Urban parks and gardens green waste: A valuable resource for the production of fillers for biocomposites applications

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Abstract

Urban parks and gardens green waste constitute a low-cost and highly available lignocellulosic-rich resource, that is currently treated in composting or anaerobic digestion processes. The present work investigated for the first time the potential of using urban green waste as raw resource for the production of lignocellulosic fillers by dry fractionation (combination of sorting and grinding processes). Five fractions of lignocellulosic fillers with controlled composition were produced : a branches-rich fraction, a grasses-rich fraction, a leaves-rich fraction, and two fractions constituted of a mixture of constituents. All the fractions were ground to reach an average median diameter around 100 µm. The reinforcing effect of each fraction was investigated and compared to that of the sample as a whole. Biocomposites based on a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) as matrix were produced by melt extrusion, with filler contents up to 30 wt%. It was shown that the branches-rich fraction displayed the best reinforcing effect (e.g. stress at break of 37 ± 1 MPa for a filler content of 15 wt%, similar to that of the neat matrix) whereas the grasses-rich fraction slightly degraded the overall mechanical performance (e.g. stress at break of 33.5 ± 1.5 MPa for a filler content of 15 wt%). The dry fractionation and formulation steps could be thus

adapted depending on the targeted application, e.g. by choosing to use the whole urban green waste resource, or to remove grasses, or to keep only branches.

Keywords : Urban green waste; dry fractionation; lignocellulosic fillers; biocomposites; biocomposites

1- Introduction

The biodegradable fraction of green garden and park waste is considered as a high volume resource flow classified in the European catalogue with the waste code 200201 (Eades et al., 2020). In the two last decades, the generation of urban green waste has raised due to the increase of worldwide urban green areas, which are considered as local ecosystems contributing substantially to the urban life quality (Eades et al., 2020; Shi et al., 2013). As an example of the increased availability of green waste, Boldrin et al. (Boldrin et al., 2011) indicated that the generation of garden waste in Denmark was 143 kg.person^{-1}.year^{-1} in 2006 against only 67 kg.person^{-1}.year^{-1} in 1994. Many studies have been carried out around the world to evaluate the availability of urban green waste to assess its potential as biomass resource. In Europe, the average quantity of urban green waste is around 150 kg.person^{-1}.year^{-1}, e.g. 165 kg.person^{-1}.year^{-1} in France in 2006 (Som et al., 2009), 143 kg.person^{-1}.year^{-1} in Denmark in 2006 (Boldrin et al., 2011) and 288 kg.garden^{-1}.year^{-1} in England in 2020 (Eades et al., 2020). At the international level, a greater variation is observed depending on region's climate: 72 kg.person^{-1}.year^{-1} in USA in 2008 (MacFarlane, 2009), 150 kg.person^{-1}.year^{-1} in Australia (Greater Brisbane) in 2012 (Hla and Roberts, 2015) or 120 kg.person^{-1}.year^{-1} in China (Beijing municipalities) in 2006 (Shi et al., 2013).

The green park and garden waste consists of a mixture of organic materials such as grass clippings, hedge prunings, leaves and bark, flowers, branches, twigs and other woody

material, and inorganic fractions such as soil and stones, and not to mention foreign objects (e.g. paper and cardboard, glass, cigarette butts or cans). It can however be considered as a lignocellulosic biomass whose composition varies according to the season, the location and also the waste management strategies (Bary et al., 2005; Boldrin and Christensen, 2010; Hanc et al., 2011). There are two main technologies of green waste management, i.e. composting by aerobic digestion (Reyes-Torres et al., 2018; Som et al., 2009; Vandecasteele et al., 2016) and bioenergy production by anaerobic digestion (Hla and Roberts, 2015; Kabir et al., 2015; Pick et al., 2012). Briquetting, i.e. compaction of residues into a product of higher density, production of bioethanol and production of bioplastics are other possible management strategies (Bhange et al., 2014).

In the recent years, the development of biocomposites made of biodegradable polymers from renewable resources and loaded with lignocellulosic fillers derived from organic solid waste and residues appeared as a sustainable solution to the reduction of our dependence on fossil resources, the reduction of environmental pollution generated by non-biodegradable plastics, while giving value to a waste, favoring a cradle to cradle concept and promoting the circular economy (Väisänen et al., 2016). However, the up-cycling of urban green park and garden waste for the production of reinforcing fillers has never been investigated. Among the different commercially available biopolymers, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is one of the very interesting family of polyhydroxyalcanoates bacterial polyester family. They are bio-sourced thermoplastic copolymers, biodegradable in natural conditions, both in soil and water. The development of the mixed microbial culture technology has shown promising prospects, as it is based on open systems that do not require sterile conditions and allow the production of PHBV from heterogeneous bio-waste feedstocks, including agricultural or urban bio-waste (e.g. excess sludge from treatment of urban wastewater) as explored in the European project RESURBIS. One main limitation for its large use at the

industrial level is its high cost that still exceeds 5€/kg (Bugnicourt et al., 2014). The use of a sustainable, inexpensive and rigid fillers allows decreasing the overall cost of the material while decreasing its overall environmental impact (David et al., 2020), without affecting its biodegradability (David et al., 2020). Furthermore, the incorporation of fillers stemming from lignocellulosic residues allowed maintaining mechanical performance and modulating barrier properties (Berthet et al., 2015; Lammi et al., 2018; Sánchez-Safont et al., 2018).

In this context, the objective of the present work was to assess the potential of eco-converting urban green park and garden waste into fillers for biocomposites applications. This resource being an heterogeneous mixture of organic and inorganic fractions, the reinforcing effect of each fraction constituting the raw material was investigated in such a way to able to understand the reinforcing effect of the overall resource, and eventually conclude on the pertinence to sort or not the resource before its conversion into fillers. For that purpose, the resource was manually sorted and five valuable fractions with controlled size and composition were produced by successive dry grinding. A representative fraction of the overall sample was reconstituted and a commercial wood flour was used as reference. Each fraction was incorporated up to 30 wt% in a PHBV matrix by melt extrusion. Thermal and mechanical properties of resulting composites were discussed in relation to the structure of materials and the composition of the fillers.

2- Experimental

2-1. Materials

Park and garden waste was supplied by the RGS NORDIC composting facility (Copenhagen – Selinevej). A sample batch, fully representative of this kind of urban waste, was collected in July 2017. The water content of the raw matter was around 50 % of wet weight basis (Boldrin and Christensen, 2010). Just after reception, the sample was sun-dried for a month until

reaching a water content of approximatively 10 wt%. A commercial spruce wood flour (apparent median diameter d_{50} in the range 70 – 150 µm, noted W) was supplied by AFT Plasturgie Company and used as reference in the present study. Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) containing a valerate content of around 1 – 3 mol% (molar fraction) was purchased from Natureplast (PHI 002 grade).

2-2. Preparation and characterization of lignocellulosic fillers from green parks and gardens waste

2-2.1 Sorting process

The raw biomass was manually sorted in order to separate the different fractions. A first manual sorting was done to remove foreign objects such as sponges, metallic cans, plastic bags, glasses, papers and boards. In a second step, big pieces of branches (noted B), leaves (noted L), grass (noted G) were manually separated from a mixture of pieces displaying a size lower than 1 – 2 cm. Then, this latter mixture was sieved on a 4.0 mm grid to separate a heterogeneous medium fraction (noted MF) from a heterogeneous fine fraction (noted FF). Five fractions were thus used for the production of fillers: branches (B), leaves (L), grass (G), a heterogeneous medium fraction (MF) and a heterogeneous fine fraction (FF).

