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Agricultural by-product filled poly(lactic acid) biocomposites with enhanced biodegradability: The effect of flax seed meal and rapeseed straw

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ABSTRACT

The purpose of this research was to develop "green" materials by combining poly(lactic acid) (PLA) with two agricultural by-products, namely flax seed meal (FSM) and rapeseed straw (RSS). The natural fillers (0–20 wt.%) were mixed with PLA through extrusion and then injection molded into specimens. The samples were analyzed for their thermal, morphological, mechanical, and physical features and biodegradability. Thermal properties and crystallinity were analyzed using Differential Scanning Calorimetry (DSC), while the morphology was investigated by Scanning Electron Microscopy (SEM). Mechanical properties were characterized through tensile, flexural, and impact measurements, while surface hardness was evaluated by Shore D tests. Water absorption and biodegradability of the samples were also examined. DSC measurements revealed a nucleating effect of both bio-fillers. Based on the tensile tests, major improvement in stiffness was found with the biocomposites having up to ~16 % higher Young's modulus than neat PLA (2.5 GPa). It came, however, at the cost of tensile strength, which decreased from 56 to 51 MPa even in the presence of the lowest amount (2.5 wt.%) of FSM. Loss in strength was due to the limited adhesion between the components, as also supported by SEM images. The hardness slightly (1–2 %) improved in the presence of even 2.5 wt.% bio-filler and it remained at that level at higher filler loading as well. Laboratory-scale composting revealed that both fillers facilitated biodegradation with FSM being superior. In the presence of 10–20 wt.% FSM, the rate of decomposition was found to be twice as fast compared to neat PLA.

1. Introduction

To tackle the issue of the gradually increasing number of landfills and the amount of waste deposited there, different products and their components are expected to be fabricated by taking into account their environmental friendliness. When it comes to plastics, the two major routes that can be followed are the facilitation of recyclability or biodegradability [1–5]. Regarding the first route, the greatest motive for the industry is the fact that the price of commodities doubled during the last three years according to the IMF, which is the largest increase since the years following the recession of 2008 (https://data.imf.org/?sk=471DDDF8-D8A7-499A-81BA-5B332C01F8B9). The second route can be achieved by manufacturing products that are derived from renewable resources or at least contain such components. For instance, in the plastic industry, great efforts are being devoted to improving the "green" nature of the material by incorporating various natural fibers into them. Accordingly, extensive research is carried out in this field [6–14].

Plastics can be classified into different categories based on their source and their biodegradability. The ones synthesized from natural ingredients and/or which are also capable of biodegradation are called biopolymers [15]. Note that even though bio-based plastics are derived from natural ingredients, they are not necessarily biodegradable and *vice versa*. The development of biopolymers and biopolymer-based multi-component materials has become a hot topic in recent years and has become of focus of much research [16–23]. As a consequence, the biopolymer industry has shown unprecedented growth in production lately [24,25]. In general, these materials are used for single-use applications, such as packaging.

One of the most widely used biopolymers is poly(lactic acid) (PLA). PLA is produced from sugarcane and cornstarch through fermentation, which makes it an eco-friendly material [26]. However, its synthesis requires an immense amount of lactose- and glucose-containing agricultural products [27], which raises ethical questions about the priority

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of food-based industrial conglomerates [28]. Lactic acid has two stereoisomers, more precisely called enantiomers, because they are mirror images of each other [29]. They are classified based on the position of the –OH group to the chiral center [27,30]. Accordingly, the most commonly produced types are the L and d-lactic acid (LLA, and DLA, respectively) [31]. In most commercial PLA grades the various stereoisomers are mixed at different ratios [32]. PLA is a thermoplastic polyester that can be processed with traditional technologies, such as extrusion and injection molding as well as novel techniques such as 3D printing [33]. PLA is widely used both in the packaging [34] and medical industry [35]. It possesses tensile and flexural strength (50–60 MPa and 90–110 MPa, respectively) comparable to other widely used thermoplastics like poly(ethylene-terephthalate) (45–55 MPa and 100–120 MPa) or polystyrene (40–50 MPa and 70 MPa). Its stiffness (Young's modulus: ~2.4 GPa, flexural modulus: ~3.4 GPa) is among the highest, manifesting in rather stiff and rigid behavior [36]. It has a rather hydrophobic nature because of the methyl group (CH_3) in its chain molecule [37]. One of the most attractive properties of PLA is its biodegradability. Since global plastic pollution has exponentially increased in the past ten years [38], manufacturers are expected to act in order to decrease the amount of accumulating waste. Thereafter, research and development on the biodegradation of PLA is a well-documented field [39–41]. To achieve faster decomposition, specific environmental conditions are required (temperature, humidity, soil, etc.). In order to facilitate biodegradation, researchers investigate combining PLA with other natural ingredients [42–44].

Natural fibers consisting of cellulose, hemicellulose, and lignin are the main structural components of plants [45]. Since plants are also a kind of natural polymers it seems straightforward to combine them with plastics, such as PLA in order to alter the mechanical and other properties of the latter. Besides the modified properties, its cost efficiency can be improved as well and its decomposition can be accelerated this way [46]. Therefore, extensive research has been performed in this area lately [47–49]. On the other hand, these composite materials have their drawbacks as well due to compatibility issues between the components. In order to overcome these limitations, researchers tend to apply various surface modifications to ensure proper adhesion between the matrix and the natural additives [50,51]. These treatments, however, often include using various chemicals that besides increasing the cost of manufacturing also severely deteriorate the "green" nature of the resulting composites. One example of such techniques is the alkali treatment, where NaOH is utilized [52].

Depending on the type of natural fiber used as filler within the biocomposite, different kinds of property enhancement can be achieved for PLA. Bamboo-reinforced PLA, for instance, is a popular choice, since bamboo is a plant widely cultivated all over the world, especially in China, where it is used extensively for construction works due to its strength and low cost [53]. Its beneficial effect on PLA is supported by a number of research articles in the literature [54,55]. Dehghan et al. [56] fabricated PLA/bamboo polymer composites using compression molding, with a fiber content ranging from 35 to 55 wt.% with 1 % addition of maleic anhydride grafted polypropylene (MAPP). The study reports a tensile strength for unfilled PLA being 48.13 MPa, while with 35 wt.% of bamboo fiber, it decreases to 37.31 MPa. The decline continues with the addition of 55 wt.% bamboo to 22.14 MPa due to the poor adhesion between the components. The study also assessed a critical aspect of biopolymer composites, investigating their biodegradability *via* fungal exposure. The authors found that the degree of decomposition increased over time due to the bamboo fibers, thereby supporting the claim that the natural fiber containing PLA exhibits superior biodegradation compared to its unfilled counterpart.

