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Preparation and Characterization of Compression-Molded Green Composite Sheets Made of Poly-3-hydroxybutyrate Reinforced With Long Pita Fibers

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Keywords:	Poly-3-hydroxybutyrate, Pita fibers, Green composites, Compression molding, Automotive parts

Preparation and characterization of compression-molded green composite sheets made of poly-3-hydroxybutyrate reinforced with long pita fibers

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ABSTRACT. In the present study, novel fully bio-based composites were successfully fabricated from bacterial poly-3-hydroxybutyrate (PHB) and plant-derived pita fibers (*Agave Americana*) by compression molding. Various weight contents (10, 20, 30, and 40 wt.-%) of pita fibers at different lengths (5, 15, and 20 mm) were successfully incorporated into PHB. The mechanical and thermomechanical properties of the PHB/pita fibers composite sheets were analyzed and related to their morphological characteristics after fracture. Preliminary results indicated that the mechanical stiffness of the PHB composite sheets was improved with both the content and length of pita fibers, though the ductility was reduced. Compared to that of the unreinforced PHB sheet, the elastic modulus was about 50% higher for PHB composite sheets with pita fiber loadings of 40 wt.-% and lengths above 15 mm. Shore D hardness also improved in the PHB composite sheets, achieving the shorter pita fibers the best improve. Longer pita fibers led to the highest values of Vicat softening point and heat deflection temperature (HDT). Due to their optimal aspect ratio, it is concluded that 20 mm-long pita fibers can potentially reinforce the PHB biopolymer. The compression molding methodology described in this work also represents as a cost-effective pathway to feasibly prepare long-fiber-reinforced thermoplastics (LFRTs). As per the obtained results, prepared green composite sheets can be of interest for the development of interior parts in the automotive industry and other advanced applications in polymer technology.

Keywords: Poly-3-hydroxybutyrate, Pita fibers, Green composites, Compression molding, Automotive parts

Introduction

A large amount of agro- and marine-waste materials are globally produced every year. The development of high-performance materials made from such renewable resources is increasing worldwide. Natural fibers represent a sustainable choice for the manufacturing of polymer biocomposites.[1] These can be either sourced from animals or plants. Animal occurring fibers basically consist of proteins (*e.g.*, hair, silk, and wool), while plant fibers from crops and sea origin are mainly composed of cellulose. Plants can be subsequently classified into bast fibers (*e.g.*, jute, flax, ramie, hemp, and kenaf), leaf fibers (*e.g.*, sisal, pineapple, abaca, and agave), grass and reed fibers (*e.g.*, rice, corn, and wheat), seed fibers (*e.g.*, cotton, coir, and kapok), and core fibers (*e.g.*, hemp, kenaf, and jute) as well as all other kinds (*e.g.*, wood and roots).[2]

The application of natural fibers as reinforcements in polymer matrices results in biocomposites with enhanced mechanical performance.[3] In comparison to classical mineral- and glass fiber-reinforced polymers, biocomposites can potentially reduce product density and the energy requirements for processing.[4] These novel materials can also offer some environmental advantages over traditional composites, for instance reduced dependence on non-renewable energy/material sources, lower greenhouse gas emissions and pollutant emissions, improved energy recovery, and end-of-life biodegradability of components.[5] Resultant natural fiber-reinforced polymer composites can be therefore considered as sustainable materials because of their relatively high renewal content.[6] Furthermore, using a bio-based and/or biodegradable polymer as the material matrix can additionally increase the green credentials of the biocomposites.[7,8] Green composites are a specific class of biocomposites, in which the matrix is a biopolymer.[9] In this regard, in the last years, the use of natural fibers such as jute, sisal, flax, hemp, bamboo, and pineapple leaf fibers as novel reinforcing fillers in biopolymers has been intensified.[10] In general, generous loadings of such plant-derived fibers are preferred since the raw materials cost for the manufacturing of the green composites is reduced.[11]

Polyhydroxyalkanoates (PHAs) are a well-known family of biodegradable bacterial polyesters with the highest potential to replace polyolefins in a wide range of applications.[12] A generic process to produce PHAs from bacteria involves fermentation, isolation, and purification from fermentation broth. In particular, more than 150 PHA monomers have been currently identified as the constituents of PHAs.[13] Such diversity definitely allows the production of aliphatic biopolymers with a wide range of properties, highly tailored for specific applications. Poly-3-hydroxybutyrate (PHB) was the first discovered bacterial PHA, identified by Maurice Lemoigne as one of the constituents of the bacterium *Bacillus megaterium*.[14] PHB is a completely linear and isotactic homopolyester that results in a highly crystalline macromolecule, *i.e.*, 60–70%. As a result it presents a typical brittle behavior and a melting temperature of *ca.* 178 °C.[15] Among PHAs, PHB, together with the co-polymer poly(3-

hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), have received so far the greatest attention in terms of pathway characterization and industrial-scale production. PHB biopolymer possesses relatively similar thermal and mechanical properties to those of polypropylene (PP). In particular, it presents a good resistance to moisture but with the advantage to have higher oxygen barrier performance than its counterpart polyolefin.[16] For this reason, PHB has been processed in existing processing equipment to produce a wide range of plastics components: Films and sheets, laminates, coated materials, spun fibers, nonwoven fabrics, foams, etc.[17] Habitually PHB is well biodegradable, printable, and, in contrast to most biopolymers, it presents a low water vapor transmission rate (WVTR). The main disadvantage of PHB, however, is related to its high brittleness[15] and low thermal instability[16] that makes difficult its drop-in-replacement in current melt-processing equipment.