2-2.2 Production of fillers by dry grinding

The five sorted fractions (B, L, G, MF and FF) were dried at 60 °C overnight before grinding. The same grinding protocol was applied to the five fractions. The different fractions were first reduced using a cutting mill type SM100 (Retsch, Germany) with a first passage on a 4.0 mm sieve and a second one on a 1.0 mm sieve. In the case of the B fraction, a preliminary cut milling step using a 10.0 mm sieve was necessary due to the presence of large pieces of branches. Thereafter, the five reduced fractions were dried at 60 °C before being ground again on an impact mill type 100UPZ (Hosokawa Alpine, Germany) operating at 18,000 rpm and

equipped with a 0.3 mm sieve (trapezoid holes), an 8-teeth rotor and an output recovery cyclone.

2-2.3 Characterization of fillers produced from urban parks and gardens green waste

The biochemical composition of lignocellulosic fillers was determined using adapted methods from TAPPI standards (Technical Association of the Pulp and Paper Industry, 2002), (Technical Association of the Pulp and Paper Industry, n.d.), (Technical Association of the Pulp and Paper Industry, 2015). The thermal stability was evaluated by thermogravimetric analysis (TGA) using a Mettler TGA2 apparatus (Mettler Toledo, USA). Thermal analysis performed from 30°C up to 900°C at 10°C.min^{-1} under nitrogen atmosphere assessed: the temperature of main thermal degradation (T_{peak}) was measured from the maximum value of weight loss derivative and the onset temperature (T_{onset}) was taken at the beginning of the derivative weight loss degradation peak, when derivative weight reached an absolute value of 0.1 %.°C^{-1}. The particle size distributions of fillers were determined by laser light scattering diffraction using a Mastersizer 2000 (Malvern Instruments Ltd., United Kingdom), where the particles were dispersed in ethanol 95 % (v/v). The morphology was qualitatively observed by scanning electron microscopy using a Desktop SEM Phenom ProX (ThermoFisher Scientific, USA). The true density was determined using a gas pycnometer Ultrapycnometer 1000 (Quantachrome Instuments, USA) at a pressure about 40 kPa under nitrogen gas flow. The color was measured using a chroma-meter CR 400 – CR 410 (Konica Minolta, Japan) in the L*, a*, b* color system.

2-3. Preparation and characterization of PHBV-based biocomposites

2-3.1 Compounding and shaping processes

The compounds constituted of PHBV pellets and different fractions of fillers were obtained by extrusion melting, after drying at 60°C overnight, using a co-rotative Eurolab twin-screw extruder (Thermo Fischer Scientific, USA) with a L/D = 40 and a screw diameter of 16 mm.

The temperature varied from the feeding to the die according to the following profile: 160 – 180 – 180 – 170 – 170 – 170 – 160 – 160 – 150 – 150 °C. The total flow rate was 1.5 $kg.h^{-1}$ and the screws rotation speed was 500 rpm. The end barrel was equipped with a rod die (3.0 mm in diameter) and the extruded compound was cooled into air before being pelletized. The fillers content increased from 5 up to 30 wt%.

The extruded compounds were injection molded after drying at 60 °C overnight. Small tensile test specimens (ISO 527-2 1BA) were produced with a small injection molding device IM15 (Zamak Mercator, Poland). The compounds were heated at 180 °C for 160 s in the heating chamber. The mold temperature was held constant at 30 °C and the injection pressure was set at 3 bars.

2-3.2 Thermal properties

The thermal stability of biocomposites was evaluated as described previously for fillers by TGA. Crystallization and melting temperatures, as well as crystallinity, were determined by differential scanning calorimetry (DSC) using a Q200 thermo-modulated calorimeter (TA Instruments, USA) operating under an inert atmosphere (nitrogen flow = 50 $ml.min^{-1}$). A heat-cool-heat cycle (heating from -20 °C to 190 °C, then cooling down to 0 °C and finally heating again up to 190 °C at a constant rate of 10 $°C.min^{-1}$) was performed to investigate the crystallization behavior of "as produced" composites as well as the intrinsic crystallization behavior after having erased the thermal history of materials. The melt crystallization temperature (T_c) was determined from the top of the exothermic peak during the cooling ramp, the melting temperatures during the first (T_{m1}) and the second (T_{m2}) heating ramps were respectively defined from the top of the endothermic peaks during the first and the second heating ramps and the melting enthalpy, ΔH_m was calculated from the area under the peak of melting temperature. The crystallinity χ was calculated by Equation 1.

$$\chi = \frac{\Delta Hm}{X \times \Delta Hm^*}$$

where ΔHm was the melting enthalpy ($J.g^{-1}$), X the fraction of polymer present in the formulation and ΔHm* = 146 $J.g^{-1}$ (Barham et al., 1984). It is worth noting that the use of DSC for the measurement of crystallinity in PHBV-based biocomposites needs to be approached with much care (Laycock et al., 2014).

2-3.3 Mechanical testing

Young modulus and ultimate tensile stress and strain were determined at room temperature by uniaxial tensile tests on dog-bone specimens (ISO 527-2 1BA) using a tensile testing machine Instron 3345 (Instron, USA) equipped with a load cell of 5 kN. The elongation speed was set at 10 $mm.min^{-1}$. Five measurements were done for each formulation. Prior to tensile testing, samples were conditioned at room temperature at 0 % RH over anhydrous silica gel during 15 days to stabilize samples. Statistical analyses were carried out using XLStat package (Addinsoft). For data of strength at break, conditions of normality and homoscedasticity were fulfilled, allowing to apply the Fisher's test. For data of strain at break and Young's modulus, the non-parametric Dunn's multiple comparison test was applied. Significance was accepted at probability $P < 0.05$.

2-3.4 SEM observations of film cross-sections

The observation of composites cross-sections after mechanical testing was carried out by Scanning Electron Microscopy using a Desktop SEM Phenom ProX (ThermoFisher Scientific, USA) after sputter-coated with gold.

3- Results and Discussion

3-1 Production of fillers from urban green parks and gardens waste

3-1.1 Composition of the raw resource

To evaluate and understand the reinforcing effect of fillers produced from parks and gardens waste, the first step was to identify the different fractions constituting the raw resource. For

that purpose, a manual protocol of sorting was applied (Figure 1). A first fraction was identified, corresponding to the unusable fraction (13 wt%), which contained a high quantity of soil, and also some stones and foreign objects such as paper and cardboard, glass, cigarette butts and cans. The significant amount of soil particles in urban gardens and parks waste was previously highlighted, and is known to be all the more important during summer (Boldrin and Christensen, 2010).

Three valuable fractions were clearly identified: (i) branches and pruning wood (23 wt% d.b., noted B), (ii) leaves (5 wt% d.b., noted L) and (iii) grasses and mosses (3 wt% d.b., noted G). After having manually removed the large pieces of these three organic fractions, a mixture of smaller particles was obtained. This latter (56 wt% d.b.) was sieved on a 4.0 mm grid to separate a coarse fraction, i.e. particles having dimensions higher than 4.0 mm (9 wt% d.b., noted MF), from a fine fraction, i.e. particles that passed through the sieve (47 wt% d.b., noted FF). The fine fraction contained small pieces of organic matter and a large amount of soil. The relative quantities of each fraction were estimated for a dry sample batch of 21 kg.