Another group of highly investigated biocomposites is the PLA/wood flour binary systems. Wood/plastic composites (WPCs) are composite materials that are already used in the construction and automotive industry [57]. The reason for the immense interest in WPCs lies in the cost-efficient acquisition of the filler and its rather simple incorporation into the polymer. Logging residues [58], wood flour [59], and other by-products of forestry can be utilized for manufacturing WPCs. One of the most notable uses of wood-filled polymers lately is in Fused Deposition Modelling (FDM), which is a type of 3D printing technique. Wood particles can reduce the overall cost of the polymer matrix; however, their presence can also lead to brittleness and reduced geometrical accuracy of the printed part [60].

Other choices for natural fiber as reinforcement in composites include hemp, jute, sisal, and many more. Although a number of review articles [61–63] have been published lately dealing with these kind of composites, it is rather difficult to properly compare the developed materials due to differences in production technique, fiber treatment, fiber size, and concentration. Another aspect worth analyzing is the difference in cellulose, hemicellulose, and lignin content of the applied natural fillers. According to the literature, fibers with higher cellulose content tend to result in superior tensile properties, while higher lignin content might increase the flame retardancy [64]. For instance, Lau et al. [65] manufactured PLA/kenaf composites for 3D printing purposes with a kenaf content of up to 20 wt.%. Kenaf is known to have a rather high cellulose concentration of 75–85 %. As a consequence, the tensile strength of PLA increased from 9.57 MPa to 47.02 MPa.

In a recent study [66] the authors investigated the biodegradation of raw natural fibers without being embedded into a polymer matrix and it was found that hemp fibers are capable of losing more than 30 % of their weight within the first 4 days of being buried in decomposing soil, making them an attractive choice for biopolymer composites, where quick disintegration is a primary requirement. In our previous research [67], rapeseed straw (RSS) particles (0–20 wt.%) of different sizes were applied as natural additives for PLA-based biocomposites. Based on the results, RSS particles were shown to act as nucleating agents facilitating the crystallization of PLA. Additionally, straw particles effectively improved the stiffness of the polymer; both the tensile and flexural modulus increased relatively by ~30 % in the presence of 20 wt.% RSS, albeit, at the cost of slightly decreasing strength. The water absorption kinetics were also studied, revealing that straw fibers, especially the largest ones (35–60 mesh) tend to absorb considerably more water than neat PLA.

As outlined above, a large body of work has been devoted to fabricating and characterizing biocomposites composed of entirely biodegradable constituents throughout the last decade. The existing body of literature pertaining to the impacts of agricultural waste utilization is primarily concerned with mechanical and thermal characterization, with inadequate attention paid to the biodegradation characteristics of these biocomposites. Therefore, this investigation aims to identify solutions that can contribute to the development of more economically and environmentally sustainable engineering practices, in addition to those that are mechanically and thermally viable. Furthermore, there are numerous lignocellulose fibers that have yet to be explored in relation to this objective. In the present study, flax seed meal (FSM) was incorporated into PLA at different concentrations (0 to 20 wt.%) as a natural filler. To the best of authors' knowledge, there has been no prior investigation that has examined the suitability of FSM agricultural waste for this particular objective. Furthermore, the benefits of combining agricultural waste materials such as FSM and RSS in a PLA matrix have yet to be researched. Therefore, RSS was incorporated as a secondary additive to investigate the potential of filler hybridization, which has been a promising but less studied area within the scope of natural fiber filled biocomposites. Accordingly, biocomposites were manufactured through extrusion followed by injection molding. PLA/FSM binary composites and PLA/FSM/RSS ternary composites were fabricated this way to determine the effect of the type and concentration of the two fillers. Subsequently, the morphological, thermal, mechanical, and physical properties of the biocomposites were examined. In order to support one of the most favorable trait of the application of vegetable fillers in PLA, laboratory-scale composting tests were performed demonstrating how FSM and RSS are promoting the biodegradation of

the polymer.

2. Materials and methods

2.1. Materials

The matrix material used in the current research was a PLA polymer labeled Natureworks Ingeo 2003D with ~4.5 % D lactid content. According to its datasheet, it has a density of 1.24 g/cm^3 and a melting temperature of 170 °C. Further parameters of the material include a melt flow rate (MFR) of 6 g/10 min, and a polydispersity index (PDI) value of 1.79 with ~100 000 g/mol number average molecular weight (M_n). The natural fibers used in this study include ground flax seed meal (<250 μm) obtained straight from a farmer (India) in pulverized form and chopped rapeseed straw provided by Mikó Stroh Borotai-Laska Ltd (Baja, Hungary). The latter was ground with a feed grinder and then sorted by a Matest A059 type sieve shaker (Matest, Treviolo, Italy) using a sieve of 250 μm gaps. RSS fibers passing the sieve were applied in order to match the size of flax seed meal particles. The bio-fillers were washed to remove any contaminations and then dried for 24 h.

2.2. Composite fabrication

Before processing, each material was dried in a Faithful WGLL 125 BE (Huanghua, Cangzhou, China) drying chamber for 4 h at 80 °C. After drying, small portions of dry mixtures (40 g) of PLA and the corresponding natural fibers were prepared with a predefined ratio of 0, 2.5, 5, 10, and 20 wt.%. The designation and the composition of the fabricated composites are collected in Table 1. Subsequently, the dry batches were fed into a LabTech Scientific LTE 20-44 twin-screw extruder (Labtech Engineering, Samutprakarn, Thailand) at regular intervals. The extrusion parameters are summarized in Table 2. The extruded strands were guided through a cooling tub and then led into a Labtech LZ120 grinder (Labtech Engineering, Samutprakarn, Thailand) to achieve small granulates suitable for injection molding.

Injection molding was performed using an Arburg Allrounder 420C Golden Edition injection molding machine (Arburg, Lossburg, Germany) equipped with a 35 mm diameter screw and a mold capable of forming specimens corresponding to the EN ISO 527–2 standard's 1A specimen. The nozzle temperature was set to 195 °C while the mold was tempered to 30 °C. Injection of the polymer melt was performed with a pressure of 1300 bar and a decreasing holding pressure of 750–650–250 bar of 15 s in total.