Some studies have already shown the potential of both PHB and PHBV as novel ecological candidates in biocomposites such as regenerated and/or recycled cellulose,[18-20] pineapple leaf fibers (PALF),[21,22] wheat straw fibers,[23] wood floor,[24,25] jute,[26] flax,[27-31] banana fiber, sisal, and coir,[30] hemp,[32] abaca,[33] bamboo fibers,[34] sugarcane bagasse fibers,[35,36] kenaf and lyocell,[37] and wood powder.[38,39] Due to the challenging processability of PHAs, these studies have shown that the most promising techniques to process them are compression molding and extrusion followed by injection molding. For instance, compression molding has been used to successfully prepare biocomposites containing 20 wt.-% of bagasse fibers.[35] In other work Kobayashi et al.[36] prepared PHB/sugarcane bagasse composites at 20–40 wt.-%, first by compounding in a twin-screw extruder and then shaping them by injection molding. Similar green composites were previously prepared by sandwiching 20–30 wt.-% PALF placed in different orientations between two PHBV films in a hot press.[21] These research works have suggested that the incorporation of natural fibers can definitely strength the intrinsic poor mechanical properties of PHB and PHBV. Some have also demonstrated that the incorporation of natural fibers could promote biodegradability.[23,27,33]

In this sense, compression molding by means of a hot press represents a simple and versatile method to prepare plate-like geometries, *i.e.*, films (below 250 µm) and sheets (above 250 µm). This includes the manufacturing of composite parts based on long-fiber-reinforced thermoplastics (LFRTs), which can find several uses in polymer engineering. Due to their excellent strength and renewability, natural fibers are increasingly used in LFRTs in the automotive and transportation sector.[40] Recent studies have showed that the market of natural fibers in the automotive industry is growing at more than 20% per year, in which European manufactures are the leaders at their implementing.[41] Advanced composite materials reinforced with natural fibers typically present lower density over those based on traditional glass fibers, which allows production of light-weight parts with the advantage of fuel and cost saving.[42]. Current uses of sustainable LFRTs are mainly centered on interior and non-structural

automotive parts such as door panels, rear shelves, seat backs, headliners, package trays, and dashboards. However, their application is fast expanding to more structural parts with higher stiffness like seat frames, load floors, pick-up beds, floor pans, drive train, and steering components. Also, the food packaging industry can benefit from the hot-pressing methodology to produce novel biocomposites and nanocomposites of hierarchical structures with passive, active, and bioactive properties.[43] During compression molding, the thermoplastic material is heated to a pliable forming temperature and then molded to a specific shape by the action of pressure for a certain time.[44] Materials may be loaded into the mold either in the form of pellets or film/sheet. As a result long fibers can be then feasibly fed without the need of using pultrusion or melt-impregnation process.[45] Main advantage of hot-press molding over other melt technologies (*e.g.*, injection molding) is its capacity to mold large and intricate plastics parts with accurately control on processing temperature[46] and lower amounts of wasted material.[47] Additionally, due to the lower mixing energies and shear peaks employed during molding methodologies, fibers attrition or breakage can be minimized.[48]

In this work, pita fibers were originally chosen as the natural reinforcement material for the formation of a sustainable LFRT. This is a hard-type fiber extracted from the leaves of the agave plant (*Agave Americana*), which is a monocotyledon plant from the sisal family of *Agave Sisalana*. The leaf of this plant mainly consists of cellulose (80%), lignin (15%), and hemicellulose (6-3%).[49] This variety of plant grows in Africa and Europe warm-weather countries, but it is native from Central America and Mexico. The leaves of agave plant contain the so-called pita fibers that are extracted either mechanically by scratching and beating or by splitting up the matrix of the leaves in seawater. Due to their optimal mechanical properties, the extracted fibers are typically employed to make ropes for marine and agriculture activities. Compared to other renewable fibers, pita fibers present higher tenacity and rupture strain, weaker initial modulus, and relatively higher rupture energy.[50] In particular, tenacity is near those of strong natural fibers such as sisal or flax. Although the mechanical characteristics of single pita fibers were recently studied,[51] to the best of our knowledge, their application in polymer technology to reinforce plastic and bioplastic matrices has never been explored.

The objective of the present work is to ascertain the mechanical and thermomechanical behavior of long pita fiber-reinforced PHB composites obtained by compression molding. Resultant fully bio-based and biodegradable sheets can be potentially applied as interior parts in the automotive industry, which can be a sustainable alternative to replace conventional LFRTs. The process is summarized in the scheme displayed in **Figure 1**, which closely symbolizes the cradle-to-cradle (C2C) concept.[52] This theoretically gives a very favorable balance of carbon dioxide emissions into the atmosphere since agave plants, from which pita fibers are obtained, sequester atmospheric carbon dioxide during their growth.

Experimental

Materials

Bacterial PHB biopolymer P226 was supplied by Biomer (Krailling, Germany) in pellets form. According to manufacturer, this PHB grade is certified as compostable, has a density of 1.25 g/cm^3, and a melt flow index (MFI) of 9–13 g/10 min (190°C, 2.16 kg). The biopolymer was received in waterproof bags.

Pita fibers, obtained from *Agave Americana*, were provided by from Productos Gol S.L. (Cieza, Spain). The fibers present a density of 1.36 g/cm^3 and a purity higher than 99%. These were used as received and cut into three different lengths: 5, 15, and 20 mm. Prior to compression molding, the mats of fibers were dried at 90 ºC in an oven for 24h.

