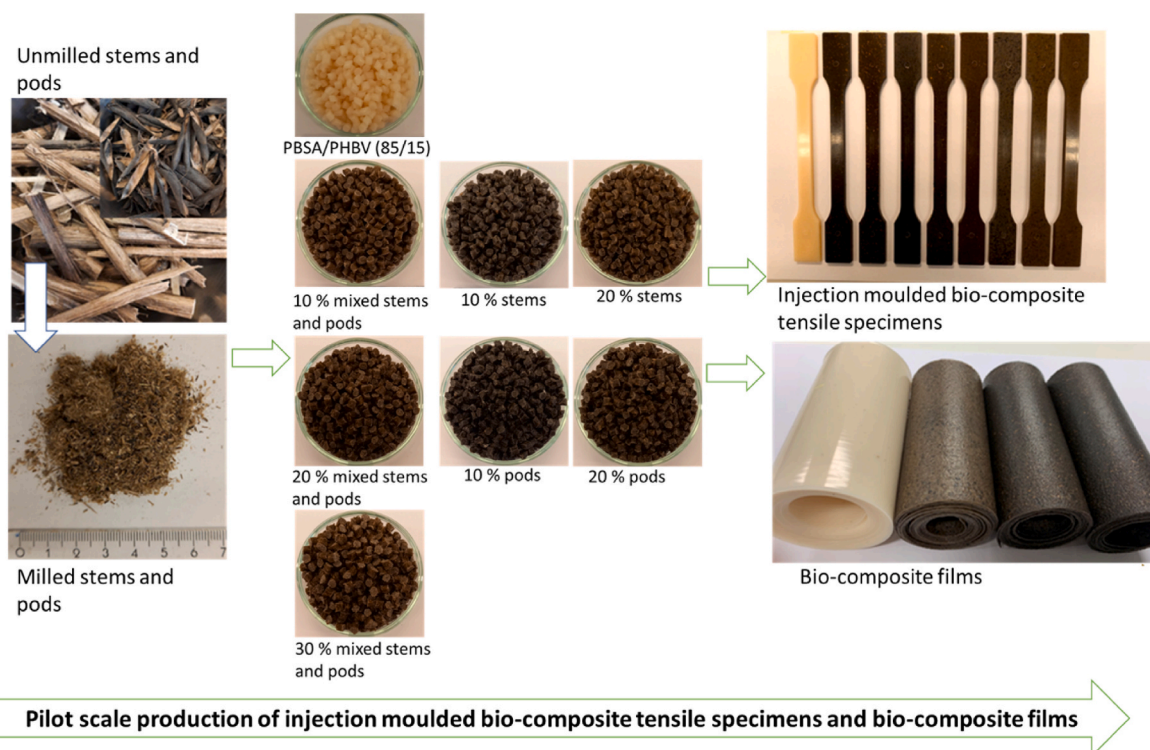


Fig. 1. Pilot scale production steps of the bio-composite films and injection moulding specimens containing faba bean sidestream fibres. On the left side of Fig. 1, dried faba bean stems and pods are shown before and after milling. Compounded PBSA/PHBV blend pellets (without fibres is whitish in colour), while the pellets of bio-composites containing fibres are brown in colour. Manufactured injection moulded tensile test specimens with a standard dog-boned structure are on the upper right corner. Film extruded bio-composite films are presented below the injection moulded tensile test specimens. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Dualperm 7002 (Industrial Physics, Johnsbury, IL, USA). The testing area of the film was 5 cm<sup>2</sup>. Four parallels were measured.

The oxygen transmission rate (ml O<sub>2</sub>/(m<sup>2</sup> × day)) of the bio-composite films (shown in Fig. 1) was measured at 23 °C, 50% RH with a Dualperm 8001 instrument (Industrial Physics, Johnsbury, IL, USA). The testing area of the film was 5 cm<sup>2</sup>. Two parallels were measured.

2.3.3. Water uptake of the bio-composite films

The water uptake of the bio-composite films (shown in Fig. 1) was carried out by immersing the films in distilled water at 25 °C. The samples were removed in water after 24 and 48 h, blot dry with a cloth to remove excess water and weighed using an analytical balance to the accuracy of 0.1 mg. Measurements were performed in triplicates.

2.3.4. Stereo microscope

The surface morphology of the bio-composite films was analysed to understand the distribution size and orientation of the fibres in the bio-composite films. The surface morphology of the bio-composite films was analysed using Wild Heerbrugg (Wild Heerbrugg, Heerbrugg, Switzerland) M5A Stereo Microscope at 12x magnification.

2.3.5. Scanning electron microscope (SEM)

The impact fractured morphology of the samples was analysed to understand the breaking behaviour of the bio-composites. The samples were sputter coated with gold using for 120 s with Baltec Balzers sputter-coater (Balzers Union, Vaduz, Liechtenstein). The cross-sectional morphology was analysed using JEOL 6360LV SEM (JEOL Ltd., Tokyo, Japan) at an accelerating voltage of 10 kV.

2.3.6. Thermogravimetric analysis (TGA) of the compounded pellets

The thermal stability of the compounded pellets (shown in Fig. 1) was analysed using STA 449 F1 Jupiter (NETZSCH, Selb, Germany).