The second step of the dry fractionation process corresponded to the dry grinding of sorted fractions, as described in the Figure 1. The same grinding protocol was applied for the five fractions, i.e. branches-rich (B), leaves-rich (L), grasses-rich (G), medium (MF) and fine (FF) fractions. After the last grinding step, a representative fraction (RF) was reconstituted from the five valuable above mentioned fractions in order to represent the urban solid waste in the whole. This representative fraction contained 26 wt% of B, 6 wt% of L, 4 wt% of G, 10 wt% of MF and 54 wt% of FF.

The intrinsic fiber characteristics of interest when considering their use as filler in composite materials are mainly their composition, having an effect on their intrinsic mechanical and surface properties, density, morphology and thermal stability (Faruk et al., 2012). That is why these parameters will be carefully studied in the following paragraphs.

Figure 1.

3-1.2. Effect of dry fractionation on the biochemical composition of lignocellulosic fillers issued from urban green parks and gardens waste

The dry matter of the different fractions produced from urban green park and garden waste was cellulose, hemicellulose and lignin, showing that they were mostly constituted of lignocellulosic compounds (Figure 2). Cellulose, hemicellulose and lignin are the three major components of lignocellulosic biomass (Wang et al., 2017). In addition to these three major components, extractives and inorganic ashes were also present in a low amount in lignocellulosic biomass as non-structural components. Wood biomass is known to contain much higher amounts of the three main components (> 90 %), while agricultural and herbaceous biomass contain more extractives and ashes. As an example, Komilis and Ham showed that grasses and yard waste presented the highest content of cellulose, i.e. 39.7 % d.b. and 27.2 % d.b. respectively, whereas branches and leaves were enriched in lignin, with values of 42.9 % d.b. and 33.9 % d.b., respectively (Komilis and Ham, 2003). The biochemical composition of the produced lignocellulosic fillers was here in agreement with the literature, although some values were slightly below due to high ashes and extractives contents (Howard et al., 2003; Malherbe and Cloete, 2002; Sánchez, 2009). The high ashes content, in particular for the grasses-rich (G), was due to the sampling during which a large amount of soil was stuck to the mulched green waste, as previously observed (Boldrin and Christensen, 2010).

More precisely, cellulose content ranged between 21 % to 37 % d.b. and increased in the order 21 % (L) < 22 % (MF) < 24 % (G) < 25 % (RF) < 26 % (FF) < 30 % (B) < 37 % (W). Ashes content ranged between 2 % to 25 % d.b. and decreased in the order 25 % (FF) > 21 % (RF) > 20 % (G) > 16 % (L) > 14 % (MF) > 7 % (B) > 2 % (W). And extractives content

ranged between 10 % to 20 % d.b. and increased in the order 10 % (B) < 11 % (FF) < 12 % (RF) < 13 % (W) < 15 % (G) < 19 % (MF) < 20 % (L). The commercial wood (noted W) used as reference, was a spruce wood flour and presented a cellulose content of 37 %, a hemicellulose content of 28 % and a lignin content of 20 %, slightly lower values than literature ones which are respectively 45 – 50 %, 21 – 30 % and 24 - 28 % (Fuqua et al., 2012). The chemical composition of branches (B) was very close to the wood benchmark sample (W). Its concentration in holocellulose (α-cellulose and hemicellulose) was the highest, with a value of 60 % d.b., and the extractives (10 % d.b.) and the ashes (7 % d.b.) contents were the lowest. On the opposite, the L fraction was more concentrated in extractives (20 % d.b.) and lignin (30 % d.b.). The chemical composition of the G fraction was an intermediate between B and L fractions except in ashes content (20 % d.b.), due to the previously mentioned presence of soil particles stuck on mulched grasses. The MF was largely constituted of small leaves particles, as confirmed the biochemical composition close to the L chemical composition. Finally, the FF was characterized by high lignin (30 % d.b.) and ashes (25 % d.b.) contents. The presence of a large amount of soil particles in FF (explaining the high ashes content) was due to the manual sorting process allowing the fine soil particles to pass through the used sieve. The presence of soil particles in the raw resource, and consequently in the grasses-rich, RF and FF fractions could play a nucleating effect in the PHBV polymer matrix.

Based on the fact that fiber mechanical properties can be related to their biochemical composition (Berthet et al., 2015), observed differences are supposed to have a significant impact on the final mechanical performance of biocomposites. The tensile strength was shown to evolve exponentially with cellulose content, and inversely exponentially with lignin content, while no clear relationship between Young's modulus and composition was recognizable (Berthet et al., 2015). It could be thus expected that the branches-rich fraction,

274 containing the highest cellulose content (after the wood benchmark sample), would present
275 the best reinforcing effect.
276 **Figure 2.**
277
278 **3-1.3 Impact of dry fractionation on thermal properties, color, density and morphology**
279 **of lignocellulosic fillers issued from urban green parks and gardens waste**
280 Thermal stability of fillers is an important criterion since they will be submitted to heating
281 cycles during the processing of biocomposites, but also during the service use or end-of-life
282 treatment of materials. The different fractions of fillers presented similar thermal behavior.
283 The derivatives curves obtained under nitrogen atmosphere showed a first peak around 100°C
284 corresponding to the water release and one major wide peak of derivative weight (from 200°C
285 up to 500°C) due to the thermal degradation of main organic compounds present in
286 lignocellulosic fibers, *i. e.* cellulose, hemicellulose and lignin. This wide peak could be
287 deconvoluted into a first fine and intense peak around 320°C and a second one, wider and less
288 intense, around 400°C. Hemicellulose is known to be the first compound to thermally degrade
289 between 225°C and 325°C, then the cellulose between 250°C and 400°C, while the
290 degradation of lignin occurs on a wide temperature range (100 – 900°C) (Pang et al., 2014).
291 Different degradation profiles were observed for the different fractions considered in the
292 present study (Figure 3 and Table 1). This was due to previously described differences in
293 biochemical compositions (Wang et al., 2017). The branches-rich fraction was characterized
294 by the most intense degradation peak, owing to its highest holocellulose content. On the other
295 hand, the derivative curve of the leaves-rich fraction demonstrated a significant shoulder
296 around 400°C, characteristic of a high lignin content. The onset degradation temperature was
297 also slightly impacted by the biochemical composition (Table 1). The T_{onset} was around 238°C
298 ± 5°C; 229°C for (L) < 232°C for (MF) < 236°C for (B) < 239°C for (RF) < 241°C for (W) <

242°C for (G) < 245°C for (FF). As expected the L and the MF presented the lowest T_{onset} due to the highest extractives and lignin contents, then the degradation of B and W which presented the highest hemicellulose content, and finally the RF, G and FF which were impacted by a large amount of inorganic matter. Based on these results, it should be pointed that thermal degradation of all produced lignocellulosic fillers occurred at temperatures higher than the melt processing temperature of the PHBV matrix, i.e. 180 °C.

Figure 3.

The different fillers fractions were also characterized in terms of color, which can be an important criterion for some applications and consumer acceptability (Table 1). The wood (W) and branches (B) fractions appeared beige and lighter while the others were brown and darker. These visual observations were quantitatively confirmed by the measurements of the colorimetric parameters L*, a* and b*, with L* characterizing the lightness from black to white, a* the range of color from green to red, and b* the range color from blue to yellow. W and B fractions presented higher L* (L^*_B = 52 and L^*_W = 69) and b* values (b^*_B = 14 and b^*_W = 20), giving the samples lighter and more yellow than the other ones. The other fractions presented similar color and similar L*, a* and b* values, except the G which appeared more green with an a* value of 1.65. The darker and browner color of G, FF and RF could be due to the presence of a high quantity of soil, while for L and MF, it was due to high lignin content.