Green composites preparation

Preparation of the PHB/pita fibers composites was carried out using a 10-Tn hydraulic press from Robima S.A. (Valencia, Spain) equipped with two hot aluminum plates and a temperature controller from Dupra S.A. (Castalla, Spain). The compression-molding process is represented in **Figure 2**. For this about 100 g of material was compression molded for 5 min at 160 °C and 4 tons by two hot plates in a hollow mold of 20 x 20 cm^2 and adjusted with screws, as represented in **Figure 2a**. Materials were initially preheated at 160 °C for 2 min without pressure in order to homogenize temperature. Five layers of PHB pellets were spread uniformly in continuous layers and then alternately sandwiched with four pita fibers nonwoven mats randomly placed, as shown in **Figure 2b**. Once the shaping process was accomplished, samples were rapidly cooled down to 60 °C by means of an internal water circulating system and taken out of the press machine.

The incorporation of pita fibers into PHB, at different lengths, was analyzed for various weight contents (wt.-%): 10, 20, 30, and 40 wt.-%. Final thicknesses of the compression-molded sheets ranged from 1.6 to 1.8 mm. Same process was followed to produce PHB sheets without pita fibers as the control.

Once compression molding was completed, the PHB/pita fibers composites were cut for characterization according to ISO 527 using a die on a hydraulic press model MEGA KCK-15A from Melchor Gabilondo S.A. (Vizcaya, Spain).

Mechanical testing

Tensile tests were carried out following ISO 527 in a universal testing machine ELIB 30 model from S.A.E Ibertest (Madrid, Spain). The machine was equipped with a 5-kN load cell. All tests were carried out in a controlled chamber at room conditions, *i.e.*, 23 °C and 50% RH,

and with 10 mm/min crosshead speed. Dog-bone shape samples were tested and the mean value of modulus of elasticity (E), tensile strength (σ_s), and strain at break (ε_b) was determined.

Hardness tests were carried out in a Shore 673-D Durometer from Instrumentos J. Bot S.A. (Barcelona, Spain). Measurements were performed as described in the norm UNE-EN ISO 868.

Thermomechanical characterization

The Vicat softening point and heat deflection temperature (HDT) of the compression-molded sheets were both measured using a standard Vicat/HDT station DEFLEX 687-A2 from Metrotec S.A. (San Sebastián, Spain). The Vicat softening point was determined following the UNE-EN 727 and ISO 306, according to the B50 method. During this, the specimens were placed in the testing apparatus so that the penetrating needle rested on its surface at least 1 mm from the edge. A load of 50 N was applied to the sample. This was then lowered into an oil bath in which the temperature raised at a rate of 50 °C/h until the needle penetrated 1 mm.

HDT measurements were carried out according to UNE-EN ISO 75-Method A and ASTM D648, using a heating rate of the medium (oil) of 120 °C/h. A specimen with dimensions of 4 x 10 x 80 mm^3 was loaded in three-point bending in the edgewise direction using a distance of 60 cm. The outer stress used for testing was 1.8 MPa and the temperature increased at 2 °C/min until the sample deflected 0.31 mm.

Microscopy

The morphology of the pita fibers was analyzed with a stereomicroscope system SZX7 model from Olympus (Tokyo, Japan) using an ocular magnifying glass of 10x. This was equipped with a KL1500-LCD light source. Pita fibers mats were deposited on a chart paper.

The morphology of the green composites was analyzed at the fracture surface after tensile tests by Scanning Electron Microscope (SEM). This was performed using a PHENOM model from FEI Company (Eindhoven, The Netherlands) with a magnification range of 525-24000x and an accelerating voltage of 5 kV. Fractured samples were covered with a 5–7 nm Au layer in vacuum conditions in a Sputter Coater EMITECH model SC7620 from Quorum Technologies Ltd. (East Sussex, UK).

Results and Discussion

Morphology

Figure 3 shows the morphology of the pita fibers mats cut at different lengths: **Figure 3a** (5 mm), **Figure 3b** (15 mm), and **Figure 3c** (20mm). In all cases fibers present a mean diameter of approximately 250 µm. **Figure 4** gathers the surface appearance of the obtained PHB composite sheets after compression molding at all different pita fibers contents and lengths. From these

images it can be seen that all green composites presented a continuous and uniform structure. It is also noticeable that pita fibers were relatively well distributed into the PHB matrix, presenting a continuous and marked randomly distribution. In general, with the increase of both pita fibers content and length, the PHB composites acquired the characteristic appearance of the natural fibers. In particular, the green composite sheets containing shorter pita fibers presented a smoother and more homogenous surface. Nevertheless longer fibers showed a more irregular surface, similar to the natural aspect of wood. A similar aesthetic effect was recently reported for wood flour composites.[53]

Mechanical properties

In **Figure 5** the mechanical response of the PHB composites was evaluated according to both the amount of pita fibers added, *i.e.*, 10, 20, 30, and 40 wt.-%, and their mean length, *i.e.*, 5, 15, and 20 mm. **Figure 5a** shows that the tensile modulus of the PHB composite sheets steadily increased with the pita fibers loading for lengths above 15 mm. In particular, it increased from 390 MPa, for the unreinforced PHB sheet, up to 610 MPa, for the 40 wt.-% PHB composite sheet containing 20 mm-long pita fibers. A similar trend in the modulus was observed in the PHB composite sheets reinforced with pita fibers of 15 mm, *i.e.*, it increased to 502 MPa. This indicates that the green composites gained elastic resistance against tensile efforts with the incorporation of long fibers, *i.e.*, 15 and 20 mm. Similar results were found for instance by Shibata et al.[20] for PHBV composites produced by compression molding. In particular, lyocell fibers contents from 17.6 to 66.7 wt.-% reported a nearly linear increase in the modulus. While the neat PHBV achieved an elastic modulus of 440 MPa, the 34.6 wt.-% PHBV/lyocell composite showed a value of 1.63 GPa.

