Overview of Agro-Food Waste and By-Products Valorization for Polymer Synthesis and Modification for Bio-Composite Production [†]

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Abstract: The increase in the world’s economic growth and global population requires a more efficient management of the Earth’s natural resources. The combined plastic and food sector forms 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 polyhydroxyalkanoates from agro-food by-products as well as synthesis of lactic acid co-polymers constitute a pathway to achieving sustainable polymeric matrices. Natural fibers, as well as polysaccharides (starch, cellulose, chitin, chitosan), cutin, and protein rich by-products, are abundantly available from the agro-food industry. Natural fibers may be modified chemically with enzymes or by treating their surface with natural waxes, with a significant improvement in adhesion and impact resistance. An overview on the availability, collection, treatment, and approach of valorization of largely available agro-food waste biomass for both polymer and biocomposite production is hereby reported, with examples of case studies and product developed in our research units, such as sustainable pots, rigid containers, active films, and non-woven tissue.

Keywords: biomass; bio-based polymers; active molecules; coatings; packaging; cosmetic; biomedical

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1. Introduction

The increase in the world population and the expansion of emerging countries’ economies require a more sustainable and performant management of natural resources with consideration given to each step of the materials’ life, including sources, logistics, use, and disposal—a complete life cycle [1,2]. In recent decades, the worldwide production of plastics increased significantly, reaching one million tonnes in 2015, with expectations of a continuous high rate of growth. The combined plastic and food sector forms an important part of the EU economy, accounting for 15 million jobs (7.6% of total employment) [3].

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 increasingly replaced with their renewable counterparts, mainly bioplastics and natural polymers. The term bioplastics refers to polymers produced from biomass and those that are carbon dioxide neutral, but not biodegradable or biodegradable polymers whose biodegradability needs to be related to a precise environment and conditions as clearly stated by normative standards. Misleading labels may increase in number when the two definitions of biobased and biodegradable are confused or not related to a precise and official standard [4].

The global sale of bioplastic utensils was estimated to be of about 845 million pieces in 2016, and a projection considers this figure to increase to 1274 million pieces in 2022 [5]. A number of bio-based materials are available on the market from companies worldwide, based mainly on starch or polylactic acid (PLA), and these are generally used for products produced by injection molding for cutlery, by thermoforming for plates or cups, and by thermo-foaming for foamed trays or shells; this latter method enables a saving of up to 60% less plant-based raw material than traditional plastic or paper products [6,7].

Another important issue in producing such trays is the low barrier-to-gas properties, and the low resistance to water and any liquid food, this represents a problem for natural polymer-based materials. For starch, and sometimes even for trays with a minor amount of PLA, coating of the tray with a second material is advised 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 with proper coatings. Natural polymer can be applied in anti-microbial coatings with a positive effect on cell vitality and regeneration; thus, health care and other general hygienic products can achieve functionalized performances with a positive effect on skin quality [8].

Polysaccharides, such as chitin and chitosan, can be considered an optimum basis for this product because of their anti-microbial and skin regenerative properties. Developments have been observed in the ECOFUNCO and PROLIFIC projects, for example, where chitin derived from shrimps or mushrooms are valorized for anti-microbial properties by coating and melt-processing with bio-polyesters and electrospinning technology.

In order to reduce the cost of items based on biodegradable polymers, either natural or synthetic are composed of 70% materials derived from renewable resources and 30% fillers, being either natural fillers or inorganic ones, such as talc or calcium carbonate. Fillers are widely used in biobased, biodegradable polymeric matrices such as PLA or other bio-polyesters such as poly hydroxyalkanoates (PHAs) due to the higher cost of the polymers and the assessed positive effect on disintegration and biodegradation induced by the presence of natural fillers in biocomposites [9]. One case study reported an example of biocomposite production in the experimental section, reporting biocomposites with PHAs and the effect of fiber compatibilization with waxes.

2. Experiments for Biocomposite Production

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) was PHI002 from Natureplast, with 1% valerate, a density of 1.25 g/cm³, a 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) was obtained from Sigma Aldrich (Sigma Aldrich, St. Louis, MS, USA) and OMYACARB[®]2, an inorganic filler with fine grain size distribution (12 µm), was from OMNYA[®] (Oftringen, Switzerland). PHBV/CaCO₃/ATBC 85/5/10 by the weight of the polymeric matrix was used to produce biocomposites with different natural fibers without and with a surface treatment to compatibilize it with the polymeric matrix. Wood, legume, potato and bran fibers were used to produce biocomposites with a PHA-based polymeric matrix. Sawdust was a commercial product from softwood; the pea fibers were provided by the “Stazione Sperimentale per l’Industria Conserve Alimentari” located in Parma, Italy. These represent the by-products of pea’s protein extraction from discarded peas. The bran fibers were the by-products of wheat flour production, and the potato fibers were the by-

