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Overview of Agro-food waste and by products valorization for polymer synthesis, and modification for bio-composite production†

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Abstract: The world economy growth and global population rising push for a more efficient management of the Earth's natural resources. The combined plastic and food sector form an important part of the EU economy, accounting for 15 million jobs. Unlocking the innovation potential in the field of packaging, and cosmetics will significantly contribute to job creation and competitiveness. Sustainable synthesis of polyhydroxyalkanaotes from agro-food by-products as well as synthesis of lactic acid co-polymers constitute a pathway to performing and sustainable polymeric matrices. Natural fibers as well as polysaccharides (starch, cellulose, chitin, chitosan), cutin and protein rich by-products are abundantly available from the agrofood industry. Natural fibres may be modified chemically, with enzymes or treating their surface with natural waxes with a significant improvement in adhesion and impact resistance.

An overview on the availability, collection, treatment and approach to valorization of largely available agro-food waste biomass for both polymers and biocomposites production, is hereby reported with exampled of case studies and product developed in our research units, such as sustainable pots, rigid containers, active films, non-woven tissue.

Keywords: Biomass; Bio-based polymers; active molecules, coatings, packaging, cosmetic, biomedical

1. Introduction

With the growth of world economy and rising of global population (9 billion by 2050) the Earth's natural resources need to be managed more efficiently throughout their life cycle, from extraction, transport, transformation and consumption, to the disposal of waste. [1] Global production of plastics has increased twentyfold since the 1960s, reaching million tonnes in 2015 and is expected to double again over the next 20 years. The combined plastic and food sector form an important part of the EU economy, accounting for 15 million jobs (7.6% of total employment) [2].

In the last decade efforts were dedicated by academics and industries to investigate and formulate new bioplastics products, but their effective presence in the market, which is increasing, needs to be promoted in a wide spectrum of applications and petro-based plastics should be more and more replaced with renewable counterparts mainly employing bioplastics and natural polymers. Bioplastics may address polymers produed from biomass, being carbon dixide neutral, but not necessarly biodegradable, or biodegradable polymers whose biodegradability needs to be related to a precise environment and conditions as clearly stated by normative ans standards. Misleading labels may raise when the two definitions of biobased and biodegradable are confused or not related to a precise and official standard [3].

The global bioplastic utensils sales was estimated of about 845 million pieces n 2016, and a projection consider it ti become 1274 million pieces in 2022 [4]. A number of bio-based materials are available on the market from companies spread worldwide, based mainly on starch or polylactic acid (PLA) addressing products produced mainly by injection moulding, for cutlery, by thermoforming for plates or cups, then by thermo-foaming for foamed trays or shells, this latter enabling to save up to 60% less plant-based raw material than traditional plastic or paper products [5,6].

Another main issue in products such as trays is the low properties of barrier to gas, and in the case of starch based materials the low resistance to water and any juicy food. For starch, and sometime even for trays with minor PLA amount, coating of the tray with a second material, to enhance resistance to gas and moisture.

In personal care applications, where petro-based tissues are often used in hygienic products, such as wipes, the cellulosic version needs to be promoted by improving its performances thanks to proper coatings. The presence of anti-microbial coatings based on natural biopolymers that can also improve cells vitality and their regeneration, can suggest the possibility of transforming some general hygienic products in more sophisticated products promoting health and beauty of skin. Polysaccharides such as chitin and chitosan can be considered an optimum basis for this product, because of their anti-microbial and skin regenerative properties, as in development in the ECOFUNCO and PROLIFIC projects, where chitin derived from shrimps, or mushrooms will be valorized for anti-microbial propertis by coating, melt-processing with bio-polyesters and electrospinning technology.