A similar trend was observed in the tensile strength for the PHB/pita fibers composite sheets. As it can be seen in **Figure 5b**, the mean length of pita fibers showed a main influence on the tensile properties of the PHB composites. Reinforcement accomplished by the longest pita fibers, *i.e.*, lengths of 20 mm, led to a slight increase in the tensile strength. The highest strength value was also observed for the 40 wt.-% PHB/pita fibers composite, which resulted in 19.4 MPa. This was followed by the 30 wt.-% PHB/pita fibers composite that increased to 18.9 MPa. Tensile strength values for the 10 and 20 wt.-% pita-reinforced PHB sheets were on a similar level, *i.e.*, 16.9 and 17.8 MPa, respectively, than the unfilled PHB sheet, *i.e.*, 17.3 MPa. However, the incorporation of 15 and 5 mm-long pita fibers slightly reduced the tensile strength. Considering some other previous works related to natural fiber-reinforced PHB composites, different trends were reported. On one hand Bodros et al.[28] described similar reinforcements for a 34 wt.-% PHB/flax fibers composite. On the other hand, Garkhail and Peijs[29] and Barkoula et al.[27] found a decrease in tensile strength for similar PHB composites based on flax fibers. In the last research work,[27] up to 44 wt.-% of flax fibers was needed to

achieve a mechanical strength on the same level than the neat biopolymer. In other recent study, Skrifvars et al.[30] produced sisal, flax, coir, and banana fiber-reinforced PHB composites by the injection molding with fibers loadings ranging from 5 to 30 wt.-%. Though minimal reinforcement was noticed for the tensile-strength value, the modulus significantly increased except for PHB composites reinforced by coir.

The lowest mechanical performance for all the studied PHB composite sheets was undoubtedly observed for the lowest lengths of pita fibers, *i.e.*, 5 mm. Both the elastic modulus and tensile strength progressively decreased with the pita fibers content and, more importantly, these values were lower than those of the unfilled PHB sheet. Therefore, interestingly, incorporation of long pita fibers at 40 wt.-%, *i.e.*, 15 and 20 mm, provided the highest mechanical strength in the PHB composite sheets. This points out the fact that pita fibers could act as an effective reinforcement for PHB when their length exceed a critical value above 15 mm. This was in agreement with the research work previously performed by Shibata et al.[54], in which the effect of the natural fibers length was investigated by flexural tests on a corn-starch based matrix. This study showed that the flexural modulus and strength rapidly decreased for fiber lengths below 2.8 and 3.2 mm of kenaf and bagasse, respectively.

Figure 5c shows the elongation at break of the PHB composite sheets as a function of pita fibers content. Addition of pita fibers clearly resulted in a drastic reduction of the elongation at break for all PHB composite sheets. In particular, it decreased from *ca.* 8.8%, for the unfilled PHB, to 2–3%. This is agreement with several preceding research works carried out for other green composites based on PHB and PHBV matrices. For instance, in the research work performed by Barkoula et al.[27], PHB/flax composites presented a significant lower elongation-at-break value than neat PHB, which was *ca.* 1.5% for all fibers contents. In this regard it should be taken into account that PHB inherently presents a low elongation at break, *i.e.*, in the range of 6-9%, which is an indication of the typical brittle behavior under load of this biopolymer.[15] Similar mechanical responses were formerly reported by Bodros et al.[28] for composites containing randomly scattered flax fibers.

Figure 5d plots Shore D hardness *vs.* the pita fiber content at different lengths. As it can be seen in the graph, unfilled PHB sheet showed a Shore D hardness of *ca.* 61. Incorporation of pita fibers, in the whole range of lengths, exerted a positive effect on the hardness of the PHB composite sheets. In particular, it increased up to 66.6 and 67.0 for the 30 and 40 wt.-% green composite sheets, respectively. Unexpectedly, highest values were observed for the 5 mm-long fiber PHB composite sheets. This can be related to the fact that shorter pita fibers could move into more optimized locations inside the biopolymer matrix because they were better dispersed. This can be supported by the previous visual observation of the surface of PHB composite sheets. Similar results were previously described by Graupner and Müssig,[37] who particularly

showed a Shore D value of 67.5 for neat PHB. By adding 40 wt.-% kenaf fibers, the hardness of the PHB composite was increased to 73.1.

In conclusion, 20-mm long pita fibers were very effective in enhancing the elasticity of the PHB composite sheets, but the ductility greatly decreased. As aforementioned, the preparation method is expected to exert a leading influence on their mechanical performance since it highly influences the remaining fibers length, distribution, and orientation of the pita fibers in the PHB matrix. This also highlights the key role of the filler aspect ratio, *i.e.*, the fiber length over fiber diameter, on the mechanical properties of polymer composites.[44] High aspect ratios are habitually needed for effective transfer of the intrinsic mechanical properties of the reinforcing fibers, in agreement with previous research works.[21,27,55] For instance, PHB/flax composites manufactured through injection molding exhibited lower impact strength than those manufactured through compression molding[27]. This was explained by the shorter fibers length attained in the injection-molded pieces.