2.3. Characterization

Microscopic images of the fracture surfaces were recorded with a Hitachi S-3400 N Scanning Electron Microscope (SEM) (Hitachi, Tokyo, Japan) using a 10 kV accelerating voltage. The aim of the SEM analysis was to examine the matrix/natural fiber interphase. Specimens were coated in a thin layer of gold with a Quorom SC7620 sputter coater machine (Quorum Technologies, Laughton, United Kingdom) to avoid charging of the material.

Table 1
Summary of designations and compositions of the prepared samples.

Designation	PLA (wt.%)	Flax seed meal (wt.%)	Rapeseed straw (wt.%)
PLA	100	0	0
2.5FSM	97.5	2.5	0
5FSM	95	5	0
10FSM	90	10	0
20FSM	80	20	0
2.5FSM/RSS	97.5	1.25	1.25
5FSM/RSS	95	2.5	2.5
10FSM/RSS	90	5	5
20FSM/RSS	80	10	10

Table 2
Extrusion parameters.

Extrusion parameters	Value
Screw diameter (mm)	20
L/D ratio (-)	44
Heating zone temperature from feeder to die (°C)	155–185
Screw speed (rpm)	30

Differential Scanning Calorimetry (DSC) was employed to determine the crystallinity and the various transition temperatures, including the glass transition (T_g), cold crystallization (T_{cc}), and melting temperature (T_m). DSC measurement was carried out with a Netzsch DSC 200 F3 type apparatus (Netzsch, Selb, Germany). Firstly, the specimens were heated at 5 °C/min heating rate up to 200 °C to erase the thermal history of PLA. Then, they were cooled at the same rate to 40 °C and then heated up once more. The crystallinity ratio (X_c) of PLA was calculated using Eq. (1):

$$X_c(\%) = \frac{\Delta H_m}{\Delta H^{\infty}_{mPLA} * \omega_{PLA}} \quad (1)$$

where ΔH_m is the measured melting enthalpy, ΔH^{∞}_{mPLA} is the melting enthalpy of 100 % crystalline PLA determined as 93 J/g by a previous study [68], while ω_{PLA} is the proportion of PLA within the composite.

The specimens were subjected to tensile tests according to ISO 527 and flexural tests following the ISO 178 standard. For these tests, an Instron 5582 universal testing machine (Instron, Norwood, USA) was applied, equipped with a 10 kN load cell. The tensile tests were started at an initial crosshead speed of 1 mm/min up to 0.3 % elongation to determine the Young's modulus and then continued at 5 mm/min. Flexural tests were carried out at a constant speed of 5 mm/min. For tensile tests, an initial gripped length of 100 mm was used, while the span length between the supports for the 3-point bending was 64 mm.

The Shore D hardness of the samples was measured with a Sauter HDD 100-1 (Balingen, Germany) hardness tester following the ISO 868 standard. The average values of hardness were calculated from the results of seven consecutive measurements.

Charpy impact tests were carried out utilizing unnotched specimens with a length of 80 mm and a cross-section of 4 × 10 mm^2 according to ISO 179. The composites were examined with a Ceast 6545 impact testing machine (Ceast, Torino, Italy) equipped with an impact hammer of 15 J using a span length of 62 mm.

Water uptake of the composites was tested for a period of 55 days by submerging specimens of 10 × 10 × 4 mm^3 size into distilled water and measuring their weight periodically. Accordingly, the percentile increase in weight (m_t) was calculated using the formula in Eq. (2):

$$m_t[\%] = \frac{m_n - m_1}{m_1} * 100 \quad (2)$$

where m_n is the measured weight after submerging for a specified time and m_1 is the weight measured before submerging.

A biodegradability test was carried out in order to examine how the presence of different natural fillers affects the decomposition behavior of PLA in compost. The test was conducted according to the ISO 20200 standard. For this purpose, rectangular specimens (25×25 × 1 mm^3) were fabricated with a Labtech LP-20B heated hydraulic press (Labtech Engineering, Samutprakarn, Thailand) at a temperature of 180 °C. As a first step, the specimens were placed in a reactor, which contained compost of specific components as described in the referenced standard. The box used as a reactor was a polypropylene chamber of 280 × 190 × 140 mm^{3}vol and a 5 mm diameter hole situated at 80 mm height in the middle of both sides of the chamber for the purpose of ventilation. The reactors were filled with ~1 kg compost in which the specimens were buried 10 mm deep. For the duration of the composting, the reactors were placed in an ACS DY110 (T) Compact climate chamber (Angelantoni Test Technologies, Perugia, Italy) and were kept at 58 °C and 50

% humidity for 28 days. Photos of the specimens were taken during the testing period at regular intervals to follow the degradation process. The layout of the test is shown in Fig. 1.

3. Results and discussion

3.1. SEM analysis

Scanning electron microscopic images of the applied fillers (FSM and RSS) are shown in Fig. 2. Based on the image in Fig. 2a FSM particles are rather globular, while RSS (Fig. 2b) has a fibrous geometry. While their cross-sectional size is quite similar, the longitudinal size of RSS is much longer than that of FSM due to the nature of sieving process. Both bio-fillers have a rough surface, which suggests the possibility of an effective mechanical interlocking between them and the polymer matrix. Further, FSM particles seem to form agglomerates, which unless broken up might negatively affect the mechanical properties due to the weak filler-filler interactions.

The fractured surfaces obtained during the Charpy impact tests were examined by SEM analysis. Micrographs of samples PLA, 10FSM, and 10 FSM/RSS are presented in Fig. 3. Fig. 3a shows unfilled PLA, which exhibits quite a smooth surface, without any distortions, which is typical for a brittle polymer such as PLA. Meanwhile, the cross-sectional images of the filler containing composites show scattered fibers on the broken surface, supporting the claim of being well dispersed in the matrix. Samples containing bio-fillers also contain pores or voids on the composite surfaces as presented in Fig. 3b-d. Pulled-out fibers and their corresponding holes paired with the clearly distinguishable gaps at the PLA/filler interphase suggest a limited adhesion between the components. These surface morphologies of natural fiber-containing polymer composites can affect the mechanical properties of the manufactured samples as reported in the literature. For instance, Yaisun and Trongsatitkul [69] worked with PLA/bamboo, while Zhang et al. [70] prepared PLA/flax and PLA/lyocell fibers observing similar morphologies as presented here.

