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Exploring the potentialities of using lignocellulosic fibres derived from three food by-products as constituents of biocomposites for food packaging

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ABSTRACT

Lignocellulosic fibres obtained by dry grinding of three different solid agro-residues, i.e. wheat straw, brewing spent grains and olive mills, were compared regarding their potential use as fillers in poly(3-hydroxybutyrate-co-valerate) (PHBV) for food packaging applications. Differences found in their composition might have influenced their grinding ability, as observed with the difference of sizes, i.e. 109 μm, 148 μm and 46 μm, respectively. Thereafter, composites structure was characterized regarding their morphology, fibre/matrix interaction, matrix molecular weight and crystallization behaviour. Poor fibre/matrix adhesion, degradation of PHBV polymer chains, and decrease of PHBV's crystallinity were evidence. Consequently, mechanical properties were degraded in presence of the fibres. Water vapour transfer rate of composites was increased with wheat straw fibres introduction while it was decreased for olive mills-based materials. Regarding the food packaging applications, PHBV/wheat straw fibres composites appeared as promising materials to reach the requirements of respiring food products, whereas PHBV/olive mills composites would be more adapted for water sensitive products.

1. Introduction

The basic right of people to the food they need is the greatest challenge facing the world community. Roughly one-third of the edible parts of food produced for human consumption is lost and/or wasted throughout the food supply chain, from initial agricultural production down to final household consumption (Gustavsson et al., 2011). In this context, one of the main challenges common to both the fields of materials and food is the development of innovative and sustainable packaging materials. This first means the development of economically competitive and efficient packaging able to reduce food losses and waste by improving shelf life for perishable foods, which is possible by judiciously selecting or designing food packaging. This means also the reduction of the overall environmental impact of the food/packaging system by taking into account the environmental impact of the packaging itself. Concretely, food packaging material properties, including mainly mechanical and gas transfer properties, have to be adapted as a function of the food product requirements to be able to guarantee its best preservation. In the particular case of respiring fresh food products, packaging gas permeability and perm-selectivity are critical parameters to be controlled when designing new packaging materials. For this category of food products, as their shelf life is short, there is no need for long-lasting packaging materials, making biodegradable materials interesting environmental-friendly solutions.

Among the different biodegradable materials commercially available, poly(hydroxy-3-butyrate-co-3-valerate) (PHBV), is a bacterial polyester presenting the advantage of being bio-sourced and potentially prepared from food industry by-products (Serafim et al., 2008). Its main drawbacks are its high cost (3–5 €/kg, Chanprateep, 2010) and its barrier properties which are too high to fit respiring products needs (Shogren, 1997). One strategy to modulate PHBV barrier properties while maintaining the full biodegradability of the materials and reducing the final cost of materials is to mix it with low cost lignocellulosic fibres such as wood fibres (Reinsch

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and Kelley, 1997), spruce fibres, ground olive stone (Dufresne et al., 2003), flax fibres (Wong et al., 2004), jute and abaca fibres (Bledzki and Jaszkiewicz, 2010), wheat straw fibres (Avella et al., 2000; Ahankari et al., 2011) or beer spent grain fibres (Cunha et al., 2014).

The cheapest and most environmentally virtuous lignocellulosic fibres are those obtained from food industry solid by-products. Their upcycling as fillers in biocomposites would also help waste reduction in food industry as well. In this context, the European project EcoBioCAP aimed at extending the state-of-the-art by developing a new range of food packaging constituents, i.e. low cost, largely available, biodegradable and functional fibres issued from the wheat, beer and oil industry solid by-products. Wheat straw is a by-product of the production of wheat grains, mainly composed of cell walls which are constituted of a lignocellulosic network. It is widely available around the world (e.g. in Europe: 80 million of tons/year, 25 € for 1000 kg with price volatility) and traditionally used for low-value purposes, mainly in cattle, livestock feeding or agricultural mulch, the rest being burnt or simply thrown away. The production of wheat straw fibres (WSF) with controlled size for food packaging applications can be easily performed by successive dry grinding processes, without any washing step, as reported by Silva et al. (2011). Spent grains are brewing by-products (BSG) resulting from wort production (Brányik et al., 2005) (around 8 millions of tons/year of dried BSG in Europe, at a cost almost nul). They are a cellulose- and lignin-rich fraction of the barley grains that is typically sold for cattle feed or disposed of in landfills. Brányik et al. (2001) devised a method to separate a lignin-rich fraction from the other spent grains components. This method has yields of ca. 10 wt% of lignin-rich material. Nowadays, in accordance with the new tendency to find solutions for food industry residues, brewing spent grains proved to be useful in applications such as human and animal nutrition, energy production, paper manufacture and absorbent material. Finally, olive pomace is the paste-like residue obtained from the olive oil production (800 kg/1000 kg olives, 7 millions of tons/year in Europe), which is composed of skin, pulp, stone and olive kernel. Its insoluble fibre fraction was determined to be 65.3 wt% (representing hemicelluloses, cellulose and lignin) (Laufenberg, 2003). The high amounts of phenolic compounds as well as dietary fibre make olive pomace as a valuable source for further processing and fractionation (Cioffi et al., 2010). However, refinery processes are not widely developed as the use of the insoluble fibre fraction is still very limited. Such moist solid wastes of olive oil but also beer industry, are highly accessible to microbial spoilage and thus cannot be stored without further intensive drying which adds on the energy bill. Potential applications are animal feed (but not always suitable due to high content of secondary plant metabolites) (Brozzoli et al., 2010) or fertilizers but mostly the by-products are disposed without any creation of value.