Thermomechanical properties

Figure 6a represents the Vicat softening point for the PHB composite sheets in relation to the pita fibers content and length. This reflects the softening degree that would be reached when the green composite is employed for an elevated temperature request. The graph interestingly revealed that the softening point of the PHB composite sheets considerably increased with the pita fibers loading. This improvement in the thermomechanical behavior of the PHB composite sheets was observed for all lengths and contents of pita fibers. It is considered that pita fibers prevented deformation of the PHB matrix and increased the heat-softening resistance of the compression-molded sheet. The highest improvement was also achieved for fibers lengths of 20 mm. In particular, it increased from *ca.* 97 up to 135 °C, *i.e.*, about 28%, for the PHB/pita fibers composite at 40 wt.-%. This improvement is related to an increase in the stiffness of the green composites, which was above quantified in the elastic modulus analysis.

HDT represents the upper use temperature limit of a given plastic. In green composites, the service temperature is typically enhanced by the stiffness and strength exerted by natural fibers in the biopolymer matrices. In the case of PHB, as a semi-crystalline biopolymer, it can also depend on the thermal history, which is related to the crystallite sizes and distribution along with the presence of impurities and other nucleating agents.[15] Nevertheless, the compression-molding technology generally provides faster cooling times than other melt-shaping technologies (*e.g.*, injection molding). **Figure 6b** shows the variation of HDT in the PHB composites according to the amount of pita fibers at the three studied lengths. It can be observed in the graph that the increase of the pita fibers content resulted in a remarkable increase of HDT. Interestingly, the length of the fibers also promoted a rise in the temperature service. In

particular, the highest HDT increase was observed for the 40 wt.-% PHB composite sheets containing 15 and 20 mm-long fibers. In particular the 40 wt.-% PHB composite sheet containing pita fibers of 15 mm showed the highest increase, which was *ca.* 21 °C, *i.e.*, an increase of about 19%, as compared to neat PHB. In this sense, Singh et al.[34] previously described the service temperatures of PHBV and its green composites with bamboo fibers. HDT for PHBV was particularly increased from 114 to 120 and 123 °C by reinforcement with these natural fibers at 30 and 40 wt.-%, respectively. According to the authors, the major contributing factor to the improved HDT was the strong fibers strengthening applied to the biopolymer matrix. In another work, Singh and Mohanty[39] were also able to increase HDT by approximately 24 °C for PHBV through the incorporation of 40 wt.-% wood fibers. The enhanced thermomechanical behavior was mainly attributed to a crystallinity increase of PHBV, in which the wood fibers surface could act as nucleating sites. Similar observations were previously reported elsewhere.[18,25]

Surface fractures

SEM investigations of the fractured surfaces after the tensile tests of the PHB composite sheets containing 10, 20, 30, and 40 wt.-% of pita fibers are displayed in **Figure 7**. Different pita fibers contents in the PHB composites showed similar morphologies in the fractures. **Figure 7a** shows a 10 wt.-% PHB composite in which it can be seen that pita fibers were successfully incorporated with a relatively good dispersion into the PHB matrix. **Figure 7b** presents the fracture of a 20 wt.-% PHB composite sheet that clearly shows that pita fibers were not preferably oriented to any particular direction during compression molding processing. **Figure 7c**, which corresponds to a 30 wt.-% PHB composite, further confirmed that pita fiber orientation was mostly random. Therefore, the resultant structure of the green composite sheets can be beneficial for anisotropic mechanical deformations. A similar morphology was also observed in **Figure 7d** for a 40 wt.-% PHB/pita fibers composite. It is worthy to mention that some remaining holes were observed in the PHB matrix in these SEM micrographs. It can be assumed that pita fibers delamination was the main failure mode during the tensile test. Similar observations were concluded in the research carried out by Singh and Mohanty,[39] in which different contents of wood fibers were incorporated into PHBV matrices. This was related to an insufficient adhesion of the natural fibers to the biopolymer matrix, which promoted the fibers pullout. Present SEM images also showed some marked straight crack fronts on the PHB matrix after fracture. The high roughness, the irregularity of the surface, and the presence of crack fronts confirmed the inherent brittle behavior of PHB. Surface fractures fully supported the above-described mechanical performance, which indicated that the PHB/pita fibers composites presented very little plastic deformation before breaking.

Detailed picture in **Figure 7e** displays the small gaps observed between the pita fibers and the PHB matrix. The presence of a remarkable discontinuity around the fibers perimeter within the biopolymer matrix denoted the lack of interaction between the PHB biopolymer and pita fibers. From a mechanical behavior point of view, this discontinuity is known to act as stress concentrator, *i.e.*, the so-called "notch effect". This generates high concentrations of stress around the pita fibers interphase that favor the initiation and spread of cracks, causing the above-reported brittle-type fracture in the PHB composites. This effect was particularly reported by Barkoula et al.[27] for PHB and PHBV composites, which was related to a poor matrix-fibers bonding. According to this, a better interface adhesion would have allowed larger stress transfer from pita fibers to the PHB matrix, accounting for a whole superior mechanical functioning.

Finally, the SEM image included in **Figure 7f** displays the fracture examination of a pita fiber embedded in the PHB matrix. This micrograph revealed that pita fibers actually exhibit a hollow structure that is composed of long channels. Indeed, pita was reported to naturally occur as technical fibers composed of cellulose microfibrils based on a structure of lignin, pectin, and hemicelluloses.[49,51] A similar porous structure was for instance formerly observed for bagasse-reinforced composites by Shibata et al.[54], who demonstrated that porous fibers were more compressible during flexural assessment than solid-like kenaf fibers.

