Biocomposites Based on Polyhydroxyalkanoates and Natural Fibres from Renewable Byproducts

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Abstract

Background and Objective: The use of biopolymers and natural fibres or fillers for production of biobased composites has attracted interest of various application sectors ranging from packaging to automotive components and other high value applications in agreement with a bioeconomy approach. In the present paper biobased composites were produced by using compostable polymers degradable even in soil and marine water such as polyhydroxyalkanoates with natural fibres or fillers derived by food wastes (legumes by-products) and by wood industry.

Material and Methods: Polyhydroxyalkanoates were processed with a biobased, biodegradable plasticizer such as acetyltributylcitrate and calcium carbonate as inorganic filler. The selected polymeric matrix was used for the production of composites with variable amounts of natural fibres. Green composites were manufactured by extrusion and injection moulding. Thermal, rheological, mechanical and morphological characterizations of the developed composites were performed.

Results and Conclusion: The bio composites properties match the requirements for production of rigid food packaging or other single use items where the market is looking for more sustainable solutions versus the products actually used and hardly recyclable, opening a route for valorization of food residue. Pukanzsky’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.

Conflict of interest: The authors declare no conflict of interest.

1. Introduction

Natural polymers, biopolymers and synthetic polymers based on annually renewable resources are the basis for the twenty-first century portfolio of sustainable, eco-efficient plastics. The interest in these polymers is considerable in the prospect to decrease the world resources in oil and in a concern to limit the contribution of plastics to the waste disposal [1,2]. The world petro-plastic production reached ca. 335 million tons (Mt) in 2015 and it is expected to double again over the next 20 years [3]. To reduce the problem of recycling of petro-based plastics and minimize their environmental impact, research efforts are rising in the field of bioplastics around the world. Petrol plastic wastes accumulation in natural environments is raising and generating the interest for new materials with high sustainability, biodegradability and relevant performances. In this contest, bio-composites produced with biodegradable, biobased polymeric matrices and fibres of natural origin, derived from by-products or over production, are one of the most important categories of material being considered by the market for applications in packaging, agriculture and even for transport, buildings and electronics [4,5].

Polyhydroxyalkanoates (PHAs) are microbial polyesters that can be synthesized by a wide range of microorganisms under conditions of nutrient stress, with thermoplastic properties similar to those of conventional plastics [6-9]. One of the main limitations in the application of PHAs, for the production of single use items, is based on their
relatively high cost (7-10 Euro kg\(^{-1}\)) compared to other polymers, restricting their use to high-value applications, such as those in medical and pharmaceutical sectors [10,11]. Due to the increasing production in emerging countries a reduction in the cost of the PHAs is envisaged. Moreover, use of largely available and low-cost natural and inorganic fillers can allow the production of cost sustainable PHA-based composites that can be proposed in those applications where the PHAs biodegradability in compost, soil and marine water represents a main plus as for example, packaging and agriculture [12]. Due to the advantages of low cost, large availability, low density, valuable mechanical and physical properties, a wide variety of lignocellulosic fibres and natural fillers coming from agricultural and industrial crops, such as corn, wheat, bagasse, orange and apple peel, abaca, kenaf, hemp, flax, and jute were used in the production of composites in various industrial sectors, such as packaging, automotive industry, and building [13-17]. As polymeric matrices PHAs have been blended with a large variety of natural materials derived from the food and agriculture sector and even with algae and sea grasses derived fibres [18-21].

The use of fibres or fillers derived from food by-products is raising of interest, even because of increased production of protein extracted from vegetal, and in particular from legumes, as integrator of vegetarian and vegan diets. Consequently the interest of using for example pea solid residue, remaining after protein extraction from pea by-products, for bio composites production is increasing in the last decade. Chen et al. [22] explored new comprehensive applications of pea products including pea’s starch and pea’s hull fibres (PHF) and the derived nano whiskers. Ralet et al. [23] evaluated the effects of extrusion-cooking on pea hulls. Two batches of pea hulls of different average particle size (80 µm and 500 µm) were extruded under various conditions; in all cases, the water-solubility of the product increased and physical properties of extruded pea hulls, and particularly their hydration properties, are not markedly modified by extrusion-cooking.

In the present paper a contribute to knowledge and advancement in research on bio-based composites has been reported, in particular bio composites were produced with biopolymers such as PHAs, specifically poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), biodegradable in different environments, with natural fillers from agro-food industrial waste (legume fibres) and lignocellulosic fibres such as soft wood sawdust. Composites based on PHAs and the natural fibres were produced by extrusion in presence of appropriate amounts of a biobased biodegradable plasticizer and inert inorganic fillers. Composite materials consist of two or more phases in particular it is possible to distinguish a continuous and a dispersed phase. The geometry, the quantity and the characteristics of the dispersed phase have an influence on the final properties of the composite material produced. In the case in which the dispersed phase is constituted by fibers one of the parameters that most affects the final characteristics of the material is the orientation and the characteristic length of the fibers. The eventual twisting of natural short fibers inside polymeric matrices can be taken into account thanks to a waviness factor [24-26]. Thus in the present paper an investigation on fibre-matrix adhesion to better explain the effect of fibres content on biocomposites performances was addressed on both composites prepared with wood fibres and pea’s fibres and the Pukanszky’s model was applied to the produced composites in order to estimate the adhesion between fibres and polymeric matrix [27].

