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Polyhydroxybutyrate/hemp biocomposite: tuning performances by process and compatibilisation

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A fully bio-sourced and biodegradable composite material has been developed based on polyhydroxybutyrate and hemp fibres (20 wt% content). Improvements of the final performances of composite materials were shown to depend highly on the filler dispersion state and on the polar filler/apolar matrix interface. Those two parameters were tuned by playing around with the processing conditions (screw profile and speed) and the formulation (possible recourse to a green compatibiliser). The so-prepared biocomposites exhibited homogeneous structures, a controlled matrix–fibre interface and suitable thermal properties. Even if the materials also suffered some matrix degradation from identified sources, their mechanical properties were maintained and their water vapour sensitivity could be tuned by the processing conditions and formulation. The strong nucleating effect provided by the fibres has been highlighted, and a clear fibre–matrix load transfer confirmed the effectiveness of the prepared compatibiliser. Concerning the end of life, the high biodegradability of the fully bio-based composites in compost was also confirmed.

Notation

D	water vapour diffusion coefficient
M_w	mass average molar mass
$T_{-50\%}$	degradation onset temperature
T_c	crystallisation temperature
T_g	glass transition temperature
T_m	melting temperature
X_c	crystallinity degree

1. Introduction

Biocomposites based on the combination of both bio-sourced and biodegradable polymer matrices and vegetal fillers have been extensively developed during the past decade in response to environmental concerns and/or to develop specific new functionalities for many sectors of applications using short-life products such as food packaging and horticulture. Among promising bioplastics are polyhydroxyalkanoates (PHAs), such as polyhydroxybutyrate (PHB), a bacterial aliphatic copolyester which is a fully biodegradable material^{1,2} that can be produced from food industry by-products³ and agricultural or urban waste.^{4,5} The main limitation of PHB, restricting its commercial application at a large scale, is its high cost and its functional properties that are

not appropriate for some applications. Taking the example of food packaging application,⁶ PHB displays too high barrier properties to correctly preserve respiring products such as fruits and vegetables. In the case of respiring products, oxygen, carbon dioxide and water vapour permeabilities of packaging materials should be designed in such a way to fit the products' respiratory activity. Mechanical breakability of PHB is also too high for the targeted packaging applications. Mixing PHB with low-cost short lignocellulosic fillers sourced from jute,⁷ hemp,^{7,8} wheat straw fibres,^{9,10} olive pomace and husk,^{9,11} coffee waste¹² or potato peel waste fermentation residues¹³ is one environmentally virtuous strategy to modulate PHB functional properties while reducing the final cost of materials and conserving the biodegradability of materials.

The incorporation of lignocellulosic fillers in PHB matrices has one major technical bottleneck, namely the poor affinity between the filler and the matrix, which results in the low wettability of the fillers by the matrix and the poor dispersion of fillers due to agglomeration into knotty masses.¹⁴ To overcome this problem, different strategies can be applied to increase the similarity of the surface properties of the composite components – that is,

modification of the fibre surface to increase its surface free energy and particularly its hydrophobicity,¹⁵ modification of the polymer matrix to increase its hydrophilicity or the introduction of amphiphilic compatibilisers.^{16–19} If the incorporation of compatibilisers is widely reported in literature, particularly using melt extrusion,²⁰ only a handful of papers depict the use of bio-based compatibilisers,²¹ while bio-sourcing plasticisers has become a common practice.²² A combination of bio-based polyethylene-*graft*-maleic anhydride with sepiolite was proposed by Samper-Madrigal *et al.*²³ to manufacture films made of polyethylene and 30 wt% thermoplastic starch. Some authors proposed glycolysis of polylactide (PLA) with bio-based polyols such as glycerol or sorbitol to yield compatibiliser oligomers to enhance compatibilisation in PLA/starch composites.²⁴ Recently, Xiong *et al.*²⁵ proposed the epoxidation of bio-based cardanol with epichlorohydrin to yield an effective bio-based compatibiliser for PLA/starch composites.

The authors' team proposes a new strategy to synthesise bio-based compatibilisers for PHB/hemp fibre composites. The intention is to design oligo-PHB with aromatic groups, which could develop interactions with hemp fibres, by depolymerising PHB with alcohol functions of bio-based aromatic groups. The authors' team deeply studied cardanol²⁶ or tannins,²⁷ which bear only phenol groups, and also lignin derivatives, including vanillin and vanillyl alcohol, which have a primary alcohol that could be a good candidate to depolymerise PHB. Indeed, vanillin and derivatives are particularly interesting as vanillin is the only monoaromatic compound currently industrially produced from lignin.^{27,28} In a previous study,²⁹ the authors' team investigated the fictionalisations of vanillin and its derivatives at different oxidation states.