Conclusions

Novel fully bio-based long pita fiber-reinforced PHB sheets were successfully prepared by compression molding at various contents and lengths. Results shows that pita fibers performed a notorious role in the reinforcement of PHB and improved the mechanical and thermomechanical properties of the biopolymer. A maximum mechanical performance was observed in the PHB composite sheets at a pita fiber loading of 40 wt.-% for lengths above 15 mm, while shorter fibers increased the hardness to a higher extent. The attained values were in agreement with other natural long fiber-reinforced PHB and PHBV composites reported earlier by other research groups. The increased elasticity observed for the green composites sheets was ascribed to the uniform dispersion, random orientation, and remaining aspect ratio of the pita fibers in the PHB matrix. This optimal morphology gave rise to an effective and uniform stress distribution. Thermomechanical tests also confirmed that pita fibers could reinforce the service temperature of PHB. SEM micrographs, acquired at the fractured surfaces of the PHB composite sheets, noticeably indicated that pita fibers were well incorporated and randomly oriented. However, in general, pita fibers presented a low interface adhesion to the PHB matrix. Further studies will explore the surface pretreatment of plant- and agro-based fibers and/or the use of renewable compatibilizers and additives capable of forming chemical bridges with the biopolymer matrix.

This will allow improving the interfacial strength between natural fibers and bioplastics, which is of key importance in discontinuous fiber-reinforced composites.

Applications of resultant green composite sheets can be aimed to the automotive industry, which currently demands for high-performing polymer materials with a lower carbon footprint. The here-developed LFRTs based on PHB and pita fibers, both from renewable resources, can be applied for interior and non-structural automotive parts. Illustrative examples of the potential use of these novel green composite sheets in the automotive industry can be door panel inserts, seatback lining, arm rests, under-floor body panels, package shelves, headliners, etc.

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Figure Captions

Figure 1. Schematic illustration of the sustainable closed-loop model for the green composites described in this research work: Compression-molded sheets are fully obtained from natural resources and finally converted to compost for the new plant to start the cycle again.

Figure 2. a) Representation of the mold employed during compression molding; b) Spatial arrangement of the poly-3-hydroxybutyrate (PHB) and pita fiber layers to form the green composite sheets.

Figure 3. Stereomicroscopy images of the pita fibers mats cut at different lengths: a) 5 mm; b) 15 mm; c) 20 mm. Graph paper features grids of 1 x 1 mm^2.

Figure 4. Surface appearance of the poly-3-hydroxybutyrate (PHB) composite sheets according to the weight content (wt.-%) and length of pita fibers.

Figure 5. Mechanical properties of the poly-3-hydroxybutyrate (PHB) composite sheets as function of the pita fiber content in weight (wt.-%) at different lengths in terms of: a) Tensile modulus; b) Tensile strength; c) Elongation at break; d) Shore D hardness.

Figure 6. Thermomechanical properties of the poly-3-hydroxybutyrate (PHB) composite sheets as function of the pita fiber content in weight (wt.-%) at different lengths in terms of: a) Vicat softening point; b) Heat deflection temperature (HDT).

Figure 7. Scanning Electron Microscope (SEM) micrographs taken on the fractured surfaces of the compression-molded poly-3-hydroxybutyrate (PHB) composite sheets containing: a) 10 wt.-% pita fibers with length of 5 mm; b) 20 wt.-% pita fibers with length of 10 mm; c) 30 wt.-% pita fibers with length of 15 mm; d) 40 wt.-% pita fibers with length of 20 mm. Images were taken with a magnification of 200x and scale marker of 500 μm; e) Detail of the pita fiber-PHB matrix adhesion. Image was taken with a magnification of 400x and scale marker of 200 μm; f) Detail of the pita fiber fracture. Image was taken with a magnification of 1500x and scale marker of 50 μm.

Figure 1. Schematic illustration of the sustainable closed-loop model for the green composites described in this research work: Compression-molded sheets are fully obtained from natural resources and finally converted to compost for the new plant to start the cycle again.
Figure 1
395x303mm (300 x 300 DPI)

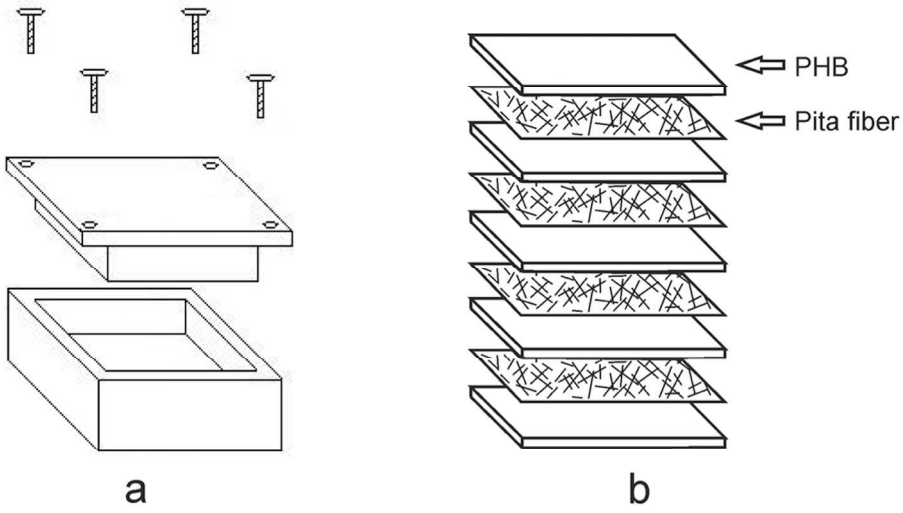

Figure 2. a) Representation of the mold employed during compression molding; b) Spatial arrangement of the poly-3-hydroxybutyrate (PHB) and pita fiber layers to form the green composite sheets.
Figure 2
150x81mm (300 x 300 DPI)