About 25 mg was weighed into 85 µl aluminium oxide pans. Heating was from 35 °C to 800 °C at a heating rate of 10 °C/min under SUPA air (N<sub>2</sub>O<sub>2</sub>).

2.3.7. Differential scanning calorimetry (DSC) of compounded pellets

The thermal properties of the compounded pellets (shown in Fig. 1) were analysed using DSC 2920 (TA Instruments, Tokyo, Japan). About 6–7 mg was weighed into aluminium pan. Heating range was from –50 to 200 °C. Heating and cooling was done twice at a heating and cooling rate of 10 °C/min to erase the thermal history.

2.4. Statistical analysis

The IBM SPSS version 20 statistical software for windows (Armonk, NY: IBM Corp.) was used for statistical analysis. Multifactor analysis of variance was performed on the data and the means were compared at p ≤ 0.05 using Turkey's B test. Independent variables were the PBSA/PHBV blends and bio-composites containing either faba bean stems, pods or mixed stems and pods, and the dependent variables were the measured values.

3. Results and discussions

3.1. Mechanical properties of the bio-composite films and injection moulded specimens

The tensile properties of the injection moulded bio-composites and bio-composite films are shown in Fig. 2. The effect of faba bean stems, faba bean pods, and unsorted faba bean sidestream (i.e. mixed stems and pods) on the tensile properties of the injection moulded specimens was investigated and the results are shown in Fig. 2a. The unsorted faba bean sidestream (i.e. mixed stems and pods) were selected to make bio-composite films, since the tensile properties of the injection moulded

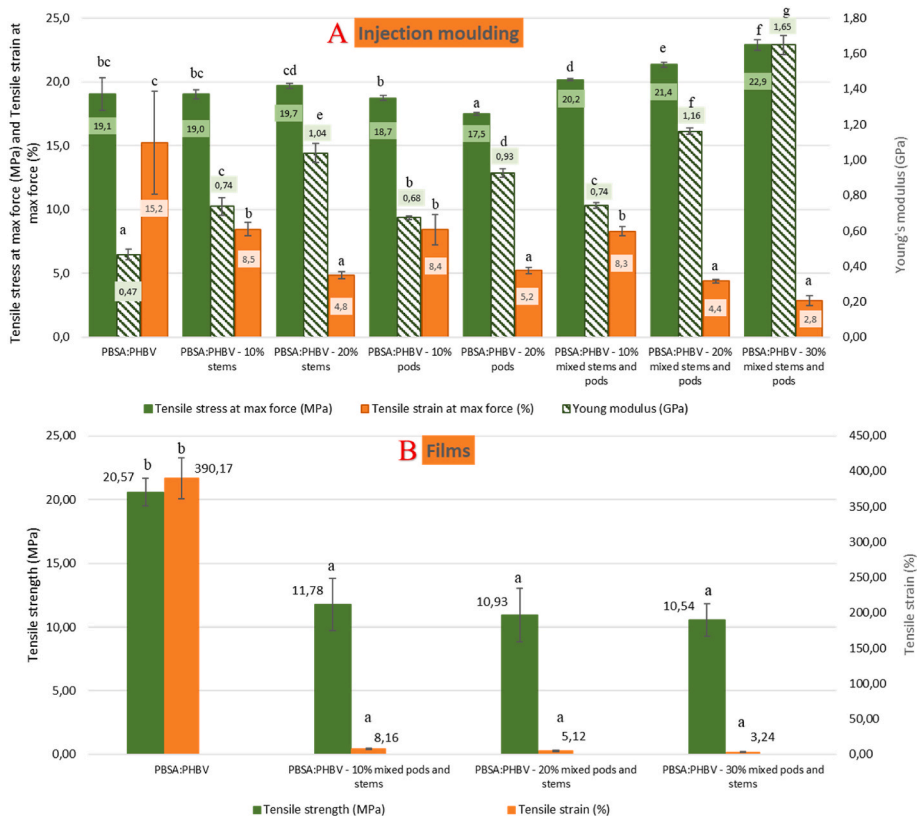


Fig. 2. Tensile properties of the injection moulding bio-composites (a) and bio-composite films (b). Means with different letters are statistically significant at P < 0.05.

bio-composites prepared from mixed stems and pods had slightly higher tensile stress and Young's modulus compared to the injection moulded specimens prepared either from the stems or pods. In addition, the use of unsorted faba bean sidestream (mixed stems and pods) would reduce the time-consuming steps of separating the stems and pods. The tensile properties of the bio-composite films are shown in Fig. 2b. The injection moulded PBSA/PHBV blend had a tensile stress at maximum force of 19.1 MPa, tensile strain at maximum force of 15.2% and Young's modulus of 0.47 GPa (Fig. 2a). The addition of faba bean pods (10 and 20%) led to a slight decrease in tensile stress at maximum force, while it remained unaffected by the addition of faba bean stems (10 and 20%) relative to the PBSA/PHBV blend. The addition of 10 and 20% faba bean stems or pods decreased the tensile strain by about 44 and 68% respectively relative to the neat blend (Fig. 2a). The Young's modulus of the bio-composite containing 10 and 20% faba bean stems increased by 36 and 55% respectively, and similarly the bio-composite containing 10 and 20% faba bean pods increased by 21 and 49% respectively in relation to the neat blend (Fig. 2a). The higher increase in Young's modulus of the bio-composite containing the stems compared to that the bio-composites containing pods may be related to the cellulose content of the faba bean stems compared to the pods. The faba bean stems contained 39% cellulose compared to the pods that contained 31%. Cellulose is semicrystalline in nature, therefore higher cellulose content in the stems provide more stiffness leading to higher Young's modulus in the bio-composite containing the stems compared to the bio-composite containing the pods at the same loading [17]. also reported higher Young's modulus for high density poly(ethylene) HDPE-based bio-composites reinforced with sweet sorghum bagasse that had higher cellulose compared to bio-composites reinforced with sugarcane bagasse and maize bagasse that had lower cellulose content. Higher cellulose content was therefore found to have positive effect on Young's modulus. In general, there were no significant difference in the overall tensile properties of the bio-composite containing the stems or the pods, despite their differences in chemical composition. Therefore, this demonstrates that there is no need to separate the faba bean stems from the pods post-harvest to prepare the PBSA/PHBV based bio-composites.