3.2. DSC results

DSC curves of the fabricated samples are shown in Fig. 4, while the data derived from those are summarized in Table 3. According to Fig. 4, the amount of filler notably affects the DSC curves. The glass transition of PLA was observed at 59.7 °C; it was manifested as a sharp shift in the baseline indicating a rather amorphous structure. When natural particles were incorporated into the polymer, its T_g reduced with growing filler content to 54.6 °C in the case of FSM-containing composites, and to 56.1 °C in the case of FSM/RSS-filled hybrid composites. This decrement in glass transition temperature can be attributed to the limited interfacial bonding between the natural fibers and PLA, which results in an increased mobility and free volume of the polymer chain molecules by loose packing of filler within the matrix. Similar observations were already reported in the literature for organic and inorganic filler-containing PLA-based composites as well [71–73]. The cold crystallization temperature of all samples is in the range of 105–110 °C. The presence of cold crystallization peak indicates that a crystalline structure was developed during the DSC measurement. Overall, a decreasing trend can be observed for T_{cc} as a function of filler content with the exception of the composites containing the most (20 wt.%) fillers, where the T_{cc} grew markedly to an even higher value than that of neat PLA. For example, in the case of PLA/FSM/RSS hybrid composites, the T_{cc} decreased from 105.2 °C to 102.1 °C when 10 wt.% natural fiber was incorporated, but it increased to 106.9 °C when the weight percentage of the filler reached 20 wt.%. An identical trend was found for the composites only containing FSM with slightly different temperature values. Haddar et al. [74] reported similar results regarding PLA/sisal fiber composites without providing a thorough explanation for this phenomenon. A potential reason is that the applied bio-fillers act as nucleation sites inside the PLA when their amount is below a certain level, thereupon facilitating its crystallization. However, at a high level of 20 wt.% filler content they rather hinder the chain mobility and thereby the crystallization process as well, shifting the T_{cc} to higher temperatures.

Regarding the melting process, a double melting peak can be observed for all samples. The presence of such a double peak originates from the nature of PLA, as it can have different crystalline polymorphs (α and α') according to the literature [75]. The melting temperatures (T_{m1} and T_{m2}) were barely affected by the filler type and content. The two melting temperatures of unfilled PLA (148.6 °C and 154.9 °C) show a very small change with the increase in filler content. Meanwhile, the relative size of the peaks corresponding to the melting of the α and α' crystalline polymorphs changes noticeably. As the amount of RSS and/or FSM grows, the second melting peak becomes larger with the first one shrinking at the same time. This indicates that the presence of fillers favors the formation of the polymorph with a higher melting temperature, thus improving the thermal stability of the composites. The melting enthalpy (ΔH_m) is almost equal to the cold crystallization enthalpy (ΔH_{cc}) for all samples, further supporting the claim of the samples being rather amorphous before the DSC test. The calculated crystallinity ratio values show that the crystallinity of PLA gradually increases with the growing filler content. For instance, compared to the 25 % crystallinity measured for neat PLA, the FSM-filled composites containing 2.5 wt.%, 5 wt.%, 10 wt.%, and 20 wt.% filler have 26.9 %, 29.1 %, 30 %, and 33.6 % crystallinity, respectively. This is similar to the results reported by Jing et al. [76], where the crystallinity of PLA increased from 5.52 % to 20.05 % in the presence of lemongrass fiber filler. The proportion of crystalline segments in FSM/RSS containing hybrid composites is slightly lower than that, suggesting that the flax seed meal is a more effective nucleating agent than the straw.

Fig. 1. A reactor with the composite specimens placed in it before being buried in the compost.

3.3. Tensile and flexural test

The summary of the tensile and flexural test results is collected in Table 4, while the characteristic stress-strain curves are shown in Figs. 5 and 6. Generally, the composites containing any bio-fillers exhibited strength values lower than neat PLA, which is a direct consequence of the limited interfacial adhesion between the components as already pointed out during the SEM analysis. The relative decrease in both the tensile and flexural strength is more prominent in the case of FSM-filled composites compared to the hybrid ones. The addition of 10 wt.% FSM reduces the tensile strength of PLA from 56.4 MPa to 41.5 MPa, and its flexural strength from 99.1 MPa to 78.5 MPa. Increasing the

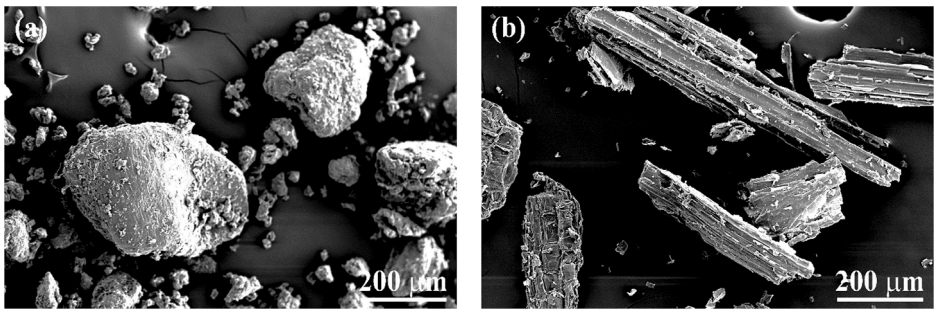

Fig. 2. SEM images of flax seed meal (a) and rapeseed straw (b) powder.