Recently, some studies were devoted to the use of BSG (Bledzki et al., 2010; Cunha et al., 2014), olive pomace fibres (Dufresne et al., 2003; Amar et al., 2010), or wheat straw fibres (Avella et al., 2000; Ahankari et al., 2011) as reinforcing agents in polymer matrices, thus opening promising outlets with added value to these food wastes. Hence, PHBV/lignocellulosic fibres food packaging materials should fulfil requirements for fresh food products, both regarding permeability needs and biodegradability. Unfortunately, too few materials of this kind were developed aiming the study of properties specific to food packaging materials application, especially permeability properties. Therefore, this study will bring more elements of knowledge answering this lack of information.

The aim of the present work is to explore the potentialities of using lignocellulosic fibres derived from three different solid food by-products, i.e. wheat straw fibres, spent grains and olive pomace, as fillers in PHBV to develop biocomposites for food packaging applications. Special attention will be first given to better understand the impact of fibre origin on their grinding behaviour, resultant intrinsic characteristics and processability through melt extrusion. Then, the paper will focus on investigating the relationships between some of the main structural characteristics of the composite and its constituents, and the composites properties. Thoroughly, the studied fibres characteristics will be their composition, size and morphology, while the studied matrix characteristics will be the polymer chain length and the crystallinity. As regards the structural characteristics of the composites, the study will focus on the fibre dispersion state, assessed by microscopic observations. And finally, the studied composite properties will be the mechanical and barrier properties, which are directly related to a potential food packaging application.

2. Materials and methods

2.1. Materials

A commercial PHBV (injection moulding grade) with 3 mol% HV and a measured molecular weight of 423,820 g mol^{-1} was purchased from Tianan Biologic Materials Company (ENMAT^{TM} Y1000P). Pellets were dried overnight at 60 °C before processing. Fresh brewing spent grains were kindly supplied by the beer industry UNICER (Bebidas, S.A., Matosinhos, Portugal). Olive pomace used in the experiments was kindly provided by Frantoio di Sant'Agata d'Oneglia di Mela C.&C. sas, Imperia, Italy. Wheat straw (*Triticum aestivum* cv. Apache) was kindly provided by Fernand Meaux (Saint Jean du Salés, Tarn, France).

2.2. Preparation and characterization of lignocellulosic fibres

Fig. 1 sums up the preparation steps of each fibre type.

2.2.1. Preparation of raw fibres

2.2.1.1. Wheat straw fibres. Wheat straw fibres were prepared as described in the work of Silva et al. (2011). Briefly, native wheat straw (stored at room temperature and relative humidity and characterised by a moisture content of 8 wt% w.b.) was reduced using a cutting mill type SM2000 (Retsch, Germany) with a 4.0 mm sieve.

2.2.1.2. Brewing spent grains. Brewing spent grains were obtained as described in details in Pires et al. (2012). Briefly, fresh brewing spent grains, as received from the beer industry, were washed in water for three times and sieved under water (500 μm) aiming at process residues thus obtaining a material with a higher barley husk content. In order to remove the remnants of proteins and sugars still in the spent grains when they are received from the brewing process, a double caustic treatment was performed in the obtained material. as follows: brewing spent grains were first heat treated at 70 °C for 20 min in NaOH 3% solution; and after that heated again at 90 °C for 20 min in a NaOH 6% solution. Finally, the material obtained at the end of the treatment was washed with acidified water (with 50 mL HCl 1 mol L^{-1} for each 10 L of water) until neutral pH and placed in an oven at 60 °C until completely dried.

2.2.1.3. Olive mills. Olive pomace, as received from olive oil producer, was milled in order to increase the available surface area, for solvent extraction of residual fat. For that purpose, the raw material was frozen with liquid nitrogen and grinded in a centrifugal mill. The particle size was controlled by a ring sieve with 500 μm mesh. The extraction of phenolic compounds was performed under conditions optimized at Fraunhofer IVV. For this the olive pomace was suspended in an ethanol-water-solution (70:30 w/w). The solid to liquid ratio was 1:15 (w/w). For extraction the suspension was stirred at 80 °C. After a treatment time of 90 min, the fibres were recovered by filtration and dried. This extraction of phenolic