In addition to this chemical strategy that reduces the lack of affinity between the components, it is necessary to disperse the fibres homogeneously within the polymer the matrix to benefit fully from the introduction of fibres. For that, processing conditions need to be optimised as largely reported in the literature, whatever the fibre type.^{30–32} Ranganathan *et al.*³³ recently reported that, when manufacturing viscose fibre/polypropylene composites at low shear, the fibre bundles remain in clusters, whereas higher-shear conditions resulted in homogenised fibre dispersion and higher mechanical performances. Further addition of a dispersing agent improves fibre dispersion along with the mechanical performance

of the composites.³³ Similarly, Kuroda and Scott³⁴ performed basic experiments concerning the dispersion mechanism of glass fibre bundles and found that complete dispersion occurs above a critical shear stress. Recently, Conzatti *et al.*³⁵ reported the use of poly(1,4-butylene adipate-*co*-terephthalate) macrocycles for the compatibilisation of hemp-based composites. Despite its very interesting properties, the reported route unfortunately needs several synthesis steps and high quantities of solvents.

The objective of the present work is to optimise the mechanical performance of PHB/hemp fibre biocomposites by investigating and combining two routes: (a) extrusion processing conditions (screw profile and speed) and (b) addition of bio-based compatibilisers produced by reactive melt extrusion from the depolymerisation of PHB with vanillyl alcohol. The impact of processing and formulation on mechanical properties, water vapour sensitivity and biodegradability has been assessed and is discussed in relation to the structure of the materials.

2. Materials and methods

2.1 Raw materials

A commercial PHB was purchased from Metabolix, Germany (P(3HB-*co*-4HB) with 5% 4-hydroxybutyrate, M2100 grade). Pellets were vacuum dried overnight at 60°C before processing. The hemp fibres were provided by Chanvriers de l'Est (France) and were retted, carded and chopped into 2–4 mm length. Their average diameter was 50–100 µm. Zinc acetate dihydrate (99% purity) and vanillyl alcohol (VA, 98% purity) were purchased from Sigma-Aldrich.

2.2 Synthesis of the compatibiliser

The compatibiliser was obtained by transesterification of PHB by VA in a batch procedure. In a two-necked flask, PHB and VA were mechanically stirred and heated at 180°C with zinc acetate dihydrate as a transesterification catalyst (1 wt% relative to the polymer) in order to obtain oligoesters exhibiting a phenol end (Figure 1). Reagents were previously dried for one night at 45°C in a vacuum oven, and three argon/vacuum cycles were applied to the flask prior to heating so as to remove residual oxygen. The reaction was maintained for 1.5 h, and the material was then put in a vacuum container during cooling and further hand-crushed in a mortar.

Figure 1. Transesterification of PHB by VA

A masterbatch of the compatibiliser that had been previously prepared was compounded in a Eurolab 16XL twin-screw extruder (Thermo Scientific). Pellets of the compatibiliser and P(3HB-co-4HB) were previously dry mixed, the coupling agent representing 30 wt% of the total throughput (2.86 kg/h). Both components were dried before extrusion, and screw speed was set to 500 revolutions per min (rpm), leading to a residence time of 70–75 s. The temperature profile was a downstream gradient from 180°C at the feeder to 150°C at the die. The so-prepared masterbatch was air-dried and further pelletised.

2.3 Preparation of PHB/hemp fibre biocomposites

Pellets of virgin PHB and compatibiliser masterbatch were dried for one night in a vacuum oven at 45°C and mixed in a plastic can before processing. Biocomposites were prepared in a twin-screw extruder with an *L/D* ratio of 28 and a screw diameter of 24 mm (Haake PolyLab, Thermo Scientific). Hemp fibres were dried at 80°C for 1 h and added to the extruder by a lateral feeder directly into the polymer/masterbatch melt. A unique and typical 20% fibre content was chosen, the temperature was moderately set to 180°C all along the screw and the total throughput was 4.5 kg/h.