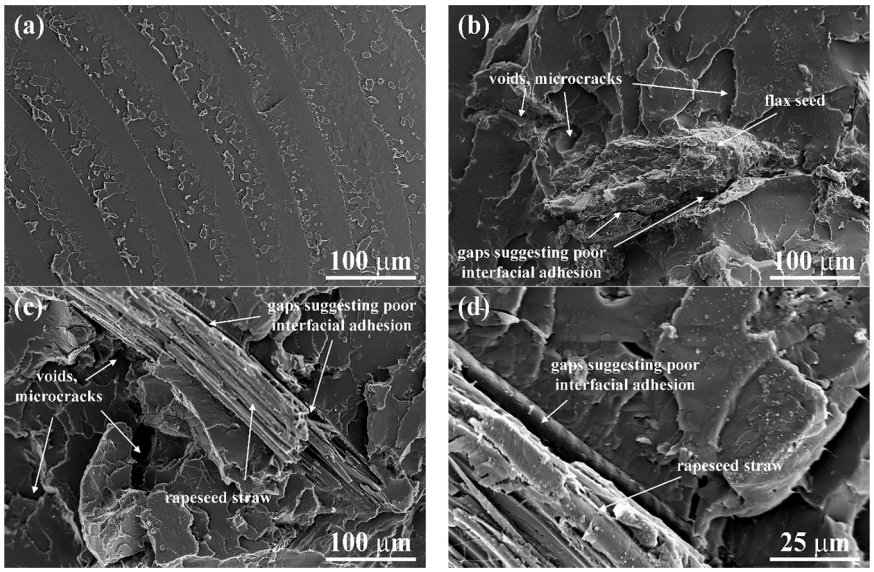

Fig. 3. SEM images of fracture surfaces of PLA (a), 10FSM (b), and 10FSM/RSS (c, d).

concentration of FSM further than that seems undesired since the strength values drop by half (19.6 and 36.9 MPa) in that case. Even though the decrease is considerable, the strength values are still comparable to those petrochemical plastics that are currently used for single-use products and packaging purposes, such as PP or PS (tensile strength = ~30 MPa), where PLA can serve as an alternative [77]. The decrease is less drastic when FSM and RSS are employed simultaneously. The tensile strength of the hybrid composites containing 10 wt.%, and 20 wt.% of both FSM and RSS is relatively 6 %, and 16 % better than the PLA/FSM composites of identical composition, which suggests a more favorable behavior of RSS compared to FSM in this respect. In our previous study [67] dealing with PLA-based composites paired with only RSS as filler, the tensile and flexural strength values were even higher, which also supports this assumption. A possible explanation for this behavior is that the rapeseed straws exhibit a fiber-like geometry, enabling a load transfer through mechanical interlocking between the polymer matrix and the natural fiber even in the absence of interfacial adhesion. Meanwhile, the globular geometry of flax seed meal (as depicted in Fig. 2a) did not allow such load transfer.

Despite the reduced tensile strength, an increase in Young's modulus occurred, which indicates the composites becoming stiffer due to the presence of the fillers. Interestingly, the ternary composites show a greater increase compared to the binary composites only filled with FSM. The hybrid composites' Young's modulus peaked at 2968 MPa when the filler loading was 20 wt.%, which is considerably higher than the FSM-filled composite at the same filler concentration (2788 MPa). The same can also be applied to flexural modulus, where the 20FSM/RSS sample outperformed all other composites with its modulus of 3880 MPa. Robledo-Ortíz et al. [78] observed similar behavior upon combining sugarcane with PLA, reporting an increasing modulus compared to the neat PLA from ~1450 MPa to ~1650 MPa at 20 wt.% filler content, both tensile and flexural. Meanwhile, the tensile strength decreased by around 10 MPa and the flexural strength by ~5 MPa. Other studies reported similar results as well [79,80].

3.4. Impact test

The results of Charpy impact tests are shown in Fig. 7. Apparently, the addition of even the lowest amount (2.5 wt.%) of bio-filler reduced the impact strength of neat PLA (15.0 kJ/m^2) by almost 5 kJ/m^2 (2.5FSM: 10.4 kJ/m^2; 2.5FSM/RSS: 10.9 kJ/m^2), which can be ascribed to the rigid nature of both FSM and RSS. The decline further continued with additional filler loading, albeit less significant, thereby bottoming at 20 wt.% filler concentration. The samples 20FSM and 20FSM/RSS exhibited an impact strength of 3.69 kJ/m^2 and 4.58 kJ/m^2, respectively. Again, the application of RSS was shown to be more beneficial than FSM, which is in good accord with the tensile and flexural tests' results and is in line with the study of Ecker and his colleagues [37], describing a decrease in impact strength from 30 kJ/m^2 to 13 kJ/m^2 at 15 wt.% wood flour content. Recall, that the SEM images of these specimens' broken surfaces showed agglomerated filler particles and voids on the interphases that both deteriorated the structural integrity of the PLA matrix and thus promoted less energy absorbance during the impact load. Up to 5 wt.% bio-filler concentration there was no marked difference between the composites containing different fillers; nevertheless, above this level of loading the rapeseed straw-containing

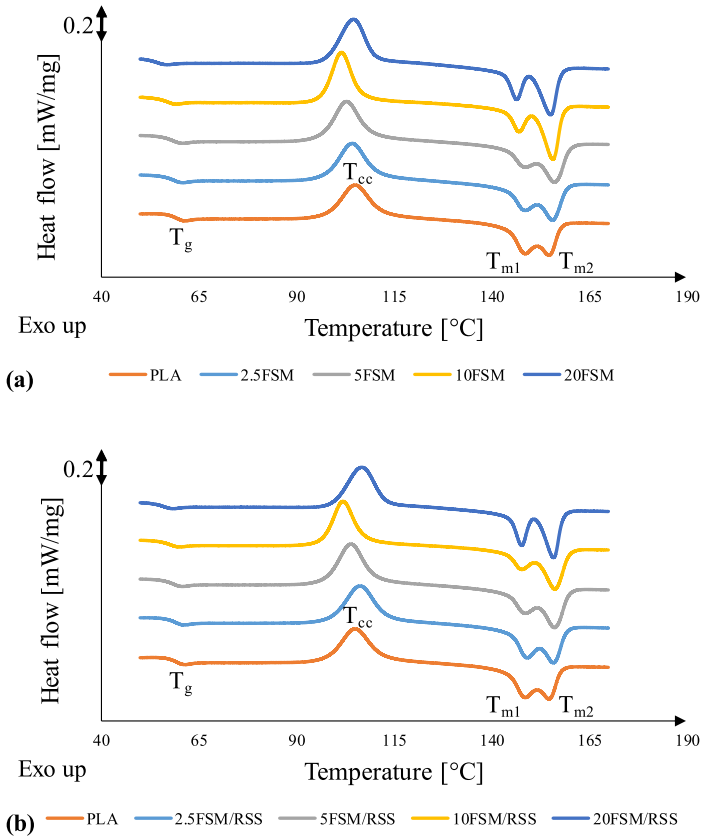

Fig. 4. DSC curves of flax seed meal (a) and flax seed meal/rapeseed straw (b) filled PLA-based composites with 0–20 wt.% filler content.