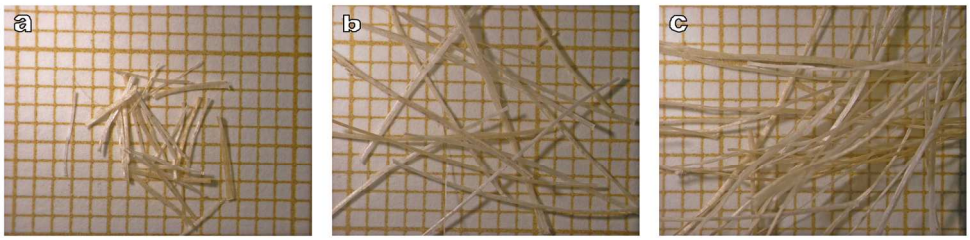

Figure 3. Stereomicroscopy images of the pita fibers mats cut at different lengths: a) 5 mm; b) 15 mm; c) 20 mm. Graph paper features grids of 1 x 1 mm2.
Figure 3
206x55mm (300 x 300 DPI)

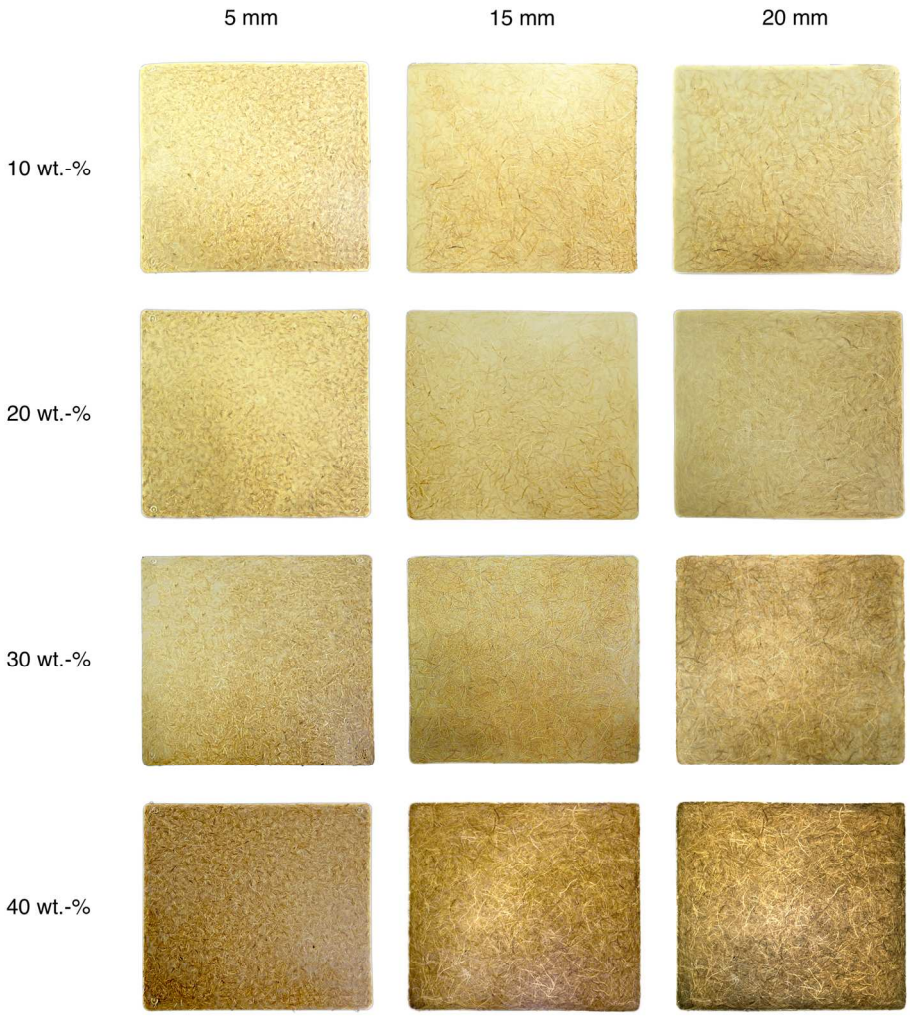

Figure 4. Surface appearance of the poly-3-hydroxybutyrate (PHB) composite sheets according to the weight content (wt.-%) and length of pita fibers.
Figure 4
186x203mm (300 x 300 DPI)

