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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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Abstract

Novel green composites were successfully prepared from bacterial poly(3-hydroxybutyrate) (PHB) and pita fibers derived from the agave plant (*Agave americana*). 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 by compression molding. The newly prepared PHB/pita fibers composite sheets were characterized in terms of their mechanical and thermomechanical properties and then related to their morphology after fracture. Attained results indicated that the mechanical stiffness of PHB significantly improved with both the content and length of pita fibers, although ductile properties were reduced. In particular, the elastic modulus of the 40 wt.-% PHB composite sheets containing 20-mm-long pita fibers was approximately 55% higher than the unfilled PHB sheet. Shore D hardness also improved, achieving the shortest pita fibers the highest improvement. Pita fibers with lengths of 15 and 20 mm also increased the Vicat softening point and heat deflection temperature (HDT) by 38 and 21°C, respectively. Due to their optimal shape, it is concluded that pita fibers with lengths above 15 mm can potentially reinforce and improve the performance of PHB biopolymer. In addition, the compression-molding methodology described in this research work represents a cost-effective pathway to feasibly prepare long-fiber-reinforced thermoplastics (LFRTs) fully based on renewable raw materials. Resultant green composite sheets can be of interest for the development of sustainable parts in the automotive industry and other advanced applications in polymer technology.

KEYWORDS
automotive parts, compression molding, green composites, pita fibers, polyhydroxyalkanoates

1 | INTRODUCTION

A large amount of agro- and marine-waste materials are globally produced every year. The development of high-performance polymer technologies made from renewable resources is increasing worldwide. Natural fibers (NFs) represent a sustainable choice for the manufacturing of polymer biocomposites.[1] NFs can be either sourced from animals or plants. Animal-based fibers basically consist of proteins (e.g., hair, silk, and wool), while plant-derived fibers are obtained from crops and sea, and they are mainly composed of cellulose. Plant-derived fibers 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), core fibers (e.g., hemp, kenaf, and jute), and other kinds (e.g., wood and roots).[2]

The term wood–plastic composite (WPC) usually refers to any biocomposites based on NFs derived from plants, including wood and nonwood fibers, embedded in a thermoset or thermoplastic matrix.[3] NFs are, in general, suitable to reinforce plastics due to their relative high strength and stiffness.[4] In comparison to classical glass fiber-reinforced plastics (GFRPs), WPCs can potentially reduce product density and the energy requirements for processing.[5] These novel materials can also offer some environmental advantages over traditional polymer composites, such as reduced dependence on nonrenewable energy/material sources, lower greenhouse gas and pollutant emissions, improved energy recovery, and end-of-life biodegradability of components.[6] WPCs are habitually considered as sustainable materials because of their relatively high renewable content.[7] Furthermore, using a bio-based and/or biodegradable polymer as the material matrix can additionally increase the green credentials of the WPCs.[8,9] Green composites are a specific class of WPCs, in which the matrix is a biopolymer.[10] In this regard, the use of NFs such as jute, sisal, flax, hemp, and bamboo fibers on biopolymers has been recently intensified.[11] In general, high loadings of NFs are preferred since the raw materials cost for the manufacturing of the green composites can be significantly reduced.[12]

Polyhydroxyalkanoates (PHAs) are a well-known family of biodegradable bacterial polyesters with the highest potential to replace polyolefins in a wide range of applications.[13] 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.[14] Such diversity definitely allows the production of aliphatic bio-based and biodegradable polyesters 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*.[15] 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. 175°C.[16] Among PHAs, PHB, together with its copolymer with 3-hydroxyvalerate, i.e., poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), has received so far the greatest attention in terms of pathway characterization and industrial-scale production. PHB biopolymer holds 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.[17] For this reason, PHB has been widely studied and processed in conventional manufacturing equipment to produce a wide range of products: Films and sheets, laminates, coated materials, spun fibers, nonwoven fabrics, foams, etc.[18] PHB is compostable, i.e., disintegrable in controlled compost soil, 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 stability[16] that gives a very narrow processing window and 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 green composites such as regenerated and/or recycled cellulose,[19–21] pineapple leaf fibers (PALF),[22,23] wheat straw fibers,[24] wood floor,[25,26] jute fibers,[27] flax fibers,[28–32] banana, sisal, and coir fibers,[31] hemp fibers,[33] abaca fibers,[34] bamboo fibers,[35] sugarcane bagasse fibers,[36,37] kenaf and lyocell fibers,[38] and wood powder.[39,40] Due to their challenging processability, 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 green composites containing 20 wt.-% of bagasse fibers.[36] In other study, Kobayashi et al.[37] prepared PHB/sugarcane bagasse fibers 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.[22] These research works have suggested that the incorporation of NFs can definitely strength the mechanical performance of PHB and PHBV. Some of these works have also demonstrated that NFs could promote biodegradability.[24,28,34]