The tensile properties of the injection moulded bio-composites containing mixed stems and pods are shown in Fig. 2. There are several factors, such as distribution and orientation of fibres, length of fibres and interfacial adhesion between the fibres and the polymer matrix that affect the tensile properties of bio-composites [18]. The Young's modulus increased linearly with an increase in the amount of mixed faba bean stems and pods, with the bio-composite containing 30% mixed faba bean stems and pods showing an increase of 71% relative to the PBSA/PHBV blend (Fig. 2a). The increase in Young's modulus is due to the reinforcing effect of the fibres. The fibres have high stiffness/rigidity compared to the polymer matrix, thus providing stiffness to the material resulting in an increase in Young's modulus [5,19].

Similarly, the tensile stress at maximum force increased linearly with an increase in the amount of mixed faba bean stems and pods, with the bio-composite containing 30% mixed stems and pods showing an increase of 17% relative to the PBSA/PHBV blend (Fig. 2a). The increase in tensile stress at maximum force with an increase in fibre loading may be an indication of good interfacial adhesion and efficient stress transfer between the polymer matrix and the mixed faba bean stems and pods when load is applied. Previous studies have shown that good interfacial adhesion between the fibres and the polymer matrix led to an improvement in tensile stress, whereas poor interfacial adhesion led to a decrease in tensile stress of bio-composites [12]. The tensile strain at maximum force decreased linearly with an increase in mixed faba bean stems and pods, with the bio-composite containing 30% fibres showing the largest decrease of 81% compared to the neat blend (Fig. 2a).

The injection moulded bio-composite containing mixed faba bean stems and pods had better performance in terms of Young's modulus and tensile stress at maximum force compared to the bio-composite containing faba bean stems and faba bean pods separately at the same

content. Therefore, this justifies our choice of manufacturing of the films using the whole sidestream (unsorted mixed stems and pods), instead of separating the pods and stems post-harvest.

The tensile strength of PBSA/PHBV blend films was 20.57 MPa, which reduced by 43% with the addition of 10% mixed stems and pods and it did not change with further addition of 20 and 30% mixed stems and pods (Fig. 2b). This trend was different from the injection moulded bio-composites that displayed an increase in tensile stress with fibre loading (Fig. 2a). This may be due to differences in processing. Injection moulding may provide better packing of the polymer chains and the fibres resulting in better performance compared to the bio-composite films prepared by film extrusion. However, the tensile strain of the bio-composite films displayed a similar trend to the tensile strain at maximum force of the injection moulded bio-composites. The PBSA/PHBV blend film had a tensile strain at break of 390% that reduced to 8, 5 and 3% with the addition of 10, 20 and 30% respectively (Fig. 2b) suggesting that the films become more brittle with fibre addition. Fibre loading is known to decrease the tensile strain of bio-composites due to rigidity of the fibres relative to the polymer matrix. In addition, the increase in fibre loading decreases the amount of polymer available for elongation [20].

The mechanical properties of the fibre-reinforced composites depend on the strength and modulus of the fibres, chemical and thermal stability of the matrix and most importantly, the effectiveness of interfacial adhesion between the polymer matrix and fibres for successful stress transfer [18]. Since the faba bean stems and pods were milled to less than 2 mm, it may be difficult to achieve efficient stress transfer between the polymer matrix and the fibres in the bio-composite films with a thickness of about 500  $\mu\text{m}$ . Therefore, the large particle size of the fibres may be responsible for the reduction in the mechanical properties of the bio-composite films containing the fibres in relation to the PBSA/PHBV blend [21].

The Charpy impact strength of the notched bio-composites containing faba bean stems, pods and mixed stems and pods was conducted to evaluate the ability of the material to withstand sudden load and the results are shown in Fig. 3. Impact strength is the measurement of the amount of energy a material absorbs during fracture propagation. The PBSA/PHBV blend matrix had the impact strength of 4.5 kJ/m<sup>2</sup> and was higher for the bio-composite containing 10% faba bean stems and pods. However, upon further increase in fibre loading the impact strength decreased (Fig. 3). Other authors have reported that the addition of fibres can in some cases decrease the impact strength relative to the neat polymer. For example [22], reported a lower impact strength of the bio-composite containing bamboo fibres compared to the PHBV matrix.