products of starch production. The natural fillers were stored in a ventilated electric oven at 80 °C for one day in order to remove moisture from them. The dried biomass was then grinded by lab-scale mill and subsequently sieved under a 500 µm sieve. In order to improve the adhesion between the natural fillers and the polymeric matrix, the biomass from bran was sprayed, respectively, with a water emulsion of Aquacer T561, which is a non-ionic aqueous emulsion of beeswax, and Aquacer T581, which is a non-ionic aqueous emulsion of carnauba wax, purchased from BYK Wesel, Germany. The prepared formulations with the polymer and natural fillers were processed in a Thermo Scientific Haake Minilab Micro-compounder (Minilab), which is a co-rotating conical twin-screw extruder. The type Haake III dog-bone tensile bars (90 × 4.8 × 1.35 mm) were produced by feeding the molten material to a Thermo Scientific HAAKE MiniJet II (Karlsruhe, Germany). The produced dog bones were tested for tensile properties.

3. Results and Discussion

The materials were produced by extrusion and subsequent injection; ATBC acted as a plasticizer promoting the melt flow of the mixtures, while the inorganic fillers promoted the release from the mold and had a significant effect on lowering the cost of the final products. Wood fibers have a typical fibrous shape with a length of up to 3 mm, while the solid residues of pea, bran, and potato fillers after the extraction of proteins, starch, or flour, respectively, were composed of platelets, as well as round-shaped fractions in the case of protein and starch (Figure 1). Thus, these latter biomasses have a shape that is more typical of a filler than of a fiber, as reflected by the mechanical performance of the produced composites [10].

Figure 1. Scanning electron microscopy image of wood fibers, pea, bran, and potato fillers.

In all of the biocomposites, with the increase in the fiber content regardless of the type fibers used (wood, bran, wheat, or pea), the elastic modulus increased, while elongation at the break decreased, as the presence of the lignocellulose fillers increased the stiffness in the material. This trend is typically observed in particle-filled materials with a polymeric matrix in the case of poor or no compatibility among the matrix and the filler, that is, the presence of weak interfacial interactions. This occurs often in composites with polymers and wood flour since the surface-free energy of both the filler and polymer is low, and, consequently, stress transfer phenomena cannot occur; in this case, the particle of the filler becomes a concentrator for stresses, and this can lead to early fracture.

To predict the behavior of materials in terms of the amount of fiber varieties, models that considered the length of the fibers, their orientation, and the geometric factors, such as the aspect ratio (ar), have been studied. For instance, Pukanszky's model is developed to predict the behavior of composite materials, in which the dispersed phase consists of particulate or short fibers, and it examines the geometric factors, the quantity of fiber contained within the material, and the adhesion between the matrix and filler [11–13]. In this formula, the strengthening action of the filler is quantified by the lowering of the effective load-bearing cross-section of the polymer.

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

$\sigma_{c,red}$ 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; 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 is related to the interfacial properties of the system and expresses the adhesion between the filler and polymeric matrix, which is higher with better adhesion.

The B parameters calculated for the prepared composites are reported in Table 1.

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

By-Product	B
Wood Fibers	2.47
Potato Fibers	2.33
Pea Fiber	1.98
Bran Fibers	0.67
Bran Fibers T581	0.45
Bran Fibers T561	1.53

The data reported in the above table confirm what was observed for the mechanical properties; thus, a higher value of B is observed for bio-composites with better values in mechanical strength. In particular, the data confirm an improvement in adhesion between the bio-polyester matrix and the natural fibers when the biomass is treated with beeswax.

5. Conclusions

Biomass from agro-food industries can be valorized in several applications from the simplest use of natural fibers and fillers in biocomposite production to biomolecule extraction and use for advanced materials to be applied in packaging, cosmetics, and agriculture.

Composites based on PHA and fibers showed good processability by injection molding, from 20% to 30% fiber content. Elongation at break values was lower when the load of fibers increased, while the tensile strength slightly decreased. Young's modulus increased with an increase in fiber loading, as well as the absorbed impact test energy. Factor B , calculated by applying Pukanszky's model, expresses the tensile behavior of the composites and, in the analyzed cases, represents medium intensity adhesion between the fibers and polymer matrix (wood, peas, and potato). Improvement of adhesion can be achieved with fiber surface treatment with natural waxes to compatibilize it with the polymeric matrix. The presence of fibers lowers the cost of biocomposites and promotes biodegradation and sustainability.

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Informed Consent Was Obtained from all Subjects Involved in the Study: The data presented in this study are available on request to the corresponding author. The data are not publicly available due to the confidentiality of the AGRIMAX project.

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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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