It is well reported in the polymer literature that not only the fiber origin and content but also the blending methodology plays a key role in the mechanical properties of the resultant green composites.[41] In this sense, compression molding in 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 long-fiber-reinforced thermoplastics (LFRTs), which can find several uses in plastics engineering. Due to their excellent strength and renewability, LFRTs made of NFs are being increasingly used as parts and components for automotive applications.[42] Recent studies have indicated that the market of NFs in the automotive industry is growing at more than 20% per year, in which the European manufactures are the leaders at their implementing.[43] Advanced green composites typically present lower density over conventional GFRPs, which allows production of lightweight parts with the advantage of fuel and cost saving.[3,44] Current uses of sustainable LFRTs are mainly focused on interior and nonstructural 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 such as seat frames, load floors, pick-up beds, floor pans, drive train, and steering components. There are also some examples of exterior parts made from green composites.[45] NFs are also being explored for thermo-acoustic insulation panels and construction uses.[46] In addition the food packaging industry can benefit from the hot-pressing methodology to prepare novel green composites and polymer nanocomposites of hierarchical structures with passive, active, and bioactive properties.[47] 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.[48] Materials may be loaded into the mold in the form of either pellets or film/sheet. As a result, long fibers can be then feasibly fed without the need of using pultrusion or melt-impregnation processes.[49] The main advantage of the hot-press molding over other melt technologies (e.g., injection molding) is related to its capacity to shape large and intricate plastic parts with accurately control on processing temperature[50] and reduced amounts of waste materials.[51] More importantly, due to the lower mixing energies and shear peaks employed during molding methodologies, filler attrition or breakage can be minimized.[52]

In this work, pita fibers were originally selected to produce a sustainable LFRT. This hard-type fiber is 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%).[53] This variety of plant grows in Africa and Europe warm-weather countries, but it is native from Central America and Mexico. Their leaves 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 with other NFs, pita fibers present higher tenacity and rupture strain, weaker initial modulus, and relatively higher rupture energy.[54] In particular, tenacity is near those of strong NFs such as sisal or flax. Although the mechanical properties of isolated pita fibers have been recently studied,[55] to the best of our knowledge, their application in polymer technology to reinforce plastic and bioplastic matrices has never been explored.

The objective of this 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 sustainable LFRTs for the automotive industry. The life cycle of the proposed green composites is summarized in the scheme displayed in Figure 1, which closely symbolizes the cradle-to-cradle (C2C) concept.[56]

FIGURE 1 Schematic illustration of the closed-loop sustainable model for the green composites described in this research work: Compression-molded sheets are fully obtained from renewable resources and they are finally converted into compost, which serves as nutrient for a new agave plant to start the life cycle again [Color figure can be viewed at wileyonlinelibrary.com]

This theoretically gives a very favorable balance of carbon dioxide emissions into the atmosphere. This is based on the fact that agave plants, from which pita fibers are obtained, capture atmospheric carbon dioxide during their growth, and this provides a positive balance on the overall carbon footprint. In addition, both raw materials are renewable and their availability is relatively unlimited.

2 | EXPERIMENTAL

2.1 | Materials

Bacterial aliphatic homopolyester PHB was Biomer® P226, supplied by Biomer (Krailling, Germany). The product was delivered in pellet form in waterproof bags. This grade is certified as compostable, presents a density of 1.25 g/cm^3, and shows a melt flow index (MFI) of 9–13 g/10 min (190°C, 2.16 kg). Productos Gol S.L. (Cieza, Spain) provided the pita fibers, which are extracted from agave plants cultivated in the Cabo de Gata-Níjar National Park. The fibers present a density of 1.36 g/cm^3.

2.2 | Compression molding

Prior to compression molding, pita fibers were cut into three different lengths: 5, 15, and 20 mm. PHB pellets and pita fibers were both dried at 90°C for 24 hr in a dehumidifying dryer MD from Industrial Marsé (Barcelona, Spain). Preparation of the green 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
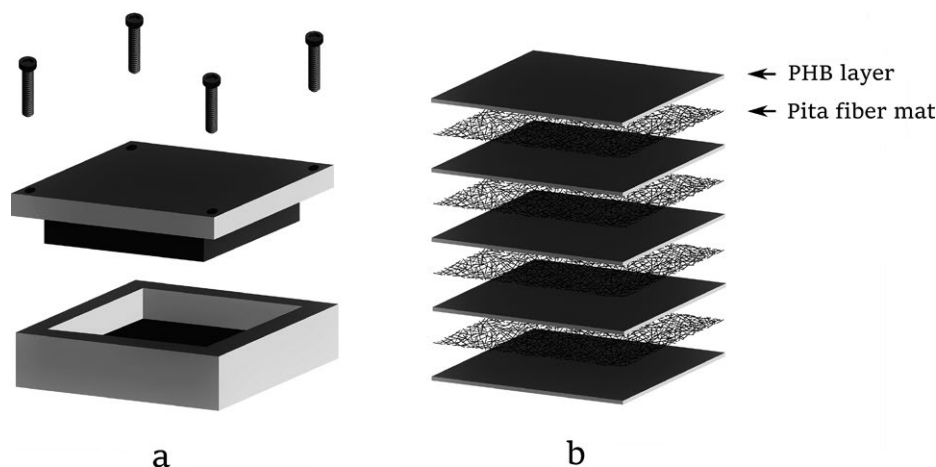
FIGURE 2 (a) Representation of the mold employed during compression molding; (b) spatial arrangement of the poly(3-hydroxybutyrate) (PHB) layers and pita fiber mats to form the green composite sheets

S.A. (Castalla, Spain). The compression-molding methodology 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 20×20 cm^2 and adjusted with screws. This process is depicted 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 and alternately sandwiched with four nonwoven mats of pita fibers placed randomly. The stacking sequence of the green composite is 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, at different lengths, into PHB was performed for various weight contents (wt.-%): 10, 20, 30, and 40 wt.-%. Resultant thicknesses of the compression-molded sheets ranged from 1.6 to 1.8 mm. Same process was followed to prepare PHB sheets without pita fibers as the control material. Once compression molding was completed, the green composite sheets were cut for characterization using a die on a hydraulic press model MEGA KCK-15A from Melchor Gabilondo S.A. (Vizcaya, Spain).