Three screw speeds were chosen (250, 500 and 750 rpm), and two screw profiles have been tested (Figure 2), providing two different shear levels to the extruded material. The first screw profile was constituted by five distribution zones (made of mixing elements) and one single dispersion zone (made of mixing elements directly followed by an inverse screw thread) and was called the ‘low-shear profile’. The second screw profile was constituted by five dispersion zones and one distribution zone and was called the ‘high-shear profile’. Residence times for the low-shear profile were 80, 50 and 40 s at 250, 500 and 750 rpm, respectively. When using the high-shear profile, the residence times were 115, 90 and 80 s when processing at 250, 500 and 750 rpm, respectively.

Extruded composites were granulated, dried for one night in a vacuum oven at 45°C and further injected as dog-bone samples with the aid of a DSM MC 15 microcompounder and a DSM IM 12 injection moulding machine. Mould geometries were chosen according to ISO 572-2³⁶ standard specifications, and injected samples were of 1B type. It is worth noting that unfilled materials could not be processed along with this last step as injection moulding requires crystallising kinetics that those compositions did not show since no crystallisation agent was employed. Samples were codified as follows: with compatibiliser – PHB-C-H; without – PHB-H. Processing conditions are labelled as follows: ‘LS’ and ‘HS’ refer to the materials elaborated with the low-shear and the high-shear profiles, respectively. The three digits in the sample codes refer to the screw speed chosen during processing, in revolutions per min.

2.4 Characterisation of PHB/hemp fibre biocomposites

2.4.1 Scanning electron microscopy

Scanning electron microscopy (SEM) observations were performed using a scanning electron microscope (S-4500, Hitachi,

Japan) with an acceleration voltage of 2 kV and a detector for secondary electrons. Prior to observation, the injection-moulded samples were frozen under liquid nitrogen and then fractured, mounted and coated with gold on an ion sputter coater.

2.4.2 Molecular weight analysis

The weight average molecular weights (M_w) were determined by gel permeation chromatography (GPC) on a Waters high-performance liquid chromatography system equipped with a Waters 410 differential refractive-index detector, a 600 mm column PLgel MixC 5 μ m. The mobile phase was chloroform (CHCl_3); its flow rate set to 0.8 ml/min at 30°C and toluene was used as a flow marker. The samples were prepared as 10 mg/ml solutions and, when containing fibres, were filtered on a 45 μ m pores filter (VWR, filter paper, qualitative 413). Then, all samples were filtered using 0.2 μ m polytetrafluoroethylene filters. A sample injection volume of 200 μ l was used in the GPC analysis, and the calibration was performed with polystyrene standards.

2.4.3 Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were performed with a Netzsch DSC 200 F3 calorimeter calibrated with an indium standard. Samples of 10 ± 2 mg were placed in the measurement heating cell and were heated under inert atmosphere from -50 to 200°C at a heating rate of $20^\circ\text{C}/\text{min}$. Two heating runs and one cooling run were recorded, and the glass transition temperature (T_g) values were measured during the second run. T_g values were calculated at the midpoint of the heat capacity jump. The crystallinity degree (X_c) was obtained from the DSC curve using the equation

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{m100\%} \times (1 - \alpha)}$$

where ΔH_m is the measured melting enthalpy for a given sample; ΔH_{cc} is the cold crystallisation enthalpy; $\Delta H_{m100\%}$ is the melting enthalpy of 100% crystallised PHB (144 J/g);³⁷ and $(1 - \alpha)$ is the weight fraction of polymer in the material.

2.4.4 Thermal stability

Thermogravimetric analyses were performed on a Q50 instrument from TA Instruments. Ten milligrams of the sample was placed in

Figure 2. Low-shear (LS, top) and high-shear (HS, bottom) screw profiles showing mixing zones (labelled ‘M’) and inverse screw threads (labelled ‘IS’). Non-labelled zones contain only conveying elements

an aluminium pan and heated from room temperature to 550°C under a nitrogen flow (60 ml/min). The experiments were carried out at a heating rate of 10°C/min.

2.4.5 Tensile tests

Mechanical tensile tests were performed on a Zwick metrology Z010 apparatus according to NF EN ISO 527-1³⁸ standard in order to determine mechanical properties of the materials. The apparatus is equipped with pneumatic grips, with 100 mm spacing, and a sensor of 500 N or 5 kN depending on the tested materials. The traction speed is 10 mm/min, controlled by position regulation, with a preload of 2 N before measurement. Results are an average of measurements performed on at least five samples.

