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Dry fractionation of olive pomace for the development of food packaging biocomposites

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ABSTRACT

Three lignocellulosic fractions with contrasted properties were produced by dry fractionation of olive pomace (OP): a stone-rich fraction (SF) rich in cellulose and having high polarity, a pulp-rich fraction (PF) richer in lignin and less polar, and a crude pomace fraction (CF) with intermediate properties. These fractions were used as fillers in two thermoplastic matrices, *i.e.* polyprolylene (PP) and polyhydroxybutyrate-co-valerate (PHBV). Tensile tests showed a decrease of both the stress and the elongation at break for all biocomposites, while the Young's modulus was not significantly affected. At low filler contents, no effect of filler composition was observed whereas at high filler content (30 wt%), the decrease in the stress at break was less pronounced for PHBV-PF, with respective reduction values of 36%, 65% and up to 78% for PHBV-PF (30%), PHBV-CF (30%)and PHBV-SF (30%) composites, as compared to the neat PHBV. The elongation at break also greatly decreased according to the filler content. The highest reduction was recorded in the case of SF fillers, with a reduction of 74% for PHBV-SF composites. Mechanical properties were better preserved in the case of the PF filler due to better interfacial adhesion towards the matrices, as revealed by work of adhesion calculations, SEM observations and mechanical modelling. Water vapour permeability (WVP) of both matrices was increased in presence of both SF and CF fillers, while oxygen permeability was not significantly affected by the fillers. As an example, WVP increased from $0.9 \pm 0.1 \times 10^{-12}\,\mathrm{mol\,m^{-1}\,s^{-1}\,Pa^{-1}}$ for the neat PHBV up to $15.1 \pm 2.6 \times 10^{-12}\,\mathrm{mol\,m^{-1}\,s^{-1}\,Pa^{-1}}$ for PHBV-CF (30%). This supports a promising use of SF/CF fractions in sustainable biocomposites packaging for respiring food products, the PF-based formulations being more appropriate for non-respiring and water sensitive products. Our results demonstrated that the conditioning of lignocellulosic biomass by dry fractionation is important for the control of bio-based fillers properties and the resulting functionalities of biocomposites. Besides, the PP-based composites developed in this study allow reducing costs and dependence to fossil resources, while PHBV-based biocomposites also have the advantage of being fully bio-based and biodegradable.

1. Introduction

Food packaging is the sector consuming most plastics, with about 40% of the global demand worldwide. Polypropylene (PP) is at the head with more than 19% of usages (Plastics-the Facts, 2016. In view of reducing food waste while limiting the harmful effects of petrochemical-derived plastic residues on the environment, the conception of fully bio-based and biodegradable packaging materials having tailored mass transfer properties constitutes one alternative to overcome these issues (Angellier-Coussy et al., 2013). Among them, polyhydroxyalkanoates (PHA) are bacterially-derived thermoplastic polymers that can be produced from renewable resources, including solid or liquid agro-residues and municipal wastes. They have gained major importance worldwide due to their macromolecular structure diversity and close properties to conventional plastics that make them highly competitive with respect to PP. The copolyester polyhydroxy-(3-butyrate-*co*-3-valerate) (PHBV) is one of the best characterized PHA (Reddy et al., 2003). Besides its higher price as compared to conventional plastics, the main limitation restricting its commercial application at a large scale is its barrier properties which are too high to fit respiring products needs such as fruits and vegetable (Berthet et al., 2016).

One environmentally virtuous strategy to modulate PHBV barrier properties while reducing the final cost of materials is to mix it with low cost lignocellulosic fillers obtained from food industry solid by-products

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(Berthet et al., 2015, 2016). Olive pomace (OP), which is the solid lignocellulosic residue of olive oil extraction, is a very good candidate for this purpose due to its very high availability and low cost. Its production is mainly concentrated in Mediterranean area, but the emergence of new producer countries leads to an intense accumulation of OP that is estimated to reach 2,881,500 tons/year worldwide (Ravindran and Jaiswal, 2016). Olive pomace is a mixture of residual skin, pulp and fragments of the crushed stone. Until now, only the part corresponding to the olive stone has been valorized in the field of biocomposites by combining it either with synthetic polymers such as unsaturated polyesters (Gharbiet al., 2014), polyvinyl chloride (PVC) (Djidjelli et al., 2007), PP (Naghmouchi et al., 2015; Siracusa et al., 2001), or biodegradable polymers such as wheat gluten (Hammoui et al., 2015), polylactic acid (PLA) (Koutsomitopoulou et al., 2014) and PHBV (Hassaini et al., 2017). Neither the whole crude OP nor the olive pulp has been yet exploited in this way. In addition, all these studies mainly focused on mechanical and thermal properties of the resulting biocomposites. Only Hassaini et al. (2017) were interested about oxygen and water vapour permeability of these biocomposites after chemical treatment of the stone-based filler to improve its affinity toward the PHBV matrix. It is also worth noting that OP is often exclusively treated using wet processes consuming a large amount of water and chemicals (hexane and/or acetone) in order to separate the pulp from the stone, thus generating pollutant and toxic effluents. In the perspective to reduce the harmful environmental impact of OP by its sustainable valorization, dry fractionation combining grinding and sorting processes (electrostatic separation, friction or sieving) has been recently demonstrated to be a sustainable technology to produce fillers from crude olive pomace. It was shown that friction in a ball mill was the most adapted mechanical treatment to produce pulp-rich and stone-rich powders with high yield and purity, and contrasted biochemical composition and polarity (Lammi et al., 2018).