2.3 | Mechanical tests

Tensile tests were carried out on the green composite sheets following ISO 527 in a universal test machine ELIB 30 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, at a cross-head rate of 10 mm/min. Samples with a dog-bone shape were tested, and the modulus of elasticity (E), tensile strength (σ_s), and strain at break (ε_b) were determined. Shore D hardness was evaluated in a durometer 676-D model from J. Bot S.A. (Barcelona, Spain) as described in ISO 868. Six samples were tested and averaged.

2.4 | Thermomechanical characterization

The Vicat softening point and heat deflection temperature (HDT) of the compression-molded green composite 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, each specimen was 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/hr until the needle penetrated 1 mm. HDT measurements were carried out according to ISO 75 Method A and ASTM D648, using a heating rate of the medium (oil) of 120°C/hr. A specimen with dimensions of $4 \times 10 \times 80$ mm^3 was placed 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.

2.5 | 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 10×. This was equipped with a KL1500-LCD light source. In order to better ascertain their dimensions, pita fiber mats were deposited on a chart paper. The morphology of the fracture surfaces from the tensile tests was analyzed by scanning electron microscopy (SEM) in a PHENOM microscope 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 gold-palladium layer in vacuum conditions in a Sputter Coater EMITECH model SC7620 from Quorum Technologies Ltd. (East Sussex, UK).

3 | RESULTS AND DISCUSSION

3.1 | Morphology

Figure 3 shows the morphology of the pita fiber mats cut at different lengths: 5 mm (Figure 3a), 15 mm (Figure 3b), and 20 mm (Figure 3c). In all cases, pita fibers showed an average diameter of approximately 250 μm.

Figure 4 gathers the surface appearance of the obtained PHB composites after compression molding at different pita fiber contents and lengths. From these images, it can be seen that all green composite sheets presented a continuous and uniform surface. It is also noticeable that pita fibers were relatively well dispersed into the PHB matrix, presenting a markedly random distribution. In general, with the increase of both pita fiber content and length, the PHB composites acquired the characteristic appearance of wood. The green composite sheets containing shorter pita fibers presented a smooth and homogenous surface. In contrast, PHB composite sheets containing longer pita fibers showed a more irregular surface, resembling the natural aspect of wood. A similar aesthetic effect has been recently reported for renewable composites based on wood flour.[57]

3.2 | 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 length, i.e., 5, 15, and 20 mm. Figure 5a shows that the tensile modulus of the PHB composites steadily increased with the pita fiber loading for lengths above 15 mm. In particular, the elastic modulus 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, i.e., ca. 55%. 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 properties against tensile efforts with the incorporation of long pita fibers, i.e., 15 and 20 mm. Similar results were found for instance by Shibata et al.[21] for PHBV composites produced by compression molding. In particular, lyocell fiber contents from 17.6 to 66.7 wt.-% reported a nearly

linear increase in the modulus. While the neat PHBV was characterized by an elastic modulus of about 440 MPa, the 34.6 wt.-% PHBV/lyocell fibers composite showed a remarkably increase to 1.63 GPa.

A similar trend was observed in the tensile strength of the green composite sheets. As it can be seen in Figure 5b, the mean length of pita fibers exerted a main influence on the tensile properties of the PHB composites. The longest pita fibers, i.e., 20 mm, led to a slight increase in the tensile strength. In particular, the highest strength value was observed for the 40 wt.-% PHB/pita fibers composite sheet, which resulted in 19.4 MPa. This was followed by the 30 wt.-% PHB/pita fibers composite sheet, showing an increase in tensile strength of up to 18.9 MPa. Tensile strength values for the 10 and 20 wt.-% pita fiber-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 NF-reinforced PHB composites, different trends were reported. On one hand, Bodros et al.[29] described similar reinforcements for a PHB composite containing 34 wt.-% flax fibers. On the other hand, Garkhail and Peijs[30] and Barkoula et al.[28] found a decrease in the tensile strength for similar PHB composites based on flax fibers. In the last research work,[28] up to 44 wt.-% of flax fibers was required to achieve a mechanical strength similar to that of the neat biopolymer. In other recent study, Skrifvars et al.[31] produced sisal, flax, coir, and banana fiber-reinforced PHB composites by the injection molding with fiber loadings ranging from 5 to 30 wt.-%. Though minimal reinforcement was observed for the tensile strength value, the modulus significantly increased except for the PHB composites reinforced by coir fibers.