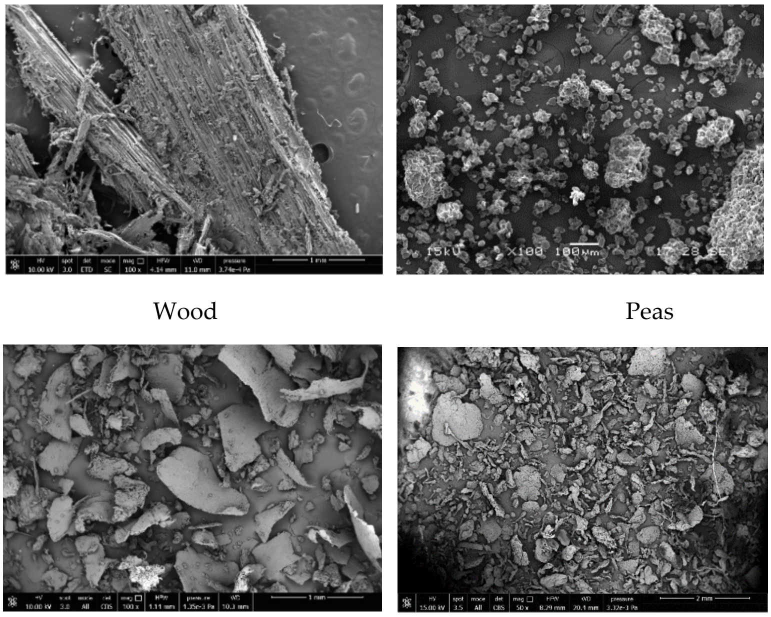
In general, the plant starch utensils are made from 70% renewable resources and 30% fillers. Non-biodegradable (PE, PP) or non biobased additives (inorganic fillers such as talc and calcium carbonate) extensively used in PLA or other bio-polyesters, such as most expensive polhydroxyalkanoates (PHAs) based materials should be progressively reduced and replaced by biobased additives, such as natural fillers. One case study reported as example of biocomposites production is addressed in the experimental section reporting biocomposites with PHAs and the effct of fibres compatibilization with waxes.

2. Experiments for Biocomposites Production

PHBV was PHI002 from Natureplast, with 1% valerate, density 1.25 g/cm^3 melting point of 145-150°C, and a melt flow index of 10-20 g (10 min)-1 (190 C, 2.16 kg). Acetyltributylcitrate (ATBC) from Sigma Aldrich (Sigma Aldrich, St. Louis, MS, USA) was used as plasticizer for PHBV, OMYACARB®2 provided by OMNYA® (Oftringen, Switzerland) as filler with fine grain size distribution (12 µm) was used to reduce the cost of the final product and facilitate the removal of the product from the mold. A PHBV/CaCO3/ATBC 85/5/10 by weight polymeric matrix was used to produce biocomposites with different natural fibers withour and with a surface treatment to compatibilise with the polymeric matrix. Wood fibres, legume, potato and bran fibres were used to produce biocomposites with PHA based polymeric matrix. Sawdust was a commercial product from softwood, pea fibres were provided by Stazione Sperimentale per l'Industrie Conserve Alimentari SSICA, Parma, Italy, as by-products of pea's protein extraction from discarded pea, Bran fibres were by-products of wheat flour production, potato fibres where by-products of starch production. All natural fibres were dried at 80°C in an electric oven for 24 h, then milled using a lab-scale mill and sieved with a 500 µm sieve. Aquacer T561 (non-ionic aqueous emulsion of beeswax) and Aquacer T581 (non-ionic aqueous emulsion of carnauba wax) purchased from BYK (Wesel, Germany) were used to wet bran fibres to improve their adhesion with the matrix and dispersion in the matrix. Mixtures were processed in a Thermo Scientific Haake Minilab Micro-compounder (Minilab), a co-rotating conical twin-screw extruder, Haake III type dog-bone tensile bars (90 × 4.8 × 1.35 mm) were produced feeding the molten material from the Minilab, directly to a Thermo Scientific HAAKE MiniJet II (Karlsruhe, Germany), and used for tensile test.