2.4.6 Water sorption kinetics

Moisture sorption isotherms were determined with the aid of a precision scale. The experiments were carried out on end parts of dog-bone injection-moulded samples. The samples were dried at 40°C in a vacuum oven for 24 h and then left to equilibrate at 0% relative humidity (RH) for 1 week before measurement. The sorption curves were conducted at 25°C with 96% RH.

$$2. \quad M(t) = \frac{w_{\text{moist}}(t) - w_{\text{dry}}}{w_{\text{dry}}} \times 100$$

The moisture uptake $M(t)$ was calculated using Equation 2, where $w_{\text{moist}}(t)$ is the sample weight exposed to 96% RH for a time t and w_{dry} is the dry weight of the sample at 0% RH. Numerous models have been developed to describe properly the moisture contamination of composite materials.^{39,40} As indicated in the ASTM standard for water diffusion in thin plates of fibre-reinforced polymers,⁴¹ this process can be adequately described by the one-dimensional Fick's second law (Equation 3), where c is the moisture concentration, D is the diffusion coefficient, t is the time and x is the position through the thickness of the plate.

$$3. \quad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

A useful closed-form approximate solution⁴² is given in Equation 4, where $M(t)$ is the evolution of the water absorbed, M_s is the water content at saturation and h is the thickness of the plate.

$$4. \quad \frac{M(t)}{M_s} \approx 1 - \exp \left[-7.3 \left(\frac{Dt}{h^2} \right)^{0.75} \right]$$

The curve were fitted thanks to a Levenberg–Marquardt algorithm applied on the asymptotic model performed in the OriginPro 2017 software. All the coefficients of determination (r^2) were higher than 0.993.

2.4.7 Biodegradation

Respirometric tests were conducted in a compost medium at 58°C to evaluate the biodegradability of the materials. The method was adapted from the US standard ASTM D 5988-03⁴³ to determine the aerobic biodegradation of plastic materials after composting. The reference material was a microcrystalline cellulose in powder (Sigma-Aldrich). As the released carbon dioxide (CO₂) is proportional to the percentage of biodegraded substrate, carbon dioxide evolution quantifies the ultimate degradation step (i.e. mineralisation) during which a substance is broken down to its final products.⁴⁴ Beforehand, materials were cut into 1–2 mm bits and carbon contents were measured with an elementary analyser (ThermoQuest NA 2500) in order to set precisely the material dose to 50 mg of carbon into 3 g of compost. Biodegradation tests were carried out in real and mature compost. Distilled water was initially added to the solid media and then regularly added throughout the experiment to maintain the moisture content of the medium at around 80–100%.

3. Results and discussion

3.1 Multiscale structure of PHB/hemp fibre biocomposites

3.1.1 Morphology of composite samples

The morphology of PHB-based composites was assessed by SEM observations of cryofractured surfaces of injected samples (Figure 3). Such observations gave information on two aspects of the impact of the elaboration conditions on the microstructure of the prepared composites. The first one was the dispersion state of the fibres, which is mainly influenced by the shear applied to the melt during extrusion and which could be assessed at low magnification (Figures 3(a) and 3(b)). Dispersion of the hemp fibres within the PHB matrix appeared homogeneous. The absence of fibre clusters was an encouraging indicator of favoured interactions between the matrix and the fibres. However, no significant impact of the processing conditions was picked up. Indeed, the composite prepared under the most severe conditions – that is, using the high-shear profile at 750 rpm (Figure 3(a)) – exhibited a uniform fibre dispersion like the one prepared under the softest conditions – that is, the low-shear profile at 250 rpm (Figure 3(b)) – indicating that the shearing forces induced by all of the chosen processing conditions were sufficient to disperse hemp fibres homogeneously within the polymer matrix.