The lowest mechanical performance for all characterized PHB/pita fibers composite sheets was undoubtedly observed for the lowest length of pita fibers, i.e., 5 mm. Both the elastic modulus and tensile strength progressively decreased with the pita fiber content and, more importantly, these values were lower than those observed for the unfilled PHB sheet. Therefore, the incorporation of long pita fibers, i.e., with lengths of 15 and 20 mm, into PHB at 40 wt.-% provided the highest mechanical strength. This points out the fact that pita
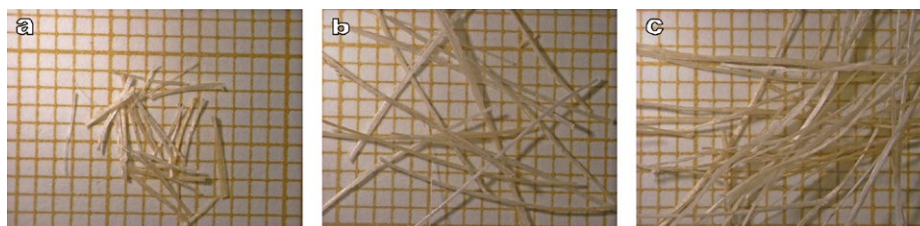
FIGURE 3 Stereomicroscopy images of the pita fiber mats cut at different lengths: (a) 5 mm; (b) 15 mm; (c) 20 mm. Graph paper features grids of 1×1 mm^2 [Color figure can be viewed at wileyonlinelibrary.com]
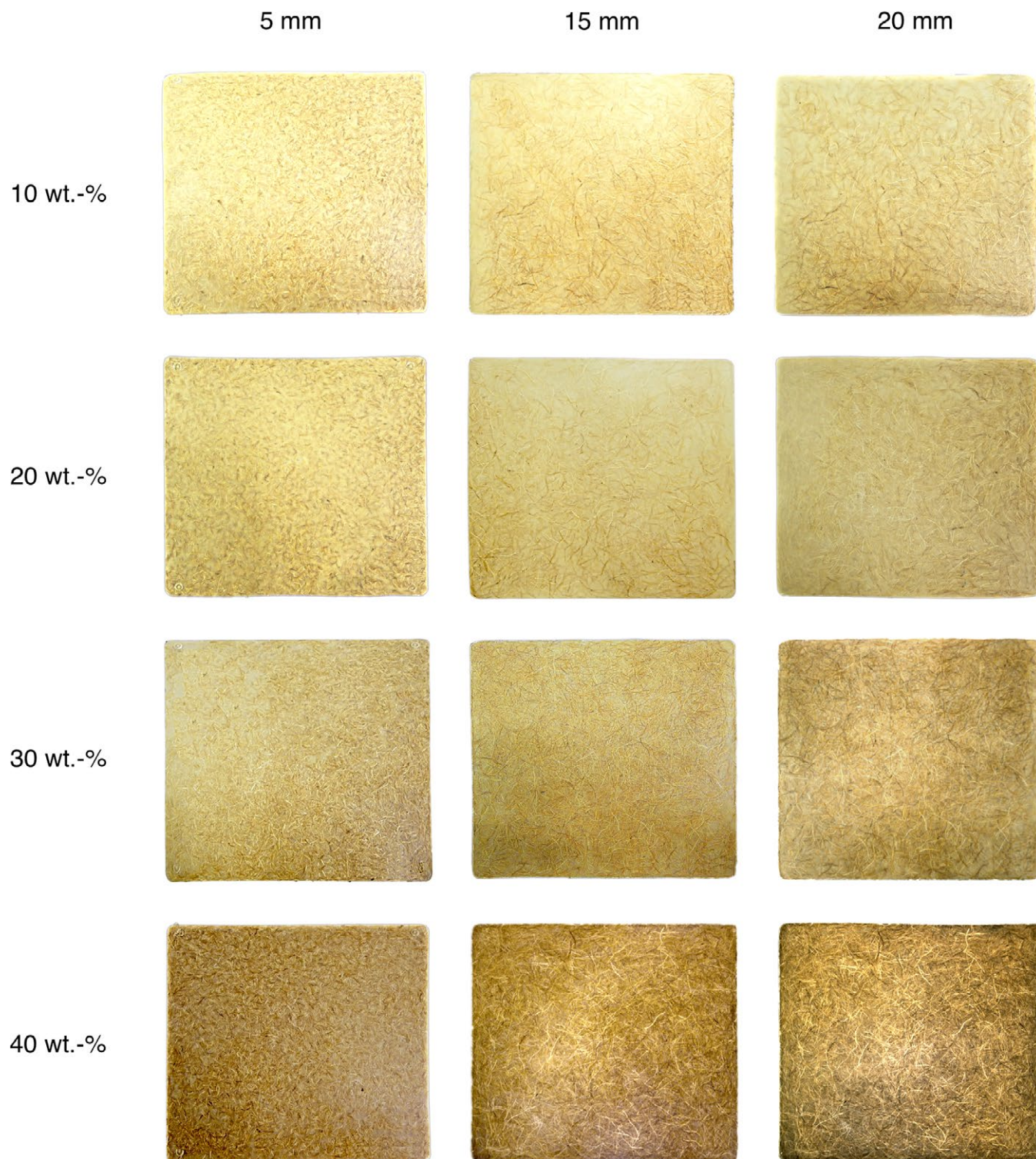
FIGURE 4 Surface appearance of the poly(3-hydroxybutyrate) (PHB) composite sheets according to the weight content (wt.-%) and length of pita fibers [Color figure can be viewed at wileyonlinelibrary.com]