Table 1.

As regards the true density, parameter impacting the final weight of materials, a significant difference was noticed according to the content of inorganic compounds (Table 2). The fillers fractions which contained a large amount of inorganic matter, i.e. G, FF and RF, had a higher true density value. It was respectively 1.65, 1.78 and 1.68 $g.cm^{-3}$ for G, FF and RF. The B, L, MF and W presented lower true density values, which were all around 1.55-1.56 $g.cm^{-3}$. It is

worth noting that the biocomposites were formulated by considering polymer/filler weight ratios, which means that for a given filler weight content, the B-, L-, MF- and W-based biocomposites had slightly higher filler volume contents. For example, PHBV-15wt%B formulations corresponded to PHBV-9.6 vol%B, while PHBV-15wt%FF to PHBV-8.4vol%FF.

The dry fractionation protocol was applied to obtain similar size distributions and median apparent diameters for the different fillers fractions, so that their reinforcing effect could be compared. All the fillers fractions presented a volume-based size distribution characterized by two particles populations of particles, i.e. a first population with a d_{50} centered around 10-20 µm and a second one centered around 100-200 µm corresponding to the main peak of size distribution (Figure 4-b). d_{50} in volume were respectively 138, 170, 119 and 90 µm for B, L, G and FF (Table 2). In spite of the same applied grinding process, d_{50} values were not exactly the same for all fillers fractions. In the case of FF, the low d_{50} value was explained by by the presence of a large amount of fine particles of soil in the fraction. On the other hand, the L fraction showed a higher d_{50} value (170 µm). This result could be explained by a high lignin content, which has been reported as the most recalcitrant component of the plant cell wall and the most resistant to chemical, biological and mechanical degradation (Hendricks and Zeeman, 2009; Barakat et al., 2013; Monlau et al., 2012). When considering the number-based size distribution, the apparent median diameter was shifted to very low values (d_{50} around 5 µm) (Figure 4-b and Table 2), due to a large quantity of fine particles inside the samples, even if they represented only a very little fraction in the total volume occupied by the whole sample. Filler morphology was qualitatively assessed by SEM (Figure 4-a). Visually, very fine particles were observed in the different fillers fractions, in agreement with laser granulometry results. However, these very fine particles seemed more numerous and whiter in the G, FF and RF, due to the presence of a large amount of soil in these fractions.

349 Bigger particles (100-200 µm) were also observed in all fractions, mainly for B and W which
350 presented elongated bigger particles. Considering these characteristics, all the fractions turn
351 out to be successfully usable as fillers in a polymeric matrix, however, the B and W fractions
352 being preferable in reason of their elongated shape.

353 **Figure 4 & Table 2.**

354 **3-2 Biocomposites reinforced by fillers issued from urban green parks and gardens**
355 **waste**

356 **3-2.1 Melting and crystallization behavior**

357 DSC was used to assess the influence of produced fillers from urban green park and garden
358 waste on the melting and the crystallization behavior of injection-molded PHBV-based
359 biocomposites. All samples were characterized by one single endothermic melting peak
360 during the heating ramp (T_{m2} = 175 °C), one single exothermic peak during the cooling ramp
361 (T_c = 126 °C) and presented a crystallinity degree X_2 of 69 ± 1 % (Table 2). This high
362 crystallinity was ascribed to the low valerate content and to the presence of boron nitride as
363 nucleating agent in the commercial grade of PHBV. The addition of fillers had no significant
364 impact on the crystallinity of materials. This indicated that the mobility of polymer chains and
365 their ability to crystallize was not affected by the presence of fillers. As previously reported
366 for cellulose, this could be explained by the presence of boron nitride that masked potential
367 nucleating or anti-nucleating effect of lignocellulosic fillers (David et al., 2019).
368 Regarding the melting temperature, it was not significantly impacted by the addition of fillers
369 (Freire et al., 2008; Pasquini et al., 2008), even for high filler contents, which led to suppose
370 that the polymer molecular weight remained also unchanged. The crystallization temperature
371 slightly decreased with the addition of fillers, this effect being more pronounced for the
372 grasses fraction. This suggested that the presence of grasses or compounds released by grasses

373 during the processing inhibited the initiation of the crystallization growth of the surrounding
374 matrix.
375 On the whole, the DSC data showed that the PHBV thermal characteristics were basically
376 maintained, indicating that biocomposites could be subjected to the same thermos-mechanical
377 processing conditions.

378 **3-2.2 Thermal stability**

379 The thermal stability was investigated by thermogravimetric analysis under nitrogen
380 atmosphere (Table 2). The PHBV thermogram displayed one main degradation peak with a
381 T_{onset} of 270.5 ± 0.5 °C and a T_{peak} of 298.3 ± 0.3 °C. PHBV belongs to the polyesters family
382 and therefore it is known to be very sensitive towards the temperature, especially in presence
383 of moisture further promotes hydrolytic degradation. Different mechanisms have been
384 proposed in literature, the random chain scission by cis-elimination being considered as the
385 general pathway of PHBV thermal degradation (Grassie et al., 1984; Liu et al., 2009).
386 Biocomposites presented a first intense and narrow degradation step around 270-300 °C
387 corresponding to the degradation of the PHBV matrix and a second weaker and wider weight
388 loss up to 400 °C corresponding to the filler degradation. This second weight loss was
389 logically more pronounced for higher filler content. On the whole, the fillers introduction
390 reduced the thermal stability, with a thermal degradation beginning at lower temperatures and
391 occurring in a wider temperature range as compared to the PHBV matrix (Table 2). Wood-
392 filled biocomposites appeared to be the most thermally stable while the grasses-filled
393 biocomposites were the least. The decrease of thermal stability did not follow a simple rule of
394 mixture according to the respective content of PHBV and fillers. If a simple rule of mixture
395 was applied, the L-filled biocomposites should have degraded first, then the MF-filled
396 biocomposites, etc. Such an unexpected behavior may be due to thermal degradation reactions
397 favored by the presence of fillers. The water content being similar for all the filler fractions

398 (around 5 – 6 wt%), it was assumed that extractives were responsible for accelerated thermal
399 degradations (Shebani et al., 2009; Sheshmani et al., 2012). The extractives content ranged
400 between 10 % to 20 % d.b. and increased in the order 10 % (B) < 11 % (FF) < 12 % (RF) <
401 13 % (W) < 15 % (G) < 19 % (MF) < 20 % (L). Although extractives contribute only a few
402 percent to the composition of lignocellulosic biomass, they have significant influence on its
403 properties (Ashori and Nourbakhsh, 2010). Regarding our results in terms of thermal
404 degradation, the amount and the type of extractives seemed responsible for accelerated
405 thermal degradation of biocomposites.

406 **3-2.3 Mechanical properties**

407 Typical curves of the stress vs. the strain highlighted a rigid and slightly brittle behavior for
408 all PHBV-based materials, including the neat matrix (Figure 5). It is worth noticed that the
409 elongation at break measured for the matrix used in the present study was higher (4.5 %) than
410 in the work of Berthet et al. (Berthet et al., 2015) (2.3 %) or David et al. (David et al., 2019)
411 (2.4 %) whereas the same grade was used (PHI002 grade from Natureplast). This could be
412 due to differences between batches, or more probably, to the fact that measured were here
413 carried out on massive samples (thickness of 2 mm) and not on films.