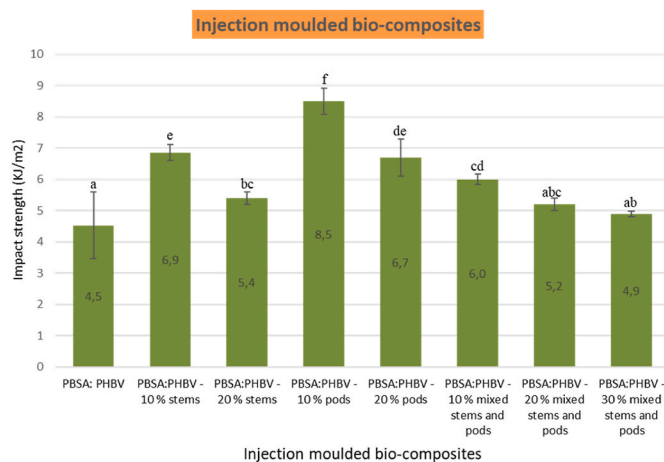


Fig. 3. Impact strength of the injection moulded bio-composites with 10, 20 and 30% of faba bean mixed pods and stems and 10, 20% stems and pods. Means with different letters are statistically significant at  $P < 0.05$ .

Similarly [12], reported high impact strength for BioPBS that decreased with addition of hemp fibres.

The bio-composites containing 10 and 20% faba bean stems or pods separately had higher impact strength compared to the bio-composites containing mixed faba bean stems and pods (Fig. 3). This is probably due to more homogeneous composition of the faba bean pods or stems separately compared to mixed faba bean stems and pods. In all the bio-composites the increase in the concentration of fibres led to a decrease in impact strength with the bio-composite containing 30% mixed faba bean stems and pods showing the largest decrease (Fig. 3). The increase in the amount of the fibres increases the chances of fibre-to-fibre contact that can act as stress raise to reduce the amount of energy required to break the sample.

### 3.2. Barrier properties of the bio-composite films

The water vapour transmission rate (WVTR) and oxygen transmission (OTR) of the bio-composite films are shown in Fig. 4.

The WVTR of the PBSA/PHBV blend film was 13.2 g/m<sup>2</sup>.24 h which increased to 16.8 g/m<sup>2</sup>.24 h after the addition of 10% mixed faba bean stems and pods (Fig. 4). With further increase in mixed faba bean stems and pods to 20 and 30%, the WVTR of the bio-composite films reduced to 11.9 and 11.5 g/m<sup>2</sup>.24 h ( $p < 0.05$ ) relative to the bio-composite film containing 10% faba bean pods and stems (Fig. 4). However, there was no statistical significance in the WVTR of the bio-composite film containing 20 and 30% mixed faba bean stems and pods and the PBSA/PHBV blend film. Many factors affect the WVTR of any fibre-reinforced composites, such as the amount of fibres, the change in crystallinity, the molecular weight and the hygroscopicity of the fibres [23]. Although the fibres are hygroscopic, the compact structure of the film as a result of fibre loading at 20 and 30% may have led to the decrease in WVTR of the bio-composite film containing 20 and 30% mixed faba bean stems and pods compared to the bio-composite film containing 10% mixed faba bean stems and pods.

The OTR of the PBSA/PHBV blend film was 76.7 cm<sup>3</sup>/m<sup>2</sup>.24 h. There was no significant difference in the OTR of the bio-composite film containing 10% fibres in relation to the PBSA/PHBV blend film (Fig. 4). However, there was a significant reduction in OTR by 29% and 52% in the bio-composite film containing 20 and 30% mixed faba bean stems and pods, respectively, compared to the PBSA/PHBV blend film (Fig. 4). This result is especially important to notice because a lower OTR is beneficial in such food packaging applications where the food products would undergo undesirable oxidative reaction, for example fat rancidity in the presence of oxygen gas [24]. prepared HDPE films reinforced with purified cellulose fibres. The increase in cellulose fibre loading led to a decrease in OTR, with the bio-composite film containing 50% cellulose fibres having 65% decrease in OTR. These authors argued that the blocking effect of the filler is more significant than the effect of

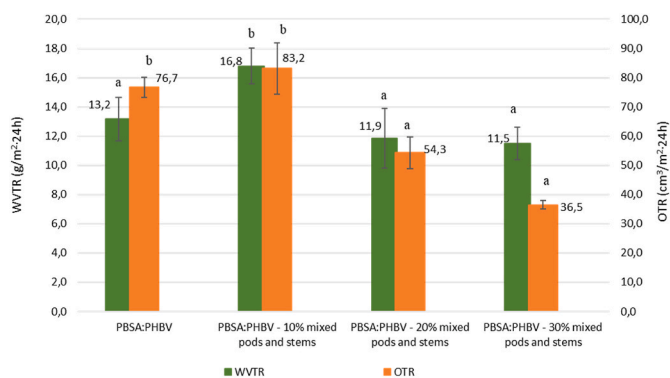


Fig. 4. Water vapour transmission rate and oxygen transmission rate of the bio-composite films. Means with different letters are statistically significant at  $P < 0.05$ .

crystallinity at a fibre content of more than 10%. The stereo-microscope images (Section 3.4) showed that the increase in fibre loading led to a more compact of structure of the fibres within the polymer matrix. Therefore, it is possible that a decrease in OTR in the bio-composite films containing 20 and 30% fibres could be due to the compact structure of the film and the presence of impermeable cellulose crystals. Lignocellulose fibres contain semi-crystalline cellulose [25], therefore, the impermeable cellulose crystals may create a more tortuous path for the non-interacting gas molecules to travel through the bio-composite film, thus reducing OTR. Therefore, the bio-composite films containing 20 and 30% fibres may be suitable for applications where reduced OTR is desired, as the WVTR was not negatively affected by fibre loading at 20 and 30% compared to the PBSA/PHBV blend film.