Table 3
DSC data obtained from the corresponding curves of PLA-based flax seed meal/rapeseed straw-filled polymer composites containing 0–20 wt.% bio-filler.

Description	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	X_c (%)
PLA	59.7	105.2	22.5	148.6	154.9	23.2	25.0
2.5FSM	58.3	104.4	24.2	148.7	155.7	24.4	26.9
5FSM	58.3	102.9	24.7	148.7	156.2	25.7	29.1
10FSM	56.9	101.7	25.1	147.1	155.8	25.1	30.0
20FSM	54.6	104.8	25.2	146.5	155.2	25.0	33.6
2.5FSM/RSS	59.1	106.4	24.1	149.3	156.0	25.0	27.6
5FSM/RSS	58.5	104.1	24.5	148.7	156.2	25.4	28.7
10FSM/RSS	57.6	102.1	22.7	147.9	156.3	23.5	28.1
20FSM/RSS	56.1	106.9	24.3	147.8	156.0	24.3	32.7

samples proved to be superior once more.

3.5. Hardness test

The results of Shore D hardness tests are presented in Fig. 8. The hardness of all samples was in the relatively small range of 82.3–85.2 Shore D with the unfilled PLA exhibiting the lowest value (82.3 Shore D). Both bio-fillers exhibit a rather rigid behavior as suggested based on previously described mechanical tests, and as such, both the FSM and the RSS hindered the penetration of the test indenter, thereupon increasing the hardness of PLA. Accordingly, the hardness test showed an increasing trend with the growing amount of filler. No marked differences were found between the two natural particles. Similar observations were made for other types of fillers in the literature, such as banana fiber in the work of Nguyen et al. [81], who reported an increase of 3 Vickers hardness in the case of 20 wt.% filler compared to pure PLA. In here, even 2.5 wt.% of FSM was enough to improve the hardness from 82.3 to 84.0 Shore D, while further addition did not result in significant improvement. The reason for the relatively low changes is that PLA itself is a rather rigid thermoplastic polymer exhibiting barely any plastic deformations.

Table 4
Summary of the tensile and flexural test results of the flax seed meal and flax seed meal/rapeseed straw-filled composites in the form of tensile strength, Young's modulus, flexural stress at conventional deflection, and flexural modulus
*Flexural strength instead of flexural stress at conventional stress is reported due to the specimens breaking before reaching the conventional deflection.

Name	Tensile strength [MPa]	Young's modulus [MPa]	Flexural stress at conv. defl. [MPa]	Flexural modulus [MPa]
PLA	56.4 ± 1.6	2552 ± 65	99.1 ± 3.4	3404 ± 63
2.5FSM	50.6 ± 0.2	2685 ± 38	93.1 ± 0.6	3447 ± 39
5FSM	48.9 ± 0.7	2711 ± 31	90.7 ± 0.5	3527 ± 65
10FSM	41.5 ± 1.2	2758 ± 34	78.5 ± 1.9*	3573 ± 101
20FSM	19.6 ± 4.4	2788 ± 132	36.9 ± 7.2*	3877 ± 40
2.5FSM/RSS	50.7 ± 0.9	2606 ± 51	93.4 ± 0.3	3471 ± 49
5FSM/RSS	48.3 ± 0.3	2716 ± 59	90.5 ± 0.3	3611 ± 30
10FSM/RSS	44.0 ± 0.5	2769 ± 49	83.2 ± 0.5*	3880 ± 42
20FSM/RSS	35.7 ± 0.4	2968 ± 89	67.5 ± 3.0*	4284 ± 79

3.6. Water absorption test

The water uptake measurement was conducted throughout a period

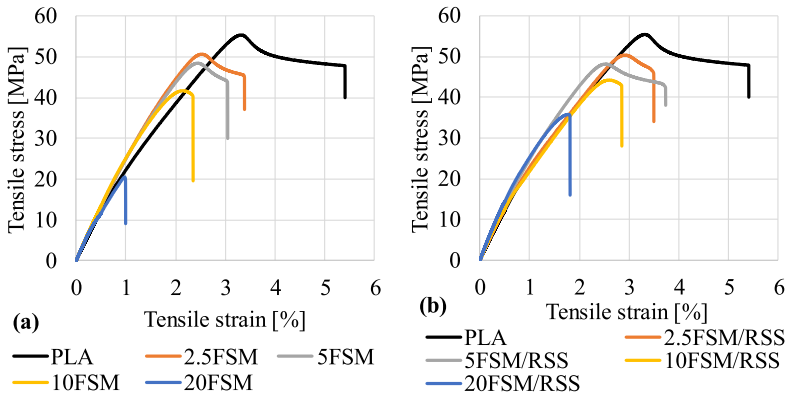

Fig. 5. Typical tensile curves of the flax seed meal (a) and flax seed meal/rapeseed straw (b) composites.

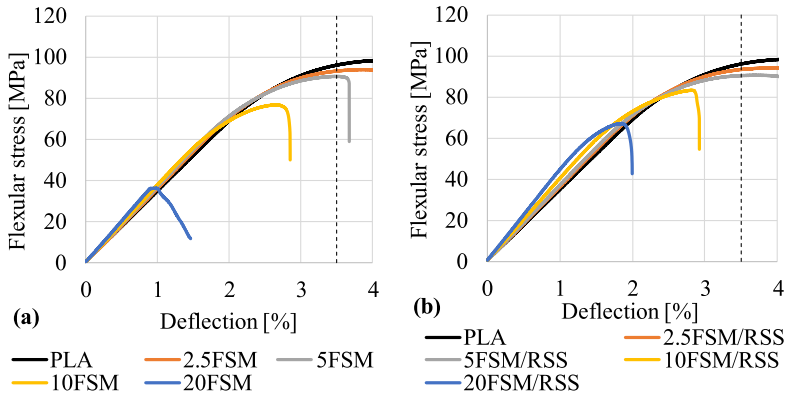

Fig. 6. Typical flexural curves of the flax seed meal (a) and flax seed meal/rapeseed straw (b) composites. The dashed line represents the conventional deflection limit.