414 **Figure 5.**

415 The introduction of lignocellulosic fillers led to an increased brittleness of materials, as
416 revealed by the significant decrease in both the strain and stress at break. Except for the B
417 fraction, the degradation of ultimate tensile properties was all the more important for
418 increasing filler contents (Figure 5), as already reported in literature for short lignocellulosic
419 fibers/PHBV composites (Avella et al., 2000; Berthet et al., 2015; Dufresne et al., 2003). In
420 the case of the B fraction, ultimate properties were almost preserved, with no negative impact
421 of increasing filler content. The accentuation of the brittleness of materials was more
422 pronounced for L, G, MF, FF and RF fractions. It seems that the behaviour of the

representative fraction (RF) of the whole resource was governed by the presence of grasses, even in low quantity. However, it is worth noting that the decrease in the elongation at break was not so pronounced as previously described for other types of lignocellulosic fillers (e.g. decrease of more than 60 % induced by the addition of 30 wt% of wheat straw fibres in the work on Berthet et al. (Berthet et al., 2015). Moreover, as largely described in the literature, the decrease in ultimate tensile properties induced by the presence of lignocellulosic fillers could be mainly ascribed to a lack of adhesion between the hydrophobic matrix and hydrophilic fibers. This assumption was supported by SEM observations of PHBV-based biocomposites cross-sections (Figure 6) displaying pull-outs and interfacial gaps between the matrix and the fibers.

Except for G and RF, the Young's modulus was slightly increased by the addition of lignocellulosic fillers (Figure 5). This increase was all the more pronounced for increasing filler contents. This was in agreement with most results obtained for short lignocellulosic fibres based biocomposites. In the case of G and RF, the Young's modulus remained constant, likely due to lower rigidity of grasses particles.

Figure 6.

4- Conclusions

In the case of the urban parks and gardens green waste considered in the present study, it was shown that up to 87 wt% (d.b.) of the raw resource could be eco-converted in valuable reinforcing fillers for biocomposites applications. More precisely, five valuable fractions of lignocellulosic fillers with controlled composition and morphology were produced using a dry fractionation process : a branches-rich fraction (23 wt%), a leaves-rich fraction (5 wt%), a grasses-rich fraction (3 wt%), a medium size fraction containing particles which were retained by a 4.0 mm sieve (9 wt%), and a fine fraction (47 wt%) containing the smallest particles

(lower than 4.0 mm) and a large amount of soil particles which passed through the sieve. The unusable fraction (13 wt%) comprised soil, stones and foreign objects (e.g. paper and cardboard, glass, cigarette butts and cans).

PHBV-based biocomposites were developed using as fillers the different sorted fractions, as well as a representative fraction of the whole resource and a wood flour as benchmark. Filler contents up to 30 wt% were used. Biocomposites with a very nice visual aspect and acceptable mechanical performance were obtained whatever the fraction used (Young's modulus ranging from 2 to 3 GPa, tensile strength ranging from 30.9 to 38.8 MPa than and strain at break ranging from 3 to 4.8 %). This study thus demonstrated that urban parks and gardens green waste represents a very interesting raw resource for the development of biocomposites, allowing to decrease the overall cost and the environmental impact of PHBV-based materials, while up-cycling solid urban waste. Other polymer matrices could of course be used. Some little but significant differences were however observed depending on the biochemical composition of fillers. It was shown that the branches fraction displayed the best reinforcing effect, whereas the grasses fraction significantly degraded the overall mechanical performance.

In conclusion, the development of biodegradable composites from urban parks and gardens green waste integrating a biorefinery concept would allow to add a usage step as valuable materials in place of polluting and non-biodegradable plastics before their final disposal, e.g. by anaerobic digestion for composting or bioenergy production. Depending on the overall targeted performance of materials, the whole sample could be used, including residues of soil or not. Furthermore, given the technical possibility to sort this heterogenous resource using dry fractionation processes, it could also be advised to remove the grasses fraction from urban green waste, and/or to keep only branches.

Regarding the applications, biocomposites based on PHBV as matrix and lignocellulosic fillers produced from simple dry fractionation of urban green waste could be used for injection moulding or thermoforming applications. Applications where full biodegradability in natural conditions is needed are the most relevant, e.g. for horticultural and agricultural purposes. Applications in the automotive sector could also be targeted. The up-scaling of the sorting step should now be investigated to consider industrial applications.

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641 Figure captions

642 Figure 1. Sorting process of lignocellulosic fillers issued from park and garden waste.

643 Figure 2. Biochemical composition of lignocellulosic fillers issued from parks and gardens

644 waste.

645 Figure 3. TGA thermograms (a) and derivative curves (b) of branches, leaves, grasses and RF

646 fractions under nitrogen atmosphere.

647 Figure 4. Morphological parameters of lignocellulosic fillers; a) SEM Images (magnitude x

648 1,500) and b) Particle size distribution of Branches, Leaves, Grasses and RF in number and in

649 volume.

650 Figure 5. Tensile properties of PHBV-based biocomposites: a) strength at break (MPa), b)

651 strain at break (%) and c) Young's modulus (GPa). Different letters above each bar indicate

652 significant difference ($p < 0.05$), using the Fisher's test for strength at break values and the

653 Dunn's test for strain at break and Young's modulus values.

654 Figure 6. SEM image of cross-sections of PHBV-based biocomposites (magnitude x 250).

655

Figure 1.