### 3.3. Water uptake

The water uptake of the PBSA/PHBV film and the bio-composite films containing 10, 20 and 30% mixed faba bean stems and pods are shown in Fig. 5. The PBSA/PHBV blend film did not show any water uptake (0%) after 24 and 48 h, which appeared to be an encouraging result for packaging application. This is due to the relatively hydrophobic surface of PBSA/PHBV films. However, water uptake increased linearly with the addition of 10, 20 and 30% fibres, with the bio-composite film containing 30% fibres showing the highest water uptake of 7% and 8% after 24 and 48 h, respectively (Fig. 5). Generally, the lignocellulosic fibres are known to increase water uptake in bio-composites due to the polar groups in hemicellulose, cellulose, and lignin [26]. [12] reported a water uptake of less than 10% in BioPBSA reinforced with 30% hemp fibres. Since lignocellulosic fibres are prone to absorb moisture and possess a porous microstructure by themselves, if not properly embedded in the polymer matrix at the film surface, water uptake is more likely to happen which may negatively affect the material properties of the films. Even though the bio-composite films containing 20 and 30% fibres showed water uptake after 24 and 48 h of immersion in water, the WVTR of these bio-composite films remained good as the neat PBSA/PHBV blend as shown in the previous section.

### 3.4. Stereo microscope

The surface morphology of the bio-composite films containing 10, 20 and 30% mixed faba bean pods and stems sidestream is shown in Fig. 6. The bio-composite film containing 10% mixed faba bean stems and pods showed that the fibres were randomly dispersed in a polymer blend matrix during processing and did not show any significant visible aggregation of the fibres within the polymer blend matrix (see white arrows) (Fig. 6a). The size of the fibres is non-homogeneous with some

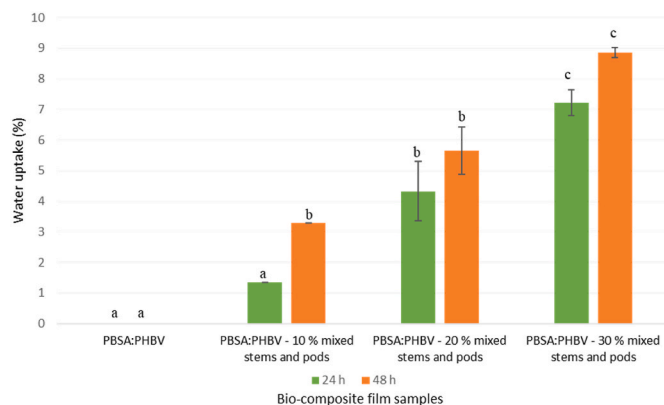


Fig. 5. Water uptake of bio-composite films containing 10, 20 and 30% mixed faba bean stems and pods after 24 and 48 h. Means with different letters are statistically significant at  $P < 0.05$ .

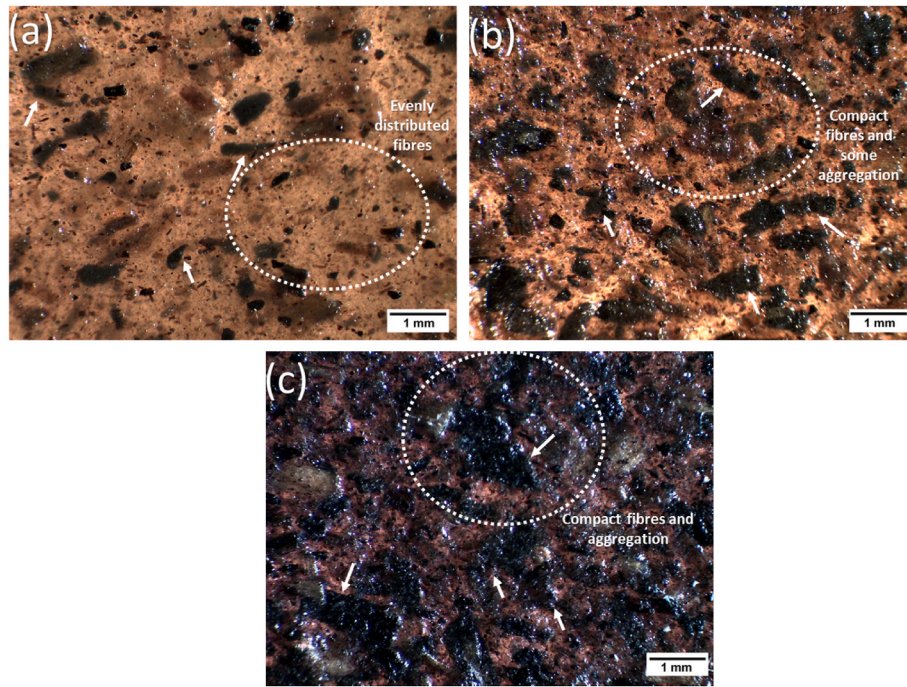


Fig. 6. Surface morphology of the bio-composite films with (a) 10, (b) 20 and (c) 30% mixed stems and pods from faba bean sidestream. Scale bar = 1.00 mm.