The second investigated characteristic of the microstructure was the level of interfacial adhesion between the matrix and the fibres, usually influenced by the chemistry of the environment. This was qualitatively assessed by high-magnification observations of the filler/matrix interface. Figures 3(c) and 3(d) show pictures of two composites elaborated with similar processing conditions (high-shear profile, 250 rpm), leading to the longest residence time of the various processing conditions. The pictures revealed dissimilar fibre/matrix adhesion levels whether a compatibiliser had been added or not. The composite prepared with a compatibiliser (Figure 3(d)) exhibited an interphase between the

Figure 3. SEM pictures of PHB/hemp fibre composites elaborated under extreme shears ((a) PHB-H HS750; (b) PHB-H LS250) and with the longest residence time ((c) PHB-H HS250; (d) PHB-C-H HS250)

fibre and the polymer, while gaps could be noticed between the hemp fibres and the matrix when no compatibiliser was employed (Figure 3(c)). This improvement of the interface revealed that this residence time (115 s) was long enough to develop an interphase, thus confirming the efficiency of the compatibiliser. However, all of the compatibilised materials (PHB-C-H) exhibited quite similar dispersion states and interphases, whatever the residence time – that is, whatever the processing conditions employed. Nevertheless, even if those various materials could not be discriminated by SEM analyses, their performances could also be linked to their macromolecular structure and molar masses.

3.1.2 Polymer molar mass

Molar mass analyses have been performed on the injection-moulded biocomposites prepared under various processing conditions and with various compositions (Table 1). The pristine PHB matrix displayed a mass average molar mass (M_w) of

150 700 g/mol and a polydispersity index (PDI) of 2.0. Although the PDI values were weakly impacted by the processing condition, analyses of the M_w provided key information regarding the process. Indeed, all samples underwent a common reduction of the molar mass when the material was submitted to an extra processing step (Table 1). This reduction comprised between –13% for the virgin PHB extruded under the softest conditions (LS250) down to –71% for the PHB-C-H extruded under the most severe processing conditions (HS750). More precisely, when comparing the two screw profiles at a similar screw speed, the M_w drop was stronger for the material processed with the high-shear profile with the low-shear one (Table 1). For instance, the two PHB-H materials processed at 250 rpm reveal M_w equal to 122 200 and 72 200 g/mol with the low-shear and the high-shear profiles, respectively, corresponding to a 19% reduction for the low-shear-processed material and to a 49% reduction for the high-shear-processed one, in comparison with pristine PHB. Those M_w reductions were even more pronounced when the screw speed

Table 1. Thermal and molecular properties of PHB-based materials

Screw profile	Screw speed: rpm	Sample	M_w : kg/mol	PDI	T_g : °C	T_m : °C	X_c : %	T_c : °C	$T_{-5\%}$: °C
Low-shear profile	—	PHB as received	150.7	2.0	4	174	3.6	Und.	280
	250	PHB	130.7	1.6	3	171	9.6	Und.	265
	250	PHB-H	122.2	2.1	0	171	41.8	78	258
	500	PHB-H	90.0	2.0	1	170	37.2	76	258
	750	PHB-H	63.7	2.0	−1	167	37.8	76	254
	250	PHB-C-H	106.5	2.3	1	171	40.7	76	258
	500	PHB-C-H	80.6	2.2	3	170	40.0	74	259
	750	PHB-C-H	69.2	2.0	2	171	41.0	77	259
High-shear profile	250	PHB	115.6	1.6	3	171	16.9	Und.	274
	250	PHB-H	77.2	2.0	3	172	40.0	76	261
	500	PHB-H	59.9	1.9	−1	169	40.9	75	264
	750	PHB-H	47.7	2.0	2	173	39.7	70	262
	250	PHB-C-H	74.9	2.2	3	168	39.6	76	259
	500	PHB-C-H	52.9	2.0	2	168	39.5	75	258
	750	PHB-C-H	43.4	1.9	1	165	40.5	74	257

M_w , mass average molar mass; PDI, polydispersity index; $T_{-5\%}$, degradation onset temperature; T_c , crystallisation temperature; T_g , glass transition temperature; T_m , melting temperature; Und., undetectable; X_c , crystallinity.
Standard deviations were as follows: lower than 1°C for T_g , T_m and T_c values; lower than 0.5°C for $T_{-5\%}$; lower than 2% for X_c ; and lower than 2000 g/mol for M_w .