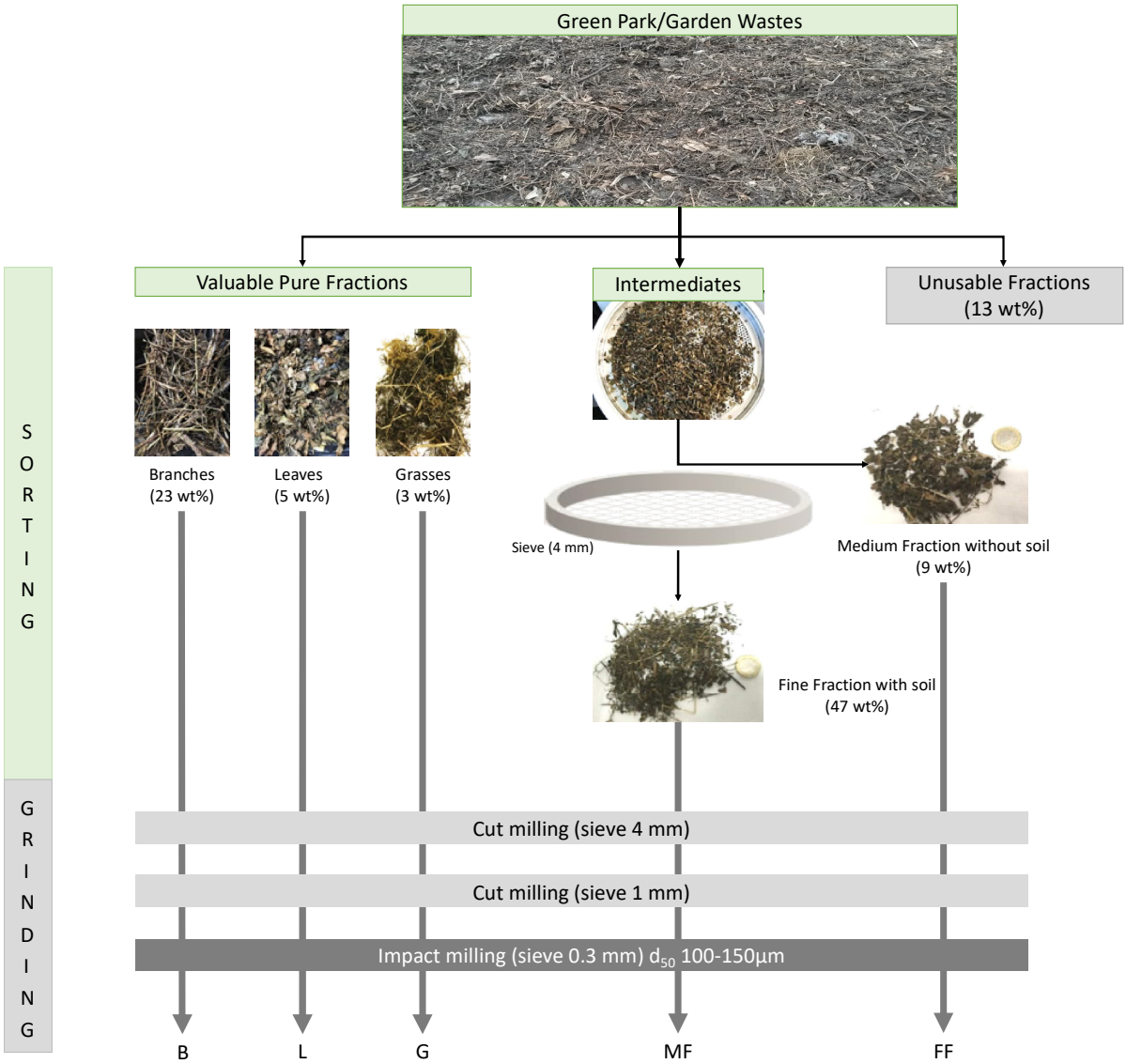
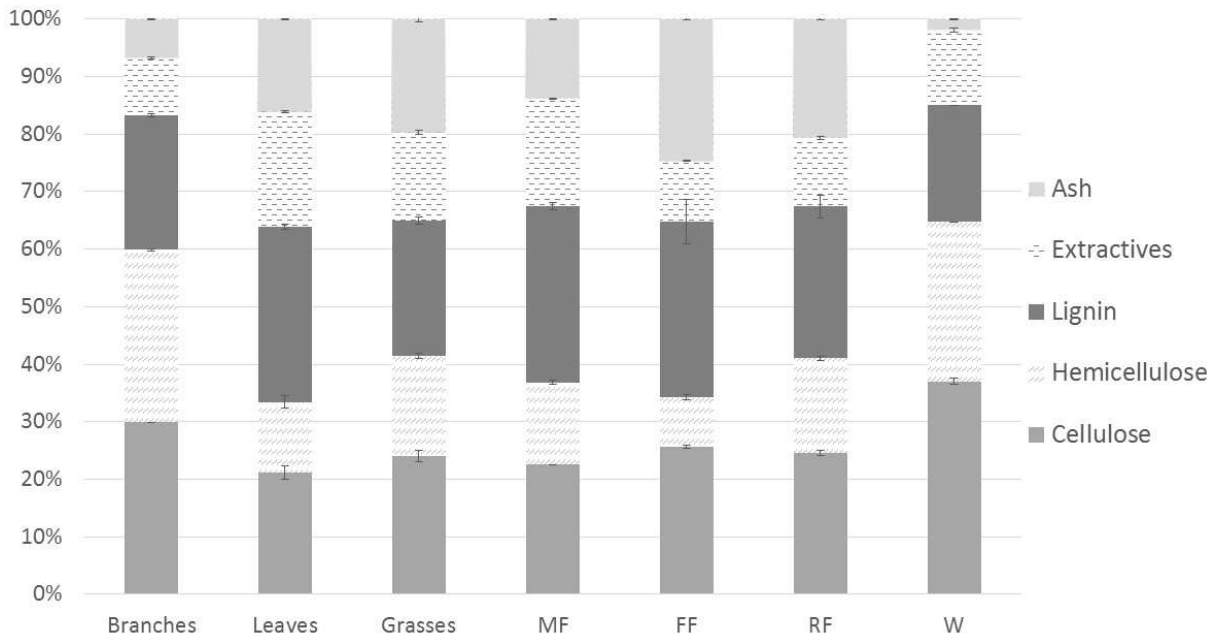
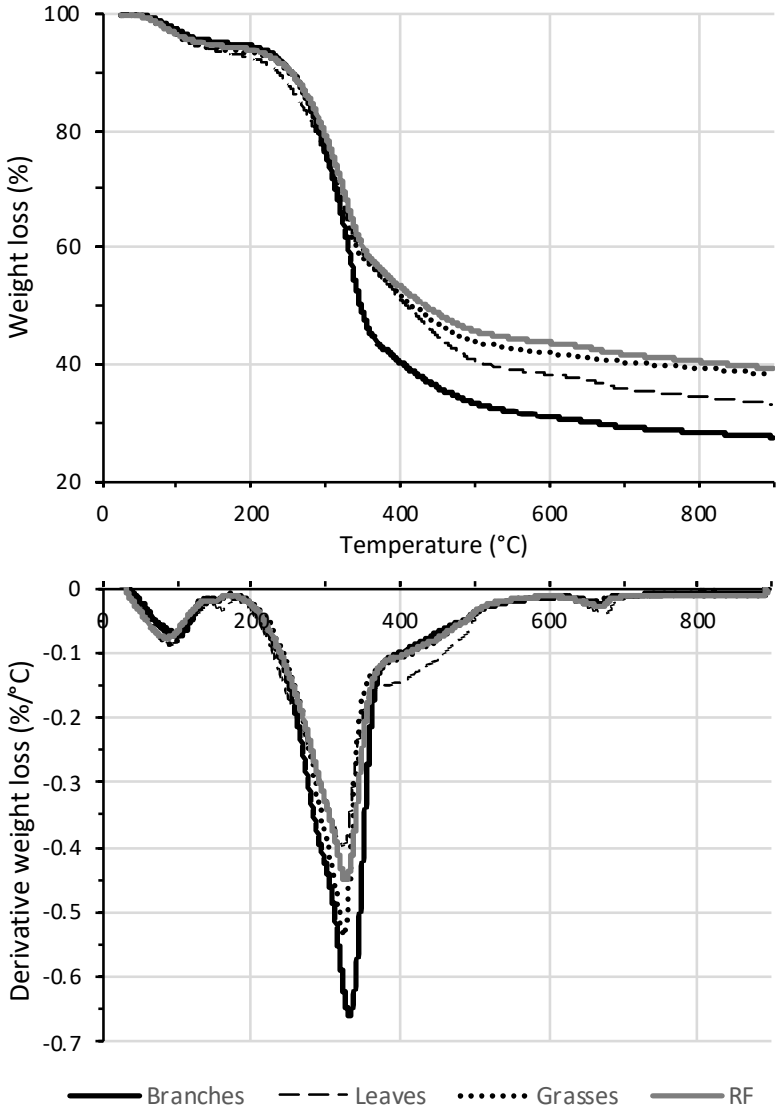

Green Park/Garden Wastes
Valuable Pure Fractions
Intermediates
Unusable Fractions
(13 wt%)
SORTING
Branches
(23 wt%)
Leaves
(5 wt%)
Grasses
(3 wt%)
Sieve (4 mm)
Medium Fraction without soil
(9 wt%)
Fine Fraction with soil
(47 wt%)
GRINDING
Cut milling (sieve 4 mm)
Cut milling (sieve 1 mm)
Impact milling (sieve 0.3 mm) d50 100-150µm
B
L
G
MF
FF

Figure 2.