fibers could act as an effective reinforcement for PHB matrices when their length exceeds a critical value above 15 mm. This was in agreement with the research work formerly performed by Shibata et al.[58], in which the effect of the NF length was investigated by flexural tests on a corn/starch-based matrix. This previous 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 plot evolution of the elongation-at-break values of the PHB composite sheets as a function of the pita fiber content. Addition of pita fibers clearly produced a drastic reduction of the elongation at break for all
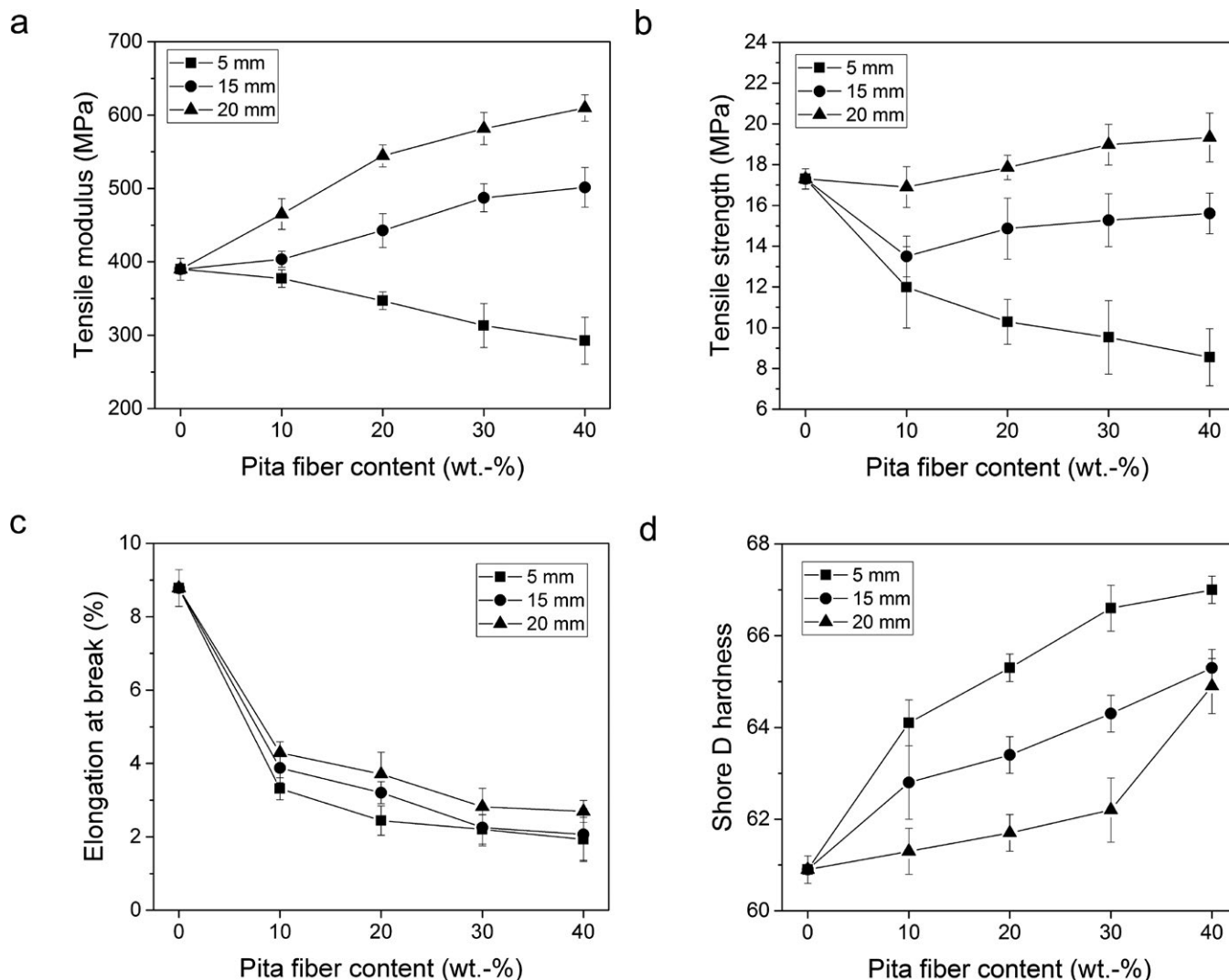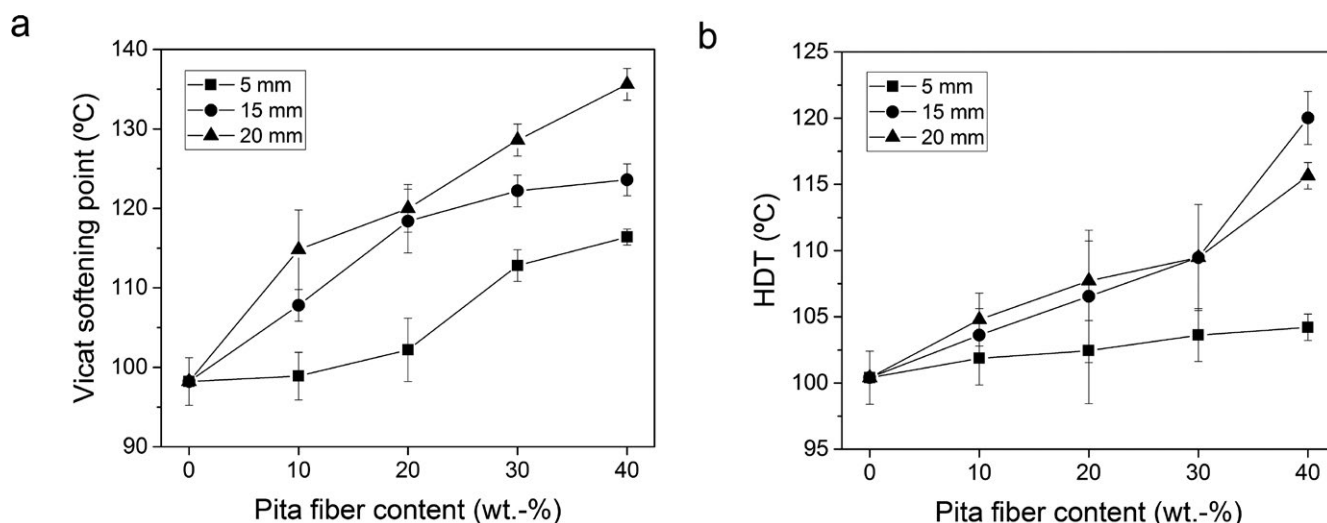
FIGURE 5 Mechanical properties of the poly(3-hydroxybutyrate) (PHB) composite sheets as function of the pita fiber content in weight (wt.-%) at different lengths in terms of (a) tensile modulus; (b) tensile strength; (c) elongation at break; (d) Shore D hardness