fibres visibly larger than 1 mm and some fibres smaller than 1 mm (see arrows) (Fig. 6a). The bio-composite films containing 20% (Figs. 6b) and 30% (Fig. 6c) mixed faba bean stems and pods showed that the fibres were organised to form a compact structure during processing with some visible aggregation of fibres within a polymer matrix (as shown in the white circles). The bio-composite film containing 20% fibres (Fig. 6b) showed a compact structure and aggregation of the fibres within the polymer blend matrix with random orientation. The bio-composite film containing 30% fibres (Fig. 6c) showed an even more compact structure and aggregation of the fibres within the polymer blend matrix with

random orientation. The aggregation of the fibres breaks the continuous matrix development and may limit the stress transfer throughout the matrix and from the matrix to the aggregated fibres thus compromising the mechanical properties. However, this type of morphology observed in the bio-composite film containing 20 and 30% fibres is believed to have led to a reduction in OTR.

### 3.5. Scanning electron microscope (SEM)

The impact fractured SEM morphology of the PBSA/PHBV blend and

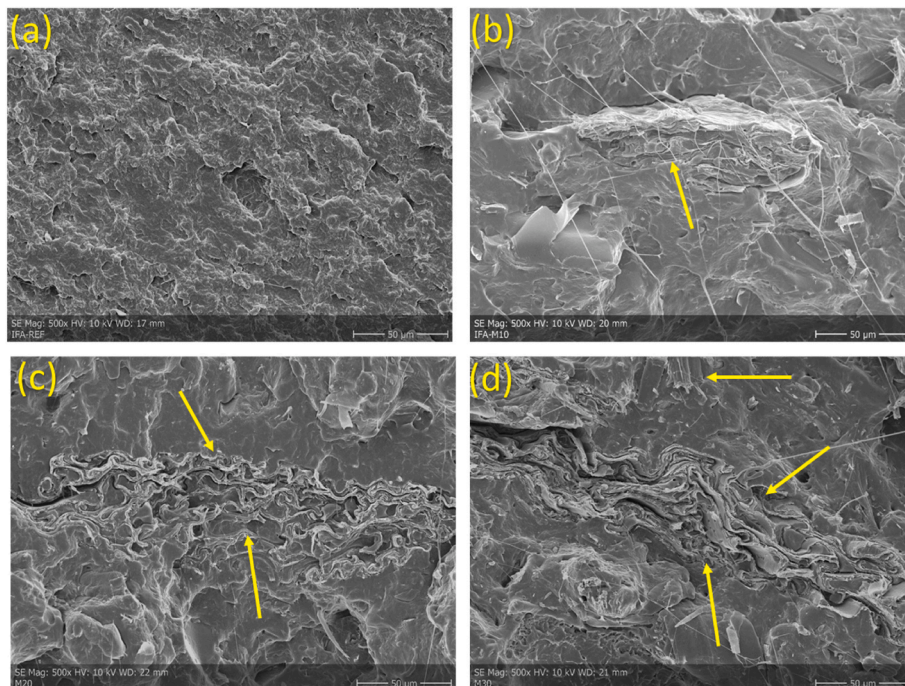


Fig. 7. Impact fracture SEM morphology of (a) PBSA/PHBV (85:15), (b) with 10%, (c) 20%, (d) 30% faba bean mixed stems and pods. Scale bar = 50 µm.

bio-composites with 10, 20 and 30% mixed pods and stems from faba bean is shown in Fig. 7. Previous studies have reported immiscible PBS/PHB blend (85/15) and PBSA/PHB blend (15/85) in which a matrix-droplet morphology was observed [27]. [28] also reported immiscible a PBS/PHBV blend (80/20) characterized by PHBV droplets dispersed in PBSA. In this study, the PBSA/PHBV blend (Fig. 7a) did not show any phase separation and a droplet dispersed morphology was not observed. Instead, a continuous non-smooth morphology was observed that is typical for a ductile material, consistent with the high elongation at break (Fig. 2). It appears that the processing conditions were sufficient to achieve miscibility of PBSA and PHBV.

The bio-composites containing 10% (Figs. 7b) and 20% (Fig. 7c) mixed faba bean stems and pods showed good adhesion of the fibres to the polymer matrix. The fibres are embedded in the polymer matrix and there is no significant interfacial gap between the polymer matrix and the fibres as shown by the arrows. In addition, there were no fibre pull outs during impact test suggesting some interfacial adhesion between the polymer matrix and the fibres. Similar observations were made with the bio-composite containing 30% mixed faba bean stems and pods (Fig. 7d). The fibres are inherently hydrophilic and may interact with the polar groups of PHBV resulting in interfacial adhesion [5]. In the next section, it will be observed that the thermal properties (TGA and DSC) of PHBV in the bio-composite were affected more by fibre addition than PBSA, this may further suggest that the faba bean fibres had higher affinity to PHBV than PBSA in the bio-composite.