increased (despite reduced residence times). Indeed, the molar mass decreased from 122 200 g/mol for the PHB-H processed with the low-shear profile down to 63 700 g/mol when the screw speed was increased from 250 up to 750 rpm. This sensitivity to mechanical stresses exhibited by polyester-based materials has already been widely studied.^{45–48} The literature also reports a decisive role played by moisture during extrusion, inducing hydrolysis reactions.⁴⁶ When adding fibres, two phenomena contributed to worsen this M_w drop: (a) PHB hydrolysis was favoured by the presence of water, alcohols and/or acids produced during biomass thermal degradation^{9,49} and (b) melt shear viscosity was higher than without fibre, which resulted in an increase of the internal warming undergone by the thermally sensitive PHB during extrusion. When the compatibiliser was introduced, PHB-C-H exhibited slightly lower M_w compared with the corresponding PHB-H. For instance, the composites processed at 250 rpm under low shear exhibit a molar mass of 122 200 g/mol without the compatibiliser and 106 500 g/mol when 2.4 wt% compatibiliser was added, indicating a 18.9% reduction for PHB-H and 29.3% reduction for PHB-C-H. This increase in the degradation level induced by the presence of the compatibiliser was expected as the composite processing conditions were similar to those of compatibiliser synthesis (transesterification in reactive extrusion with catalyser still in media). The required experimental conditions being fulfilled, the transesterification reaction occurred during the compounding process, thus favouring an extra reduction of the PHB molar mass.

3.1.3 Thermal and crystallisation behaviour

DSC analyses revealed that introducing hemp fibres resulted in two concomitant effects on the crystallisation behaviour of the matrix polymer (Table 1). First, a plasticising effect was noticed as a reduced glass transition temperature (T_g) for PHB-H in comparison with PHB. This T_g reduction was limited (−4°C was the largest T_g shift) and attributed to the production of PHB

oligomers during processing. Indeed, the already reported strong diminution of mass average molar mass indicated a shift of the molar mass distribution towards lower values and the appearance of PHB oligomers, which acted as plasticisers of the PHB matrix. However, considering the strong M_w reduction and the limited T_g shift, the plasticisation by PHB oligomers may have been counterbalanced by a contradictory phenomenon to be identified.

The second effect induced by the introduction of hemp fibres was a strong nucleating effect. Crystallinities of the unfilled extruded matrices were rather low (Table 1), while the biocomposites exhibited much higher X_c values, around 40%. Another clear evidence of the nucleation effect is the T_c shift towards high temperatures (Table 1). Moreover, DSC cooling curves of the unfilled materials hardly exhibited crystallisation regions, between 50 and 0°C in comparison with the biocomposites, which presented clear crystallisation peaks around 75°C. On heating DSC curves, unfilled materials exhibited cold crystallisation peaks, which disappeared totally for the fibre-filled materials. This nucleating effect was already noticed visually during the biocomposite elaboration. At the extruder die, the melt material exhibited some rigidity, whereas the unfilled material flew out of the extruder as a liquid. When the compatibiliser was used, the previously detailed plasticising effect was slightly compensated for by a reduction in the macromolecular mobility induced by improved fibre/matrix interactions and/or better fibre dispersion (Table 1).

Concerning the thermal stability of the materials, the effect of the process was clear, as revealed by the degradation onset ($T_{-5\%}$) provided in Table 1. The raw PHB pellets exhibited a degradation onset of 280°C, which was slightly reduced down to 274°C after one extra extrusion step (high-shear process). The drop was even higher for the low-shear process ($T_{-5\%}$ = 265°C). This sensitisation was caused by the extrusion step, which led to random chain scissions⁵⁰ and creation of crotonate-ending PHB oligomers and

crotonic acid.⁵¹ Such reactions, confirmed by M_w measurements, contributed to reduction in the thermal stability of the material (Figure 4). However, the difference observed between the two extruded polymers may be linked to their crystalline content (16.9% for the high-shear-extruded polymer and 9.6% for the low-shear-extruded one). Indeed, in the highly ordered state found among crystalline phases, macromolecules do not move as easily as in the amorphous phases. Consequently, additional forces must be overcome by the crystalline phase during the transformation towards the unordered fluid state.⁵² This energy difference was maintained after polymer melting and appeared as a difference among degradation onsets. For the fibre-containing materials, the $T_{-5\%}$ reduction was higher than that of the unfilled extruded PHB. Such results confirmed the fibre-induced sensitisation previously discussed when detailing M_w results, the hemp fibres favouring PHB hydrolysis and intensifying the internal warming of the matrix by increasing the melt shear viscosity.

3.2 Mechanical properties

Given the concomitant reductions in both the M_w and thermal performances of the biocomposites when a compatibiliser was introduced and/or when high shear rates were applied during processing, the mechanical performances of the so-prepared materials were expected to be impacted negatively by these two processing parameters.