PHB composites. In particular, it decreased from ca. 8.8% for the unfilled PHB to 2%–3% for all pita fiber-reinforced PHB sheets. This is in 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.[28], PHB/flax fibers composites showed a significantly lower elongation-at-break value than neat PHB, which was ca. 1.5% for all fiber 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%. This is an indication of the typical brittle behavior of PHB under load.[16] Similar mechanical responses were previously reported by Bodros et al.[29] for composite parts containing randomly scattered flax fibers.

Figure 5d plots Shore D hardness of PHB composites vs. the pita fiber content at different lengths. As it can be seen in the graph, the 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 properties

of PHB. In particular, it increased up to 66.6 and 67.0 for the 30 and 40 wt.-% green composite sheets, respectively. Unexpectedly, the highest values were observed for the PHB composites containing 5-mm-long pita fibers. This can be related to the fact that shorter pita fibers could be better dispersed and then moved with more freedom into more optimized locations inside the biopolymer matrix. This can be supported by the previous visual observations carried out on the surface of the green composite sheets. Similar results were previously described by Graupner and Müssig,[38] who particularly showed a Shore D value of 67.5 for neat PHB. By adding 40 wt.-% kenaf fibers, the hardness of PHB increased to 73.1.

In conclusion, 20-mm-long pita fibers were very effective in enhancing the elasticity of the PHB composite sheets. However, the ductility decreased significantly. As aforementioned, the preparation method is expected to exert a leading influence on their mechanical performance since it highly influences the remaining length, distribution, and orientation of the pita fibers within the PHB matrix. This also highlights the

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)

key role of the filler aspect ratio, i.e., the fiber length over fiber diameter, in the mechanical properties of the polymer composites.[59] Therefore, high aspect ratios are habitually required for effective load transfer between the polymer matrix and the reinforcing fibers. This is in agreement with previous research works related to green composites.[22,28,60] For instance, PHB/ flax fibers composites manufactured by injection molding exhibited lower impact strength than those manufactured through compression molding.[28] This was explained by the shorter fiber length attained in the injection-molding process.

3.3 | Thermomechanical properties

Figure 6a shows the evolution of the Vicat softening point for the PHB composite sheets in terms of the pita fiber content and length. This reflects the softening degree that would be reached when the green composites are subjected to technical applications at an elevated temperature. The graph revealed that the softening point of the PHB composites remarkably increased with the pita fiber loading. This improvement on thermomechanical behavior was observed for all pita fiber lengths and contents. It can be considered that pita fibers prevented deformation of the PHB matrix and increased the heat-softening resistance of the compression-molded sheets. The highest improvement was also achieved for pita fiber lengths of 20 mm. In particular, it increased from approximately 97 up to 135°C, i.e., about 38°C, for the PHB/ pita fibers composite sheet at 40 wt.-% in comparison to the unfilled PHB sheet. This improvement can be related to the stiffness increase of the green composites, which was previously quantified during the analysis of the elastic modulus.