The SEM morphology is consistent with an increase in tensile stress of the bio-composite films containing the fibres compared to the PBSA/PHBV blend (Fig. 2a). Good interfacial adhesion between the fibres and the polymer matrix provided enough stress transfer between the polymer blend matrix to the fibres thereby increasing the tensile stress [5]. also made similar observations. In their study they prepared bio-composites using either poly(propylene) PP or PHBV as a polymer matrix and soy stalk, corn straw and wheat straws as fibres. These authors reported good interfacial adhesion between PHBV and wheat straws with no interfacial gap. This resulted in an increase in tensile strength. In contrast there was poor interfacial adhesion between PP and wheat straws leading to a reduction in tensile stress.

Tensile strain is also dependent on the interfacial between the filler material and the polymer matrix. Although the interfacial adhesion

between the polymer matrix and the fibres was good there was a decrease in tensile strain. This is because the fibres are stiff and have high modulus compared to the polymer matrix, they provide stiffness to the material resulting in an increase in Young's modulus and a decrease in tensile strain.

### 3.6. Thermal properties of the bio-composites

Polymer blending and the addition of fibrous material is known to affect the thermal properties of the resulting polymer blend and their bio-composite materials. The thermal stability of the bio-composites was evaluated by TGA, and the melting/crystallisation behaviour was evaluated by DCS, and the results are shown in Fig. 8. The TGA and derivative TGA curves of the bio-composites are shown in Fig. 8a and b, respectively. The DSC second melting curves and the DSC second cooling curves of the bio-composites are shown in Fig. 8c and d, respectively.

The PBSA/PHBV blend and the bio-composites containing 10, 20 and 30% faba bean stems and pods showed a two-stage degradation behaviour, with the first peak degradation temperature ( $T_{deg1}$ ) corresponding to PHBV and the second peak degradation temperature ( $T_{deg2}$ ) corresponding to PBSA (Fig. 8b) [8]. also reported a two-stage degradation behaviour for BioPBS/PHBV-based composite containing mineral filler, with the degradation at lower temperature corresponding to PHBV and the one at higher temperature corresponding to BioPBS. The dTGA curves evidenced a minor degradation peaks/shoulder occurring between  $T_{deg1}$  and  $T_{deg2}$  (Fig. 8b) potentially due to the complex thermal degradation behaviour of lignocellulosic fibres.

The onset degradation temperature ( $T_o$ ),  $T_{deg1}$  (corresponding to PHBV) and  $T_{deg2}$  (corresponding to PBSA) were 296.33 °C, 307 °C and 407 °C respectively (Supplementary Table 1). These values decreased with an increase in fibre loading suggesting that the addition of fibre decreased the thermal stability of the bio-composites.  $T_{deg1}$  (corresponding to PHBV) decreased by 38 °C while  $T_{deg2}$  (corresponding to PBSA) decreased by 13 °C in the bio-composite containing 30% fibres relative to the PBSA/PHBV blend (Supplementary Table 1). The thermal stability of PHBV appeared to be more impacted by the addition of fibre than PBSA in the bio-composite material. The PBSA/PHBV blend completely degraded leaving no ash residue (0%). However, with the addition of fibre the ash residue increased, with the bio-composite

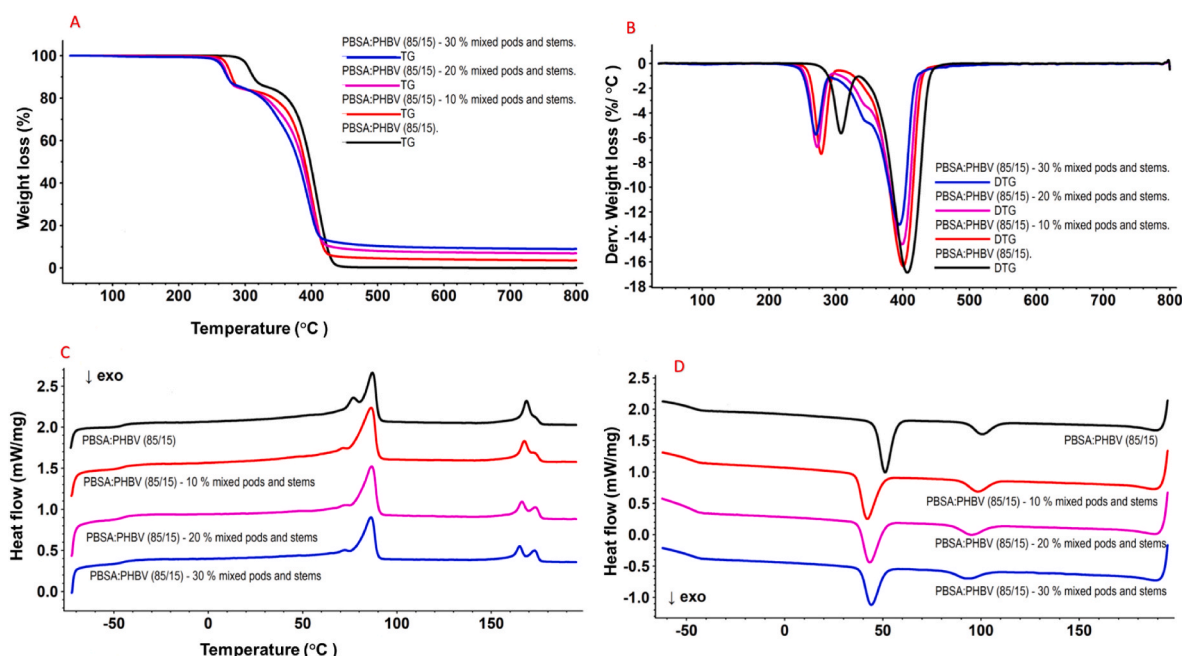


Fig. 8. TGA curves (a) and (b) dTGA curves of the bio-composites. DSC curves showing second heating (c) and (d) second cooling of the bio-composites.



containing 30% fibres having mass residue of 9% (Fig. 8a). This mass residue is due to the ash from the fibres.