The effects induced by the processing conditions (screw speed and profile) were rather weak regarding Young's modulus. Indeed, the stiffnesses of the various biocomposites prepared without

Figure 4. Thermogravimetric curves of the biocomposite and of constitutive materials (hemp fibres and PHB) and their first derivatives

compatibiliser (PHB-H) ranged between 304 and 336 MPa, without significant differences (Figure 5). However, the processing conditions had a much clearer impact onto the ultimate properties and notably onto stress at break, which frankly decreased when the screw speed increased, from 33.9 MPa for PHB-H LS250 down to 29.5 MPa for PHB-H LS750. This drop was even higher for the material processed with the high-shear profile. The stress at break was reduced by 49% when the screw speed increased from 250 to 750 rpm for PHB-H under high shear. Concomitantly the ductility of the materials was significantly reduced. Such a trend can be explained as when the processing conditions became more severe, antagonist phenomena occurred on fibre dispersion (positive), possible degradation of fibres (negative) and degradation of polymers (negative).

The introduction of the compatibiliser significantly increased the materials' stiffness, and this load transfer was more noticeable for the materials that stayed in the melt state for a longer time. For instance, Young's modulus increased by 19, 50 and 40% when the compatibiliser was added to PHB-H LS250, PHB-H LS500 and PHB-H LS750, respectively. The higher residence time induced by the low-shear process improved the transfer of the compatibiliser towards the fibre/matrix interface and finally resulted in better compatibilisation mechanisms, as observed when the materials underwent limited shear levels. For higher shear levels, the addition of the compatibiliser had a smaller

Figure 5. Tensile properties of PHB-based biocomposites

effect. Indeed, the stress at break was only slightly impacted, thus indicating that the fibre/matrix interfacial adhesion could still be improved.

Contrary to the clear trends observed for the low-shear-processed materials, where coupling the fibres and the matrix was an efficient way to tune the mechanical performances, the results reported for the high-shear-processed materials were unpredictable. This absence of correlation was attributed to the severe degradation mechanisms induced by the process, which deleted the influence of the compatibiliser.

Figure 6. Water vapour sorption isotherms of biocomposites and fitted curves

3.3 Water sensitivity

In addition to the mechanical performances, an extra aspect of the elaborated biocomposites was investigated, being a key property for the targeted packaging application. Transfer properties have been assessed by evaluating the water vapour permeation of the biocomposites (Figure 6), and by modelling the behaviour of the materials, the water vapour sorption parameters were obtained (Table 2).

The moisture content adsorbed by the materials at equilibrium was around 2 and 3% for all of the composites, whatever the processing conditions and the composition. Similar results were provided by Srubar *et al.*,⁵³ who reported that compatibilising a PHB matrix with lignocellulosic fibres slowed moisture transport into the composites without modifying the equilibrium moisture content. The present equilibrium was linked to the hemp fibres (20 wt% content), which were much more sensitive to water vapour than the PHB matrix, which was reported to sorb at equilibrium less than 0.4 wt% moisture in similar conditions.⁴⁰ Moreover, Christian and Billington⁵⁴ reported moisture contents at equilibrium for PHB/hemp biocomposites of 6.8–8.1% with 40 wt % fibre content, which is consistent with the values of the present work. In addition to the fibre content, the matrix degradation state and the presence of compatibiliser are considered as secondary parameters influencing the final moisture content. Despite the similar equilibrium observed, the observed kinetics of reaching it, assessed by the water vapour diffusivity (D), highly depended on the process used to elaborate the material. Furthermore, similar to what has been observed for the mechanical properties, the water vapour sorption highly depended on the screw profile used for the elaboration. Notably, when the low-shear profile was used, the influences of the screw speed and the composition were clear. Indeed, by improving the dispersion state (through higher screw speed and the recourse to compatibilisation) and the interphase quality (by adding a compatibiliser), the fibres were less percolating and better coated, which limited the diffusion of water vapour among the material. This reduction in the D value observed when a compatibiliser was introduced into the composition (Table 2) was higher for the materials elaborated at a low screw speed – that is, with a longer residence time, enabling better compatibilisation processes. For the composites elaborated under low shear, the D value reduced 66% at 250 rpm, 40% at 500 rpm and 17% at 750 rpm when a compatibiliser was