100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Branches
Leaves
Grasses
MF
FF
RF
W
Ash
Extractives
Lignin
Hemicellulose
Cellulose

662 Figure 3.



663

664

Figure 4.

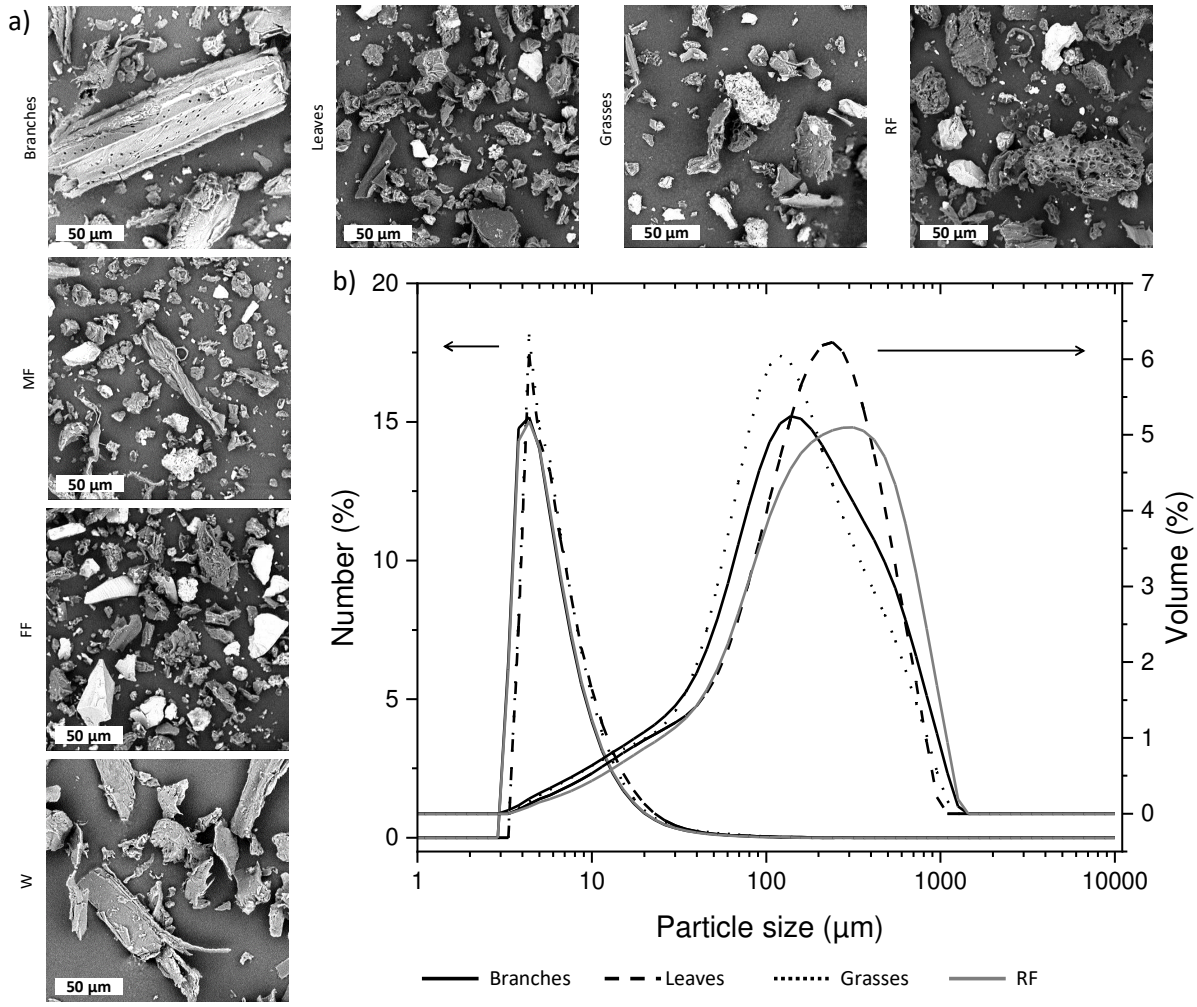
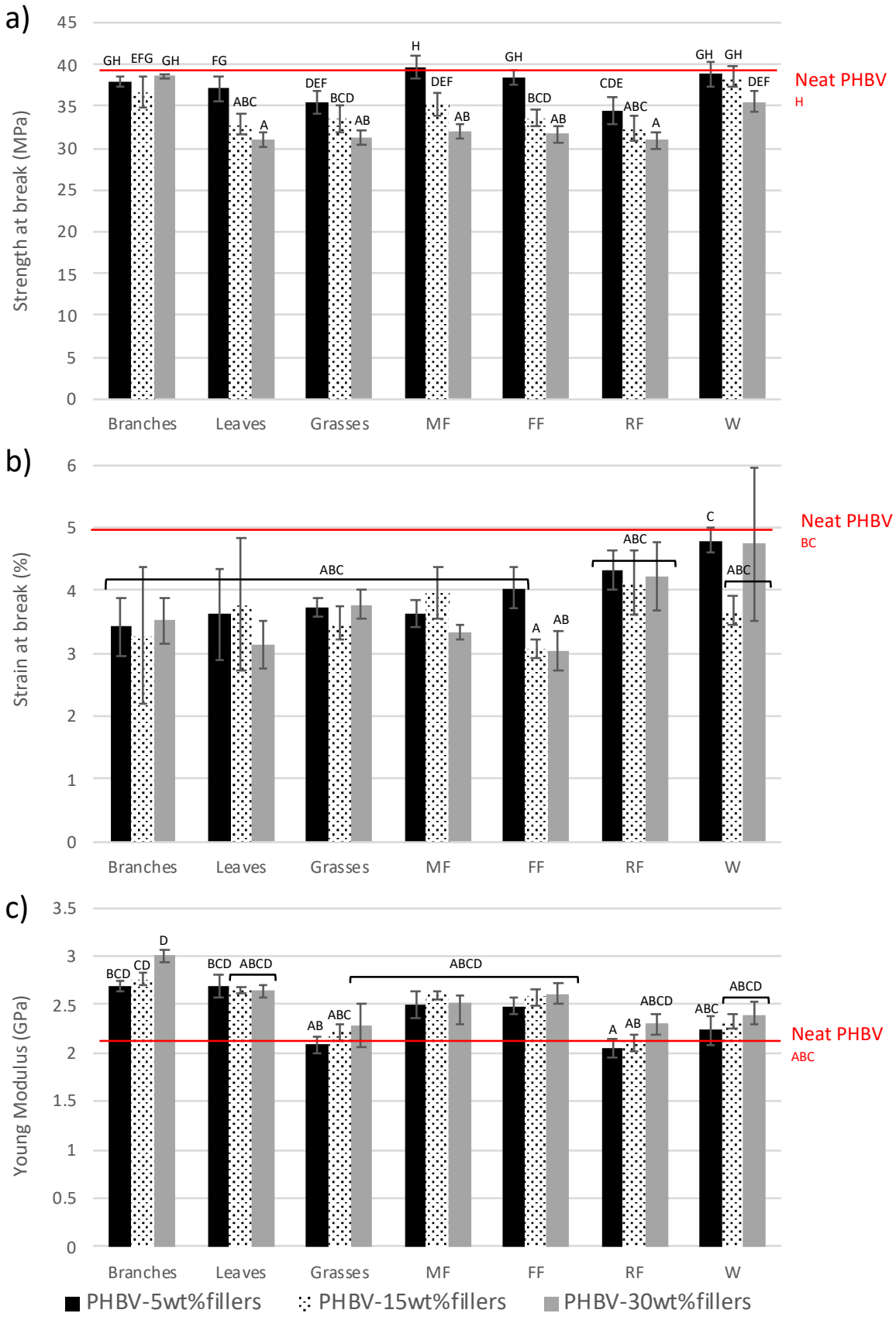
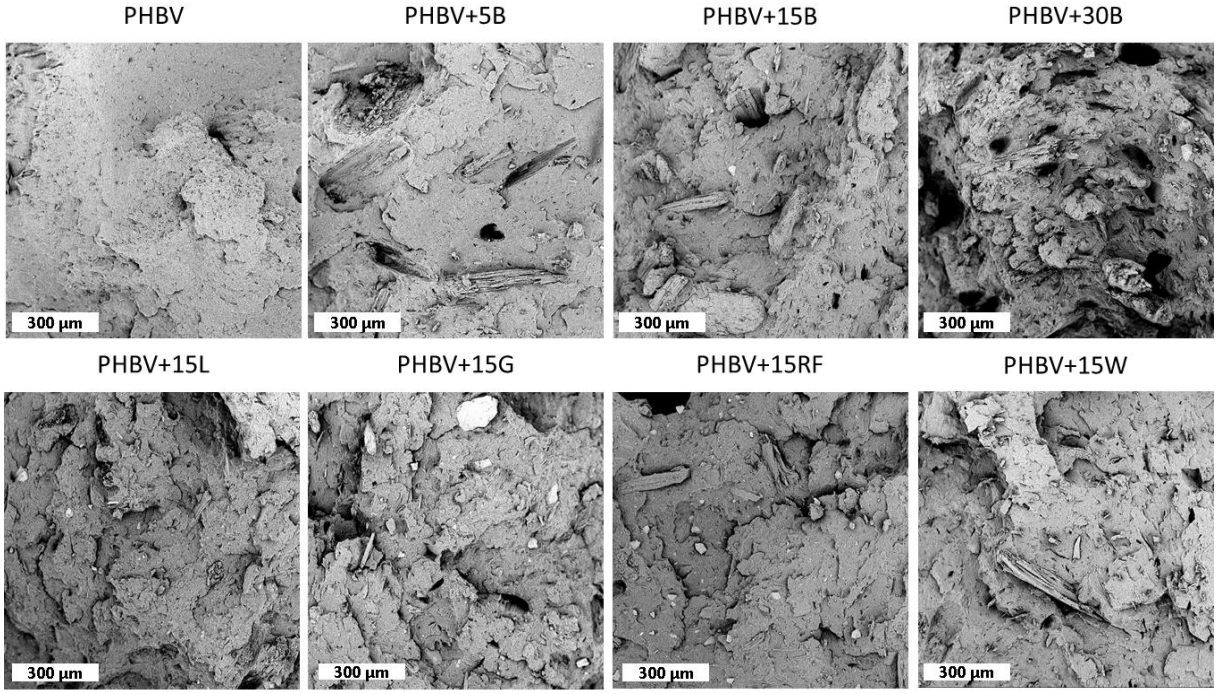