3. Results and Discussion

Wood fibres have a typical fibrous shape, with length up to 3 mm, while pea's solid residue, as well as bran and potato fillers remaining after respectively extraction of proteins, starch or flour production are composed even by platelets and round shaped fraction as residue of protein and starch (Figure 1). Thus these last biomasses has a shape more typical of a filler than of a fibre, as reflected by the mechanical performance of the produced composites [7].



Wood Peas

Bran fillers Potato

Figure 1. Scanning Electron Microscopy Image of respectively wood fibres, peas, bran and potato fillers.

In all the biocomposites, with increasing the fibres content regardless of type fibres used (wood, bran, wheat, or pea) the Young's modulus slightly increased and the elongation at break significantly decreased due to the stiffening effect induced by the lignocellulosic fillers. The observed behaviour is typical for particle-filled polymeric matrices with poor or no compatibility between the components, thus weak interfacial interactions are typical for wood flour filled composites, because the surface free energy of both the filler and the polymer is very small so that stress transfer phenomena cannot occur and the filler particle becomes a stress concentrator leading to early fracture.

To predict the behavior of materials as the amount of fibre varies, models have been studied that take into account the length of the fibers, their orientation and geometric factors such as aspect ratio (ar). For examples the The Pukanszky's model is developed to predict the behavior of composite materials in which the dispersed phase consists of particulate or short fibers taking into account geometric factors, the quantity of fiber contained within and the adhesion between matrix and filler [8] where the reinforcing effect of filler is expressed quantitatively by considering the effect of the decrease in effective load-bearing cross-section of the polymer

$$\ln \sigma_{c,red} = \ln \frac{\sigma_c\left(1 + 2.5\, V_p\right)}{1 - V_p} = \ln \sigma_m + BV_p \quad (1)$$

$\sigma_{c,red}$ is the reduced tensile strength, i.e., the tensile strength normalized to the cross-section perpendicular to the load direction, σ_c and σ_m are the break stress of the composite and the matrix, respectively, V_p is the filler volume fraction and B is a parameter connected to the matrix/filler interaction. From the slope of the logarithm of $\sigma_{c,red}$ against V_p, the value of the B parameter can be evaluated. *B* has no direct physical meaning, but it is connected with the interfacial properties of the system. In a simplified way the higher is B better is the adhesion.

The B parameters calcilated for the prepared composites are sumamrised in Table 1.

Table 1. Parameter B for each type of filler used.

By product	B
Wood Fibres	2.47
Potato Fibres	2.33
Peas fibre	1.98
Bran fibres	0.67
Bran fibres T581	0.45
Bran Fibres T561	1.53

[1] Tables may have a footer.

These results confirmed the better mechanical performances of the composites containing wood fibres, and the improvement of adhesion between the bio-polyester matrix and the natural fibres, when treated with beeswax

5. Conclusions

Biomass from agro-food industries, can be valorsed in several applications from the simplet us of natural fibres abd fillers in biocomposites production to biomolecules extraction and use for advanced materials to be applied in packaging, cosmetics, agriculture.

Composites based on PHA and fibres showed a good processability by injection moulding up to 20% to 30% of fibre content. The elongation at break decreased significantly with increasing fibres loading, while the Tensile strength decreased slightly. Young's modulus increased with increasing the fibre loading, as well as impact test energy absorbed The Pukànzsky's model predicts with good accuracy the tensile behavior of the composites showing a medium intensity adhesion between fibres and polymer matrix in both cases analyzed (Wood, peas, potato and wood Fibres). Improvement of adhesion can be achieved with fibres surface treatment with natural waxes, to compatibilize with the polymeric matrix. The presence of fibres loweers cost of the biocomposites and promotes biodegradation and sustainability

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Abbreviations

The following abbreviations are used in this manuscript:
EU: European Community
PHA: polyhydroxyalkanoates
PLA: Poly lactic acid
PE: Polyethylene
PP: Polypropylene
SEM: scanning electron microscopy

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