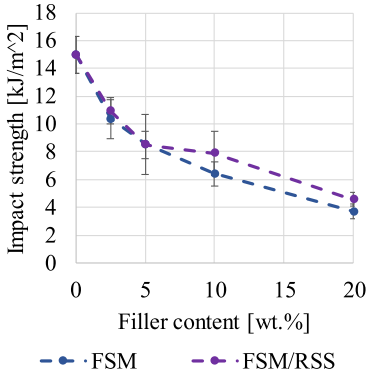

Fig. 7. Impact strength of PLA-based composites filled with flax seed meal and flax seed meal/rapeseed straw at various concentrations.

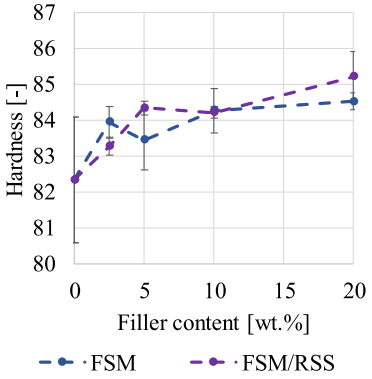

Fig. 8. Shore D Hardness of PLA-based composites filled with flax seed meal and flax seed meal/rapeseed straw composites at various concentrations.

of 55 days; by that time all samples reached saturation and their weight no longer increased significantly. The results of the water absorption test are shown in Fig. 9. As PLA is hydrophobic by nature, it took around a week to reach its equilibrium weight after submerging in water, and its weight barely increased by 0.7 % over the soaking period. This changed greatly when natural fillers were incorporated into it since these are hydrophilic due to the –OH groups on both their cellulose and lignin components. The voids corresponding to their cellular structure also contributed to the water seeping rather easily into them. Accordingly, the growing filler content increased the water absorption capability of the composites. The rate of water uptake is similar between the two sets of composites (FSM and FSM/RSS), but the absolute increment is much higher for the FSM-filled samples, especially at 20 wt.% filler content. A possible explanation for that was reported by Lazouk et al. [82]. The authors investigated the moisture content of various oilseeds, including flax seed, rapeseed, and sunflower seed. According to their study, flax seed contains 12 % mucilage, which is strongly hydrophilic and which is absent from rapeseed. Consequently, FSM is capable of absorbing a high amount of water at a fast rate. After 55 days, the composite 20FSM showed a 9.1 % weight increase, while the 20FSM/RSS sample only 5.5 %. The results of the water absorption test align with other researchers' work, such as the study of Klaai et al. [83], in which the authors paired PLA with prickly pear seed fiber. At 20 wt.% filler content the composites gained 5.2 % weight after 300 h, which is considerably more than PLA (3.87 %) or the composite containing 10 wt.% pear seed (3.93 %). The paper published by Sherwani et al. [84] presented similar

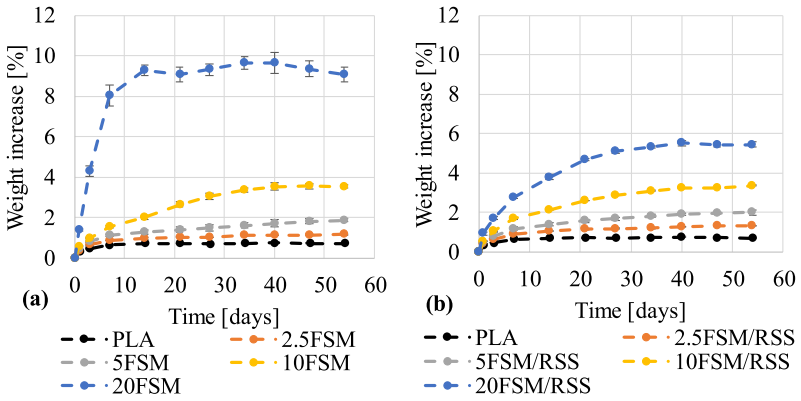

Fig. 9. Water absorption of PLA-based composites filled with flax seed meal (a) and flax seed meal/rapeseed straw (b) at various concentrations.

results; the authors incorporated sugar palm fibers from 10 to 40 wt.% into PLA and a gradual increase in water absorption capability was shown along with the increased filler concentration.

3.7. Biodegradability during composting

The biodegradability test was performed according to ISO 20200, which is a standardized method to analyze the disintegration of plastic materials when exposed to a laboratory-scale composting environment.