Heat deflection temperature determines the upper use of a given plastic in terms of the temperature limit. In green composites, the service temperature is typically enhanced by the stiffness and strength provided by NFs. In the case of PHB, as a semi-crystalline polymer, it can also depend on the thermal history. This is in turn related to the crystallite sizes and distribution, along with the presence of impurities and nucleating agents.[16] The compression-molding technology generally provides more control on the cooling time 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 that the increase in the pita fiber content resulted in a remarkable increase in HDT. Interestingly, the length of the pita fibers also promoted a rise in the service temperature. The highest improvement in HDT was also observed for the 40 wt.-% PHB composite sheets containing 15- and 20-mm-long pita fibers. In particular, HDT increased approximately by 21°C when PHB was reinforced with pita fibers of 15 mm. In this sense, Singh et al.[35] previously described the service temperatures of PHBV and its green composites obtained with bamboo fibers. HDT for PHBV particularly increased from 114 to 120 and 123°C by reinforcement at 30 and 40 wt.-%, respectively. According to the authors, the major contributing factor to the improved HDT was the enhanced fiber strengthening applied to the biopolymer matrix. In another work, Singh and Mohanty[40] were also able to increase HDT by approximately 24°C for PHBV through the incorporation of 40 wt.-% wood fibers. The improved thermomechanical behavior was mainly attributed to a crystallinity increase of PHBV, in which the surface of the NFs could act as nucleating sites. Similar observations have been previously reported elsewhere.[19,26]

3.4 | Fracture surfaces

SEM investigations of the fracture surfaces after the tensile tests of the PHB composite sheets containing 10, 20, 30, and
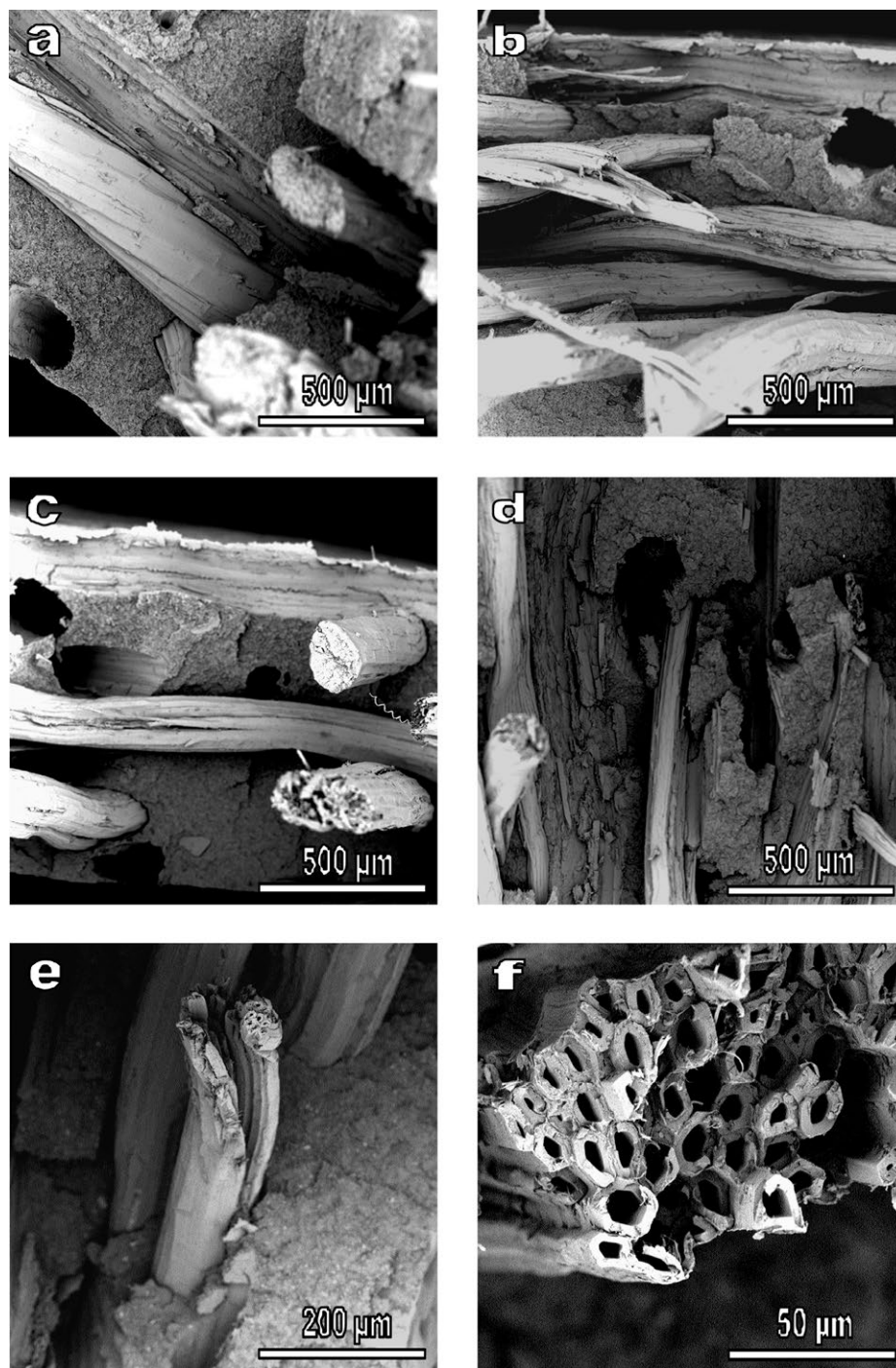
FIGURE 7 Scanning electron microscope (SEM) micrographs taken on the fracture surfaces of the compression-molded poly(3-hydroxybutyrate) (PHB) composite sheets containing (a) 10 wt.-% pita fibers of 5 mm; (b) 20 wt.-% pita fibers of 10 mm; (c) 30 wt.-% pita fibers of 15 mm; (d) 40 wt.-% pita fibers of 20 mm. Images were taken with a magnification of 200× and a scale marker of 500 μm; (e) detail of the pita fiber-PHB matrix adhesion. Image was taken with a magnification of 400× and a scale marker of 200 μm; (f) detail of the pita fiber fracture. Image was taken with a magnification of 1,500× and a scale marker of 50 μm