In this context, the present work aims at exploring the potential use of the two main parts of olive pomace, *i.e.* the stone and the pulp, as fillers in biocomposites and to compare it to that of the crude OP. For this purpose, pulp-rich and stone-rich fractions with contrasted biochemical composition and physico-chemical surface properties were produced by dry fractionation and used as fillers in a petroleum based polymer matrix, polypropylene (PP), and a bio-based polymer matrix, polyhydroxy-butyrate-co-valerate (PHBV). Biocomposites with increasing filler contents were prepared by melt compounding and thermo-compression and their optical (color), microstructural, thermal, mechanical (tensile) and barrier (water vapour and oxygen permeability) properties were characterized. Changes in material functional properties are discussed in relation to the intrinsic characteristics of olive pomace-based fillers, including their color, density, size, morphology, biochemical composition, thermal stability and surface free energy. Special attention is given to understand the impact of the composition of OP-based fillers and especially their physico-chemical affinity with the thermoplastic matrices on biocomposites functional properties. Finally, their possible application in the food packaging sector was discussed.

2. Materials and methods

2.1. Raw materials

Algerian crude olive pomace (OP) of the *Chemlal* variety was kindly provided in December 2016 by local olive producers in the region of Azeffoun (Tizi-Ouzou) located in north-central of Algeria. OP was stored in a cold room at 4 °C ± 1 until its use. This residue was composed of partially crushed stones, pulp and skin and displayed an initial moisture content of 53 wt%. Prior to dry fractionation, the fresh olive pomace was dried in an oven at 60 °C for 24 h until reaching a moisture content of 9 wt%.

A commercial grade of polyhydroxy-(butyrate-co-valerate) (PHBV) containing 5% of valerate was purchased from NaturePlast company (France) in the form of pellets (PHI002 grade). Data given by the supplier were the following: PHBV density of 1.25 ± 0.05, melt flow index ranging between 15 and 30 g 10 min^{-1} (190 °C/2.16 kg) and melt temperature ranging from 145 to 155 °C. Pellets were dried overnight at 60 °C before processing. Polypropylene (PP) in the form of pellets (PPH 9020 grade) was purchased from Total Petrochemicals (Belgium). Data given by the supplier were the following: PP density of 0.905, melt flow index of 25 g 10 min^{-1} (230 °C/2.16 kg) and melt temperature of 165 °C.

Sulfuric acid, arabinose, xylose and glucose (Sigma-Aldrich), formamide, diiodomethane (Acros Organics, Geel, Belgium), ethylene glycol (Aldrich chemical Co. Inc., Milwaukee, USA) and glycerol (Merk, Darmstadt, Germany) were used for characterization of olive pomace fractions.

2.2. Preparation of olive pomace-based fillers

A dry fractionation process was applied to separate the pulp and the stone from the crude olive pomace (OP). Dry OP was first submitted to frictional forces in a ball mill (Marne n°55, FAURE, France) operating at ambient temperature, 86 rpm and during 30 min. A jar of 2 L was used, with 1/3 in volume of ceramic balls (diameter of 15, 20 and 25 mm) and 1/3 in volume of crude OP. The resulting powder was then passed into an electric sieve (RITEC, model 400, France) through a 1.25 mm mesh. Two fractions were obtained: the fine fraction was recovered at the bottom of the sieve and corresponds to the pulp-rich fraction (PF), while a coarse fraction was retained on the sieve (Lammi et al., 2018). This coarse fraction was further ground using a knife milling (SM 300, Retch, Germany) with a grid size of 1 mm and speed of 1500 rpm. The ground product was then sieved through a 0.4 mm mesh in order to separate the stone-rich fraction (SF) from the intermediate fraction (Fig. 1). Finally, in order to obtain powders with similar particle sizes, the SF and PF fractions as well as the crude OP, corresponding to the starting biomass (named CF), were first reduced by knife milling using a 0.25 mm grid at 1500 rpm and then further reduced using a 0.3 mm impact milling (Hosokawa-alpine, type 100UPZ, Augsburg, Germany) operating at 18000 rpm (Fig. 1).

2.3. Preparation of olive pomace-based composite films

2.3.1. Compounding

To minimize hydrolytic degradation, all constituents (PHBV pellets, CF, SF and PF powders) were dried in a vacuum oven at 60 °C over night prior to compounding. Composites were blended at various polymer/filler ratios (100/0, 95/5, 85/15, 70/30 w/w) using a HAAKE Rheomix internal mixer. The polymer pellets and the OP-based fillers were first mixed manually. The resulting mixture was then introduced all at once into the mixer operating at a rotor speed of 60 rpm. The mixture was blended during 5 min at temperatures of 170 °C and 180 °C for PHBV and PP matrices, respectively. The obtained compounds were cooled to room temperature and then, ground in a knife mill (SM 300, Retch, Germany) at a speed of 2200 rpm through a 4 mm grid to obtain composite pellets, which were then stored in sealed plastic bags containing silica gel. The codification of sample was done as follows: matrix-OP based fraction (weight filler content). For example, PHBV-CF (5%) corresponds to a PHBV-based composite filled with 5 wt% of the CF fraction.

2.3.2. Film shaping

Compounds were dried at 60 °C for at least 8 h before the preparation of films. Biocomposite films (10.5 cm wide squares, average thickness about 250 μm) were prepared by hot pressing the pellets between two Teflon coated plates, at 170 °C and 180 °C for PHBV and PP-based biocomposites respectively, using a hydraulic thermopress (PLM 10 T, Techmo, Nazelles, France). Samples were allowed to melt for