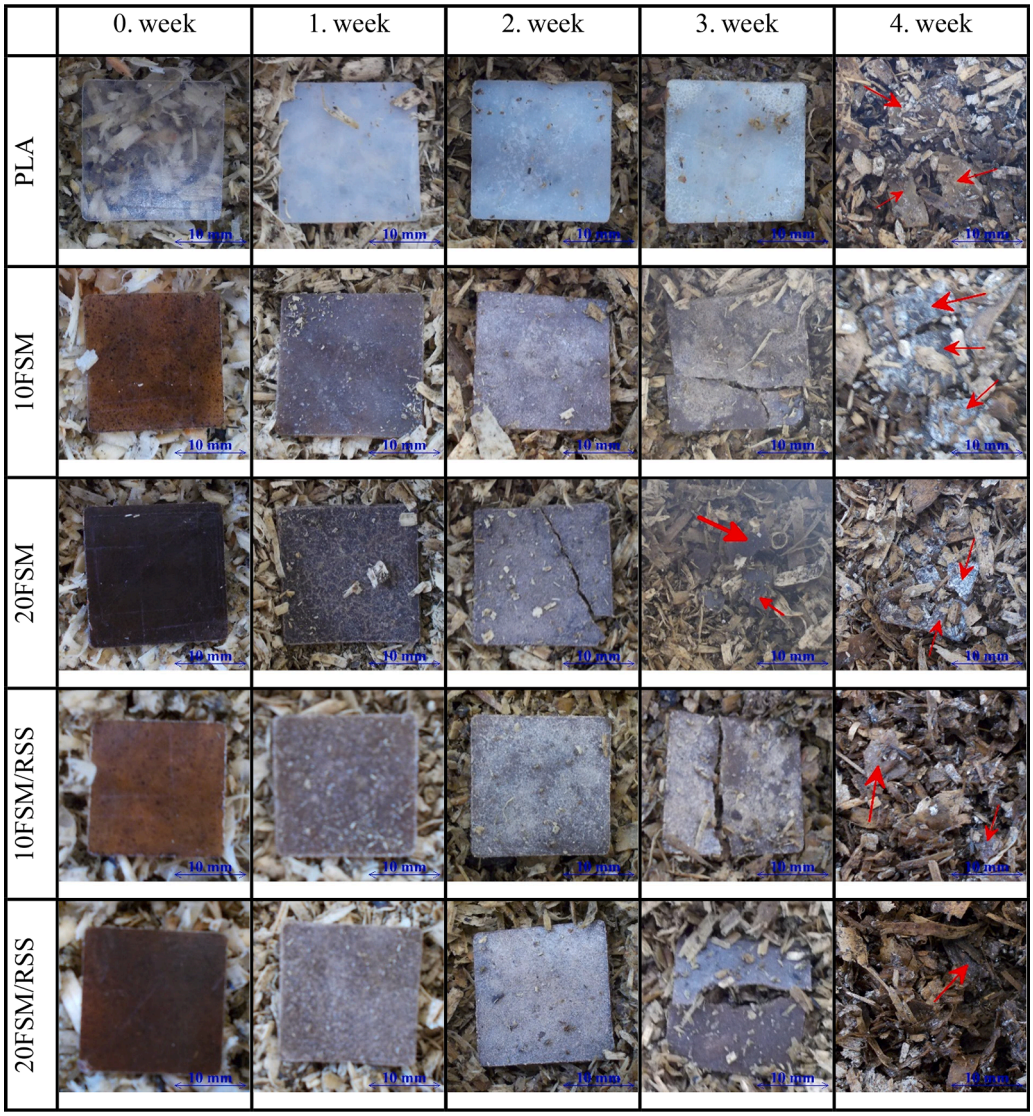

Fig. 10. The visual aspect of the disintegration test in controlled compost soil of PLA-based composites containing flax seed meal and flax seed meal/rapeseed straw at 10 wt.% and 20 wt.% concentrations throughout 4 weeks.

Each time the samples were observed, they were excavated from the compost, and carefully cleaned with a soft brush of any contaminations before taking a photo.

The photo collage prepared of the samples week by week is shown in Fig. 10. Neat PLA and the composites containing 10 wt.% and 20 wt.% bio-fillers were subjected to this experiment. Prior to digging the specimens into the compost, PLA exhibited transparent optical features, which can be attributed to its amorphous molecular structure, while the composites had a brownish, slightly translucent color due to the incorporated natural particles. After the first week of composting, the unfilled PLA specimen turned white, losing its transparency, and indicating a crystallization of the polymer. The crystallization can be ascribed to the decreasing molecular weight, which promoted molecular mobility and thereby allowed the molecules to form ordered crystallites. At this time, the composites also lost their translucency, becoming entirely opaque, suggesting the crystallization of these samples too. At the same time, cracks occurred on the surface of the 20FSM sample, which is considered a harbinger of the disintegration to come. After the second week, PLA was still intact, while sample 20FSM broke into pieces, and the remaining composites started to develop cracks. The third week was the first time the PLA started showing some cracks. At this point, sample 20FSM shattered into multiple pieces that had such low mechanical stability that it became impossible to clean the fragments from the surrounding contaminations without damaging them. Therefore, it is rather difficult to separate the individual pieces of the composite from the surrounding compost in the photo (pointed out by red arrows in Fig. 10). As such, this composite was the first one to be considered degraded. Meanwhile, all the remaining composites started to disintegrate, breaking into multiple pieces. By the end of the fourth week, all other samples, including PLA degraded into small parts making it difficult or entirely unfeasible to separate the fragments from the compost. These results align with the reports from previous studies, where the increase in filler resulted in a faster rate of biodegradation for the composites [85,86].

Overall, it can be concluded that both bio-fillers effectively facilitate the biodegradation of PLA with FSM being the more effective of the two. Since the degradation is greatly dependent on the rate of hydrolytic chain scission, the amount of moisture absorbed by the composites from their environment is expected to play a prominent role in the disintegration process. Recall, that during the water absorption tests, 20FSM was the sample absorbing the largest amount of water by far, which also supports the fact that FSM is an effective additive to facilitate the disintegration of biodegradable plastics.

4. Conclusion

Flax seed meal and rapeseed straw can be effectively used as fillers in PLA to alter its properties and to achieve enhanced biodegradability. In this study, PLA was modified by the addition of FSM and RSS biomass. Binary composites of PLA/FSM and ternary hybrids of PLA/FSM/RSS were prepared using melt compounding in a twin-screw extruder followed by injection molding. The concentration of the agricultural wastes was varied in the range of 0 to 20 wt.%. Thermal, morphological, mechanical, physical and biodegradation properties of the prepared samples were investigated.

According to the DSC results, both bio-fillers were found to act as nucleating agents in PLA. Even though the fabricated samples were rather amorphous due to the intense cooling during injection molding, throughout the heating cycle of DSC the developed crystallinity ratio in PLA increased from 25 % to 33–34 % when agro-wastes were incorporated into it. Tensile and flexural tests revealed a growing stiffness with increasing natural fiber content; however, it came at the cost of slightly reduced strength. The drop in strength is ascribed to the limited adhesion between the components, which is also supported by the gaps and voids at the interphase as shown in SEM images. The presence of rapeseed straw proved favorable, since the PLA/FSM/RSS hybrid composites had superior mechanical properties compared to the PLA/FSM ones of identical filler content. The hardness of PLA (82.3 Shore D) improved with increasing filler content regardless of its type and peaked at 20 wt. % natural fiber content (84–85 Shore D). Water uptake of the polymer matrix was markedly affected by the presence of the incorporated biomass. Due to the hydrophilic nature of the lignocellulose particles, the composites absorbed a higher amount of water than unfilled PLA, especially the ones filled only with FSM. Considering biodegradability, the composite with 20 wt.% flax seed meal showed the most promising results. The corresponding specimen decomposed entirely within three weeks, while for the other samples it took at least four weeks.

Overall, both flax seed meal and rapeseed straw particles were found to have a prominent potential as additives in PLA-based biodegradable polymer composites. The findings of this study provide a detailed insight into biocomposites filled with low-cost natural fillers through their extensive mechanical, thermal and physical characterization. Additionally, the composting test demonstrated enhanced decomposition features, which can make these composites attractive in many fields, especially for single-use applications.

CRediT authorship contribution statement

Sándor Kálmán Jakab: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis. **Tej Singh:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Imre Fekete:** Investigation. **László Lendvai:** Writing – review & editing, Writing – original draft, Supervision, Resources, Investigation, Funding acquisition, Data curation, Conceptualization.

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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