The neat PBSA has a melting temperature ( $T_m$ ) of 86.6 °C, and a melt crystallisation temperature ( $T_{mc}$ ) of 9.8 °C [14], while PHBV has a  $T_m$  of 171 °C and  $T_{mc}$  of 122 °C [29]. The PBSA/PHBV blend displayed two major melting phenomena (Fig. 8c) and two melt crystallisation phenomena (Fig. 8d), corresponding to PBSA and PHBV, respectively. In the PBSA/PHBV blend, PBSA displayed double melting peaks, with the first less intense melting peak ( $T_{m1}$ ) at 77.40 °C and the second main melting peak at ( $T_{m2}$ ) 87.40 °C (Fig. 8c). Similarly, PHBV displayed double melting peaks with the first main melting peak ( $T_{m1}$ ) at 168 °C and a second minor melting peak or shoulder ( $T_{m1}$ ) at 173 °C (Fig. 8c). The double melting behaviour of polymers, such as PBS, has been widely reported in literature. It is ascribed to the melt recrystallisation behaviour of polymers during the heating process. Imperfect crystals may melt at lower temperatures, recrystallise and subsequently melt at higher temperatures, leading to the double melting peaks [14,30,31]. In general, the melting temperatures of PBSA and PHBV in the blend and in the bio-composites containing the fibres occurred in the same range, with  $T_{m1}$  for both PBSA and PHBV decreasing with fibre loading (Supplementary Table 1).

The PBSA/PHBV blend had two melt recrystallisation peaks, with first melt recrystallisation peak ( $T_{mc1}$ ) at 51.33 °C corresponding to PBSA and second melt recrystallisation peak ( $T_{mc2}$ ) at 100 °C corresponding to PHBV (Fig. 8d). Both the melt crystallisation temperatures ( $T_{mc1}$  and  $T_{mc2}$ ) of PBSA and PHBV shifted to lower temperatures with the addition of fibres. This indicates that the crystallisation of both PBSA and PHBV were restricted by the presence of the fibres due to the suppressed nucleation. Another possible reason for a decrease in the crystallisation growth rate could be due to the dilution effect of the fibres that reduced the PBSA and PHBV chain segments towards growing crystals [22]. also reported a decrease in the rate of crystallisation of PHBV with the addition of 30% bamboo fibres.

#### 4. Conclusion

In this study, novel bio-composite films and injection moulded bio-composites were produced using agricultural sidestream of a climate smart African crop, faba bean as a filler. Faba bean stems and pods were added at 10, 20 and 30% in the PBSA/PHBV (85/15 ratio) matrix. The addition of the mixed faba bean stems and pods resulted in an increase in Young's modulus, tensile stress at maximum force, but resulted in a decrease in tensile strain and impact strength. The bio-composite containing 30% mixed fabae bean stems and pods showed maximum increase in Young's modulus by 71% and an increase in tensile stress at maximum force by 17%. The SEM morphology revealed good interfacial adhesion between the fibres and the polymer matrix resulting in an improvement in the mechanical properties in relation to the bio-composite without the fibres. The oxygen transmission rate improved with the addition of 20 and 30% mixed faba bean stems and pods, with the bio-composite containing 30% showing the optimal improvement relative to the PBSA/PHBV blend film. This study has demonstrated that bio-composites containing PBSA/PHBV (85/15) with faba bean sidestream can be prepared by extrusion compounding followed by film extrusion and injection moulding. The resulting materials have balanced mechanical properties and improved barrier properties compared to the PBSA/PHBV blend without the fibres. Therefore, the use of locally available sidestream from African crops, such as faba bean have a potential for use in the development of environmentally friendly flexible and rigid bio-packaging materials. For future work, the thermo-mechanical, rheological and TEM should be conducted to gain more insights into the fibres-polymer interaction. In addition, food trials can be conducted on these bio-composite film to test their potential in food applications.

#### CRedit authorship contribution statement

Mondli Abednicko Masanabo: Validation, Methodology, Investigation, Writing - Original Draft, Writing - Review & Editing, Visualisation. Amélie Tribot: Conceptualisation, Methodology, Investigation, Writing - Original Draft, Writing - Review & Editing. Enni Luoma: Conceptualisation, Methodology, Investigation, Writing - Original Draft, Writing - Review & Editing. Nusrat Sharmin: Methodology, Investigation, Resources, Writing - Review & Editing. Morten Sivertsvik: Resources. M. Naushad Emmambux: Validation, Resources, Writing - Review & Editing, Supervision. Janne Keränen: Conceptualisation, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Supervision, Project administration.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymeresting.2023.108047>.

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