a)
Branches
Leaves
Grasses
RF
MF
FF
W
50 µm
b)
Number (%)
Volume (%)
Particle size (µm)
Branches
Leaves
Grasses
RF

Figure 5.


a)
Strength at break (MPa)
45
40
35
30
25
20
15
10
5
0
GH EFG GH
FG ABC A
DEF BCD AB
H DEF AB
GH BCD AB
CDE ABC A
GH GH DEF
Neat PHBV
H
Branches
Leaves
Grasses
MF
FF
RF
W
b)
Strain at break (%)
6
5
4
3
2
1
0
ABC
A AB
ABC
C ABC
Neat PHBV
BC
Branches
Leaves
Grasses
MF
FF
RF
W
c)
Young Modulus (GPa)
3.5
3
2.5
2
1.5
1
0.5
0
BCD CD D
BCD ABCD
AB ABC
ABCD
A AB ABCD
ABC ABCD
Neat PHBV
ABC
Branches
Leaves
Grasses
MF
FF
RF
W
PHBV-5wt%fillers
PHBV-15wt%fillers
PHBV-30wt%fillers

670 Figure 6.



671

672

673 Table 1. Water content, temperatures of thermal degradation, colorimetric parameters[a], size

674 parameters and true density of lignocellulosic fillers produced from urban parks and gardens

675 green waste

Fillers	Water content (%)	T_{onset} (°C)	T_{peak} (°C)	L*	a*	b*	d_{50} in volume (µm)	Span[b]	True density ($g.cm^{-3}$)
Branches	5.2 ± 0.3	236 ± 0	330.8 ± 0.3	52.0	4.8	14.3	138 ± 3	3.42 ± 0.07	1.56 ± 0.00
Leaves	6 ± 0	229.3 ± 0.8	323 ± 1	37.1	3.3	9.1	170 ± 2	2.50 ± 0.03	1.55 ± 0.01
Grass	6 ± 0	242 ± 0	324 ± 0	39.7	1.6	9.1	119 ± 1	3.26 ± 0.05	1.65 ± 0.02
MF	6.8 ± 0.3	232.3 ± 0.8	324 ± 0	38.6	3.3	9.5	103 ± 3	3.18 ± 0.09	1.56 ± 0.01
FF	5.3 ± 0.3	245.3 ± 0.3	323.8 ± 0.3	38.1	3.2	7.7	90 ± 3	3.50 ± 0.09	1.78 ± 0.02
RF	5.3 ± 0.3	239 ± 0	327 ± 0	40.6	3.3	9.1	118 ± 1	3.28 ± 0.06	1.68 ± 0.02
W	4.8 ± 0.3	240.5 ± 0.5	337 ± 0	68.9	5.2	20.3	131 ± 3	3.46 ± 0.05	1.56 ± 0.02

676 [a]Standard deviations values lower than 0.1 for all the values of colorimetric parameters

677 [b]Span = $(d_{90}-d_{10})/d_{50}$

678 Table 2. DSC and TGA results for PHBV-based biocomposites

Formulations	T_c (°C)	T_{m1} (°C)	χ_1 (%)	T_{m2} (°C)	χ_2 (%)	T_{onset} (°C)	T_{peak} (°C)
PHBV	126	178	62	175	69	270.5 ± 0.5	298.3 ± 0.3
PHBV/5wt%Branches	125	177	62	175	68	266 ± 0	292 ± 0
PHBV/15wt%Branches	123	176	64	174	70	256 ± 0	278.5 ± 0.5
PHBV/30wt%Branches	121	175	63	173	70	250.5 ± 0.5	270.5 ± 0.5
PHBV/15wt%Leaves	121	176	63	174	70	257.5 ± 0.5	276 ± 1
PHBV/15wt%Grass	119	174	62	172	69	251.5 ± 1.5	272 ± 1
PHBV/15wt%MF	120	175	63	174	70	255.5 ± 1.5	273 ± 1
PHBV/15wt%FF	122	176	66	174	69	257 ± 0	277 ± 0
PHBV/15wt%RF	122	175	65	174	71	257.5 ± 0.5	277.5 ± 0.5
PHBV/15wt%W	123	175	65	175	72	261.5 ± 1.5	290.5 ± 0.5

679

Urban Parks and Gardens Green Waste

Conversion of 87 wt% of the raw resource into fillers by simple dry fractionation

Lignocellulosic fillers

Production of biocomposites by melt extrusion and injection molding (filler content up to 30 wt%)

PHBV-based biocomposites