40 wt.-% of pita fibers are displayed in Figure 7. In general, different pita fiber contents showed similar morphologies in the fractures. Figure 7a shows the morphology a 10 wt.-% PHB/pita fibers composite in which it can be observed that pita fibers were successfully incorporated with a relatively good dispersion into the PHB matrix. The fracture surface of a 20 wt.-%

PHB/pita fibers composite (Figure 7b) clearly shows that pita fibers were not preferably oriented to any particular direction during compression molding. Figure 7c, which corresponds to a 30 wt.-% PHB/pita fibers composite, further confirmed that pita fibers were randomly dispersed in the PHB matrix. Therefore, the resultant structure of the green composite sheets can be

beneficial for anisotropic mechanical deformations. A similar morphology was also observed for a 40 wt.-% PHB/pita fibers composite (Figure 7d). It is also worthy to mention that some remaining holes were observed in the PHB matrices in the SEM micrographs. It can be assumed that fiber delamination was the main failure mode during the tensile tests. Similar observations were concluded in the research carried out by Singh and Mohanty,[40] in which different contents of wood fibers were incorporated into PHBV matrices. This was related to an insufficient adhesion of the NFs to the biopolymer matrix, which promoted fiber pullout. The here-provided 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 these crack fronts confirmed the inherent brittle behavior of PHB. Examination of fracture surfaces fully supports the above-described mechanical performance, which indicated that the PHB/pita fibers composites present very little plastic deformation before mechanical failure.

SEM micrograph included in Figure 7e displays a better detail of the small gaps between the pita fibers and the surrounding PHB matrix. The presence of a remarkable discontinuity around the fibers perimeter within the biopolymer matrix denotes the lack of interaction between the PHB biopolymer and pita fibers. From a mechanical 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 interface that favor the initiation and spread of cracks, causing the above-reported brittle-type fracture in the PHB composites. In addition, it is evident that the presence of this gap does not allow proper load transfer from the PHB matrix to pita fibers. This effect was particularly well reported by Barkoula et al.[28] for PHB and PHBV composites, which was related to a poor matrix-fiber bonding. According to this, a better interfacial adhesion would have allowed a larger stress transfer, accounting for a superior mechanical performance.

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 and continuous channels. Indeed, pita fibers have been reported to naturally occur as technical fibers composed of cellulose microfibrils with a structure of lignin, pectin, and hemicelluloses.[53,55] A similar porous structure was, for instance, previously observed for bagasse and kenaf fiber-reinforced composites by Shibata et al.[58] This previous work demonstrated that porous fibers, i.e., bagasse, were more compressible during flexural assessment than solid-like fibers, i.e., kenaf.

4 | CONCLUSIONS

Novel PHB composite sheets were successfully prepared by compression molding of different layers of pita fibers at various contents and lengths. Results showed that long pita fibers are able to play a notorious role in the reinforcement of PHB. In particular, pita fibers with lengths of 15 and 20 mm contributed to an overall improvement of the mechanical and thermomechanical properties of PHB. The highest mechanical performance was observed for the PHB composite sheets reinforced with 20-mm-long pita fibers at 40 wt.-%. In contrast, the shortest pita fibers improved hardness properties to a higher extent. Attained values were in agreement with other NF-reinforced PHB and PHBV composites previously reported by other research groups. The enhanced elasticity observed for the green composite sheets was ascribed to the uniform dispersion, random orientation, and remaining length of the pita fibers within the PHB matrix. This optimal composite morphology gave rise to an effective and uniform stress distribution. Thermomechanical tests also confirmed that 15- and 20-mm-long pita fibers improve the service temperature of PHB. SEM micrographs, acquired at the fracture surfaces of the compression-molded composite sheets, confirmed that pita fibers were efficiently incorporated into PHB and their orientation was predominantly random. However, in general, pita fibers presented a low interfacial adhesion with the PHB matrix. Further studies will focus on exploring the surface pretreatment of renewable fillers by physical or chemical methods and/or the use of reactive coupling agents capable of forming chemical "bridges" with biopolymer matrices. This will allow improving the compatibility of green composites, which is of key importance in discontinuous fiber-reinforced polymers.

Applications of resultant green composite sheets are 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 long pita fibers, which are both obtained from renewable resources, show a great deal of potential for the development of interior and nonstructural automotive parts. Illustrative examples of their application in the automotive industry can be door panel inserts, seatback lining, armrests, under-floor body panels, package shelves, headliners, etc.

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