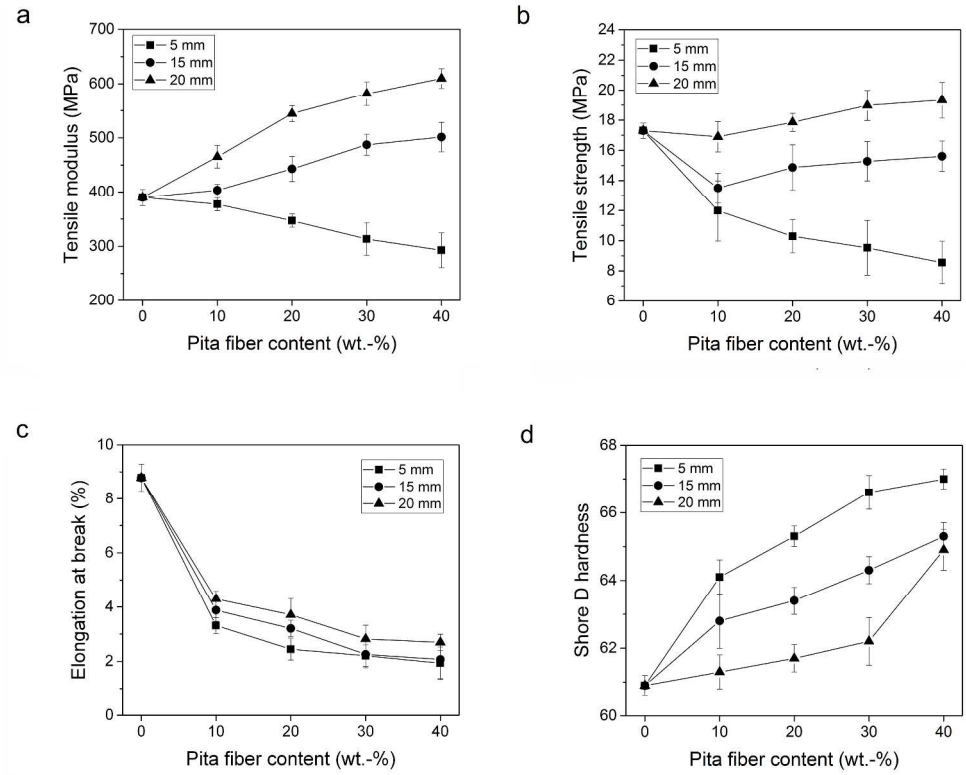

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Figure 5
372x296mm (300 x 300 DPI)

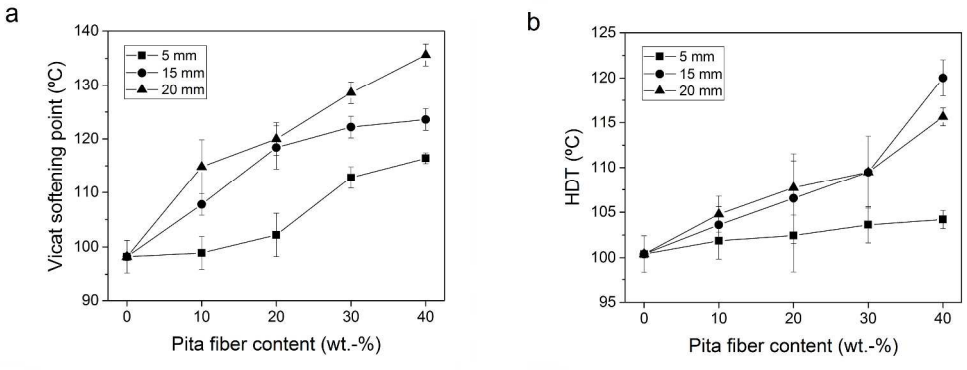

Figure 6. Thermomechanical properties of the poly-3-hydroxybutyrate (PHB) composite sheets as function of the pita fiber content in weight (wt.-%) at different lengths in terms of: a) Vicat softening point; b) Heat deflection temperature (HDT).

Figure 6
372x144mm (300 x 300 DPI)

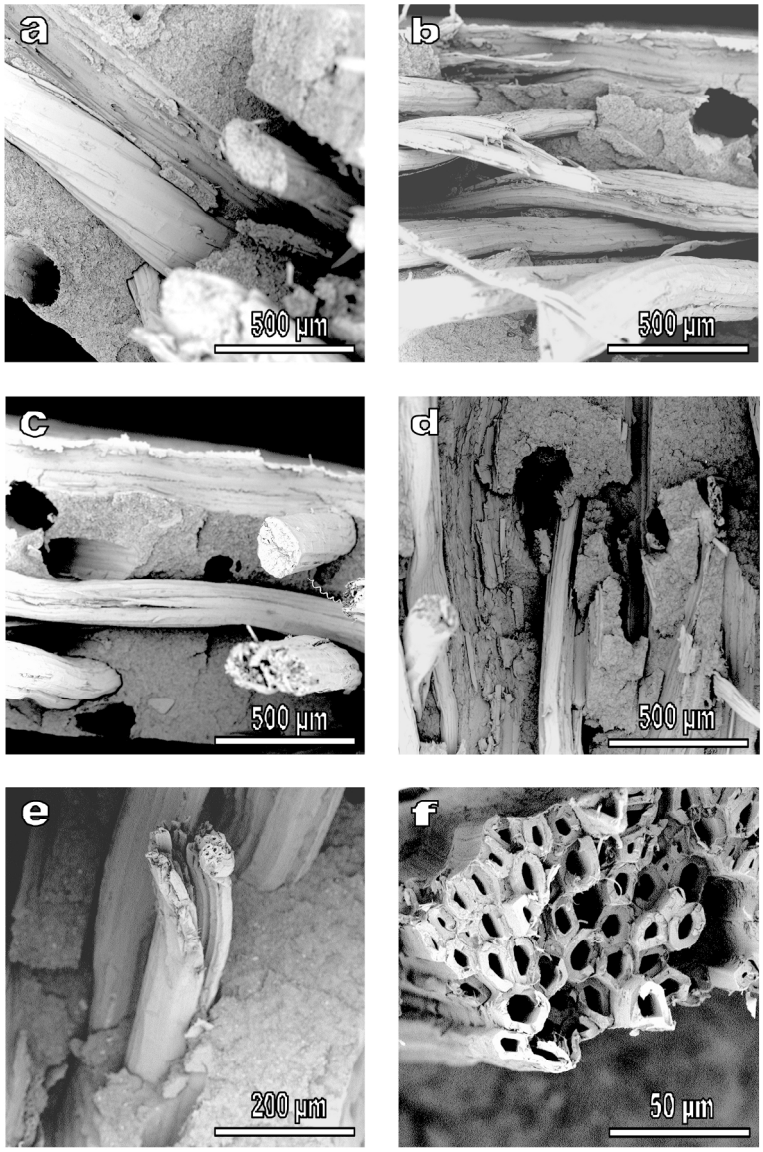

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Figure 7
171x254mm (300 x 300 DPI)