Table 2. Water vapour sorption fitted parameters obtained at 25°C

Screw speed: rpm		$D: \times 10^{13} \text{ m}^2/\text{s}$		Moisture uptake at equilibrium (percentage of initial weight): %	
		PHB-H	PHB-C-H	PHB-H	PHB-C-H
Low shear rate	250	4.0 (0.06)	1.4 (0.01)	2.7 (0.04)	2.9 (0.03)
	500	3.8 (0.06)	2.3 (0.04)	2.9 (0.04)	2.2 (0.03)
	750	3.3 (0.06)	2.8 (0.04)	3.5 (0.07)	2.0 (0.03)
High shear rate	250	3.9 (0.08)	3.7 (0.08)	3.1 (0.06)	2.8 (0.06)
	500	11.3 (0.19)	4.5 (0.11)	2.6 (0.04)	2.9 (0.07)
	750	11.6 (0.27)	5.3 (0.22)	2.2 (0.05)	3.1 (0.13)

Root mean square error values are indicated in parentheses

introduced. For the composites elaborated under high shear, the water vapour diffusions were much higher than when the low-shear profile was used during the elaboration process. The whole set of resulting D values obtained by the various processing routes ranged from 1.4 to $11.6 \times 10^{-13} \text{ m}^2/\text{s}$, enabling the application as packaging materials for various food products.

3.4 Biodegradability

The end of life of the elaborated biocomposites has been assessed by respirometric tests held in compost conditions. Biodegradation patterns of two biocomposites (PHB-H LS250 and PHB-C-H HS750) are presented in Figure 7, in addition to the one related to the pure PHB matrix. The well-known ‘priming effect’ occurred here and made final biodegradation levels exceed 100%, without any effect on the materials’ biodegradation ranking.⁵⁵ The pure PHB material degraded faster than the reference (cellulose). Indeed, after 27 d incubation, PHB exhibited around 80% biodegradation, while the reference underwent only 60% biodegradation. Moreover, the addition of fibres did not impact negatively this high biodegradability, as indicated by the slightly higher biodegradation level exhibited by PHB-H after 92 incubation days (Figure 7). This result is consistent with the literature,⁵⁶ which reveals that the biodegradation of biocomposites containing lignocellulosic fibres is mainly driven by the ability of the matrix to biodegrade. As far as PHAs are concerned, the introduction of natural fibres was reported to improve the biodegradability of the composite in comparison with that of the pure matrix⁷ by creating additional pathways for moisture, enzymatic and microbial ingress, leading to fibre swelling, increased damage at the fibre/matrix interface and cracking, further accelerating degradation.⁵⁷

Introducing fibres and the compatibiliser into the PHB matrix resulted in the most severe M_w reduction and probably the highest PHB oligomer content. However, there was no statistical difference with the two other PHB-based materials in terms of biodegradation

Figure 7. Biodegradation patterns of PHB-based materials in compost conditions

patterns (Figure 7), contrary to what has been reported by Hong *et al.*⁵⁸ The authors showed that the presence of PHB oligomers increased the biodegradation rate of PHB.⁵⁸ All in all, whatever the composition and processing conditions, the biodegradation of the PHB-based biocomposites was revealed to be fast and high.

4. Conclusion

PHA/hemp fibre biocomposites have been successfully prepared by reactive extrusion with various processing conditions, namely, variable shear rates (screw profile and speed), applied during the extrusion step and variable formulation (possible use of a compatibiliser). Structural analyses revealed homogeneous fibre dispersion states and the development of an interphase when a compatibiliser was introduced. Introducing fibres resulted in two main effects concerning the processed matrix. First, the crystallisation kinetics of the polymer strongly improved and made the usual recourse to nucleating agents unnecessary. Second, the polymer matrix underwent some thermal sensitisation. Indeed, in the case of severe processing conditions, the fibre dispersion state was improved but severe degradation reactions occurred at the same time, hindering the possible improvement provided by the compatibiliser. For the materials processed under a low shear rate, mechanical performances were preserved and even improved when the compatibiliser was added. This degradation issue made the recourse to low-shear screw profiles advisable for the elaboration of similar PHB composites containing lignocellulosic fibres. All in all, the introduction of hemp fibres into a bio-based and biodegradable matrix with an original compatibilisation route led to the composites exhibiting water vapour diffusivities ranging from 10^{-13} to $10^{-12} \text{ m}^2/\text{s}$, which are targeted values for various food packaging materials, fitting various food products’ requirements. Moreover, the maintained mechanical performances, the maintained biodegradability and the significative cost reduction are encouraging points for spreading the use of such biocomposites for food packaging.

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