2. Materials and methods

2.1. Materials

PHAs was PHI002™ used as a thermoplastic matrix, supplied in pellets by Naturplast® (Caen, France). It is a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), with 5% w valerate content, characterized by a melting point of 145-150°C, a density of 1.25 g (cm\(^3\))\(^{-1}\), and a melt flow index of 10-20 g (10 min\(^{-1}\))(190°C, 2.16 kg). In order to improve the processing ability of the composites at high content of fibres, acetyltributylcitrate (ATBC) from Sigma Aldrich (Sigma Aldrich, St. Louis, MS, USA) was selected as plasticizer for PHBV. ATBC is almost colourless and odourless oily liquid. In order to reduce the cost of the final product and facilitate the removal of the product from the mold calcium carbonate OMYACARB® provided by OMNYA® (Oftringen, Switzerland) as filler with fine grain size distribution (12 µm) was used. The Sawdust was a commercial product from softwood, and pea fibres were provided by Stazione Sperimentale per l’Industria Conserva Alimentari SSICA, Parma, Italy, as by-products of pea’s protein extraction from discarded pea. Sawdust and pea’s fibres were dried at 80°C in an electric oven for 24 h, then the materials were milled using a lab-scale mill and sieved with a 500 µm sieve. An image, recorded with a scanning electron microscopy (100x and 300x) of respectively the pea’s fibres (Figure 1a) and wood fibres (Figure 1b) is reported in Figure 1.

![Figure 1. SEM Image of respectively a) peas fibres and b) wood fibres](image-url)
2.2 Composites preparation and characterization

Formulations with 10, 20, 30% by weight respect to the total weight of different fibres (pea, wood fibres), were produced using the 85:5:10 w%:w%:w% PHBV/CaCO₃/ATBC blend as polymeric matrix. The nomenclature of the samples was as follows: The acronym PCA was used for the polymeric matrix based on (PHBV/CaCO₃/ATBC) and PCAWF10, PCAWF20, PCAWF30 for the composites containing the different wood fibre (WF) loadings: 10, 20 and 30 w%, and PCAPEF10, PCAPEF20, PCAPEF30 for the composites containing the different pea’s fibre loadings: 10, 20 and 30 w% on the total composite weight, respectively. The composites were prepared by mixing the different components and then the obtained mixtures were processed in a Thermo Scientific Haake Minilab Micro-compounder (Minilab), a co-rotating conical twin-screw extruder. The extruder operating conditions adopted for all the formulations are reported in Table 1, where by melting and mixing an extruded filament exited through the flush orifice. During the melting process in Minilab the torque momentum and the pressure were recorded to evaluate the fiber effect on the melt fluidity, as reported in Figure 2. For each formulation, specimens for the tensile test (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).

Tensile tests were performed on the injection moulded Haake Type 3 dog-bone tensile bars of composites in accordance with ASTM D 638. Stress-strain tests were carried out at room temperature, at a crosshead speed of 10 mm/min, by an Instron 5500R universal testing machine (Canton, MA, USA) equipped with a 10 kN load cell and interfaced with a computer running the Testworks 4.0 software (MTS Systems Corporation, Eden Prairie, MN, USA) at least five replicates were carried out at room temperature for each sample. Impact properties were evaluated on V-notched specimens using a 15 J Charpy pendulum (CEAST 9050, Instron, Canton, MA, USA) following the standard method ISO 179: 1993.

3. Results and discussion

3.1 Composite production and mechanical properties

As reported in Figure 1, the shape and morphology of wood and pea’s fibres appeared quite different. Wood fibres have a typical fibrous shape, with length up to 3 mm, while the pea’s solid residue, after extraction of proteins, is composed even by platelets and round shaped fraction as residue of protein and starch. Thus this last biomass has a shape more typical of a filler than of a fibre, as reflected by the mechanical performance of the produced composites. Consequently we envisage a benefit in the use of peas fillers in terms of improved degradability, improved content of low cost biobased biomass residue, and thus reduced cost and environmental impact of composites, versus a mode rate loss in mechanical properties that still meet the technical requirements for rigid packaging applications.

Table 1. Processing parameters

<table>
<thead>
<tr>
<th>Extrusion temperature (°C)</th>
<th>Screw speed (rpm)</th>
<th>Cycle time (s)</th>
<th>Injection temperature (°C)</th>
<th>Injection pressure (bar)</th>
<th>Moulding time (s)</th>
<th>Mould temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>170</td>
<td>100</td>
<td>60</td>
<td>170</td>
<td>300</td>
<td>20</td>
<td>60</td>
</tr>
</tbody>
</table>

Figure 2. Torque trend in processing of composites with PCA and respectively wood fibres and peas fibres at 10%, 20%, 30% by weight. PCA= poly (3-hydroxy-butyrate-co-3-hydroxyvalerate), CACO₃, acetyl tributyl citrate (ATBC).
In Figure 2, are reported the values of the torque recorded during processing of the formulations used for the production of the composites in the minilab extruder. The torque values trend attest for a smooth processing and for no degradation of the polymeric matrix during the processing time frame.

The mechanical properties of the composites, evaluated by tensile tests, are reported in Table 2 and by impact test in Table 3.

Table 2. Mechanical properties of the composites with different fibres

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s modulus (GPa)</th>
<th>Stress at break (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCA</td>
<td>2.2 ± 0.1</td>
<td>27.9 ± 0.9</td>
<td>2.9 ± 0.3</td>
</tr>
<tr>
<td>PCAWF10</td>
<td>2.3 ± 0.2</td>
<td>23.2 ± 0.6</td>
<td>3.2 ± 0.3</td>
</tr>
<tr>
<td>PCAWF20</td>
<td>2.5 ± 0.2</td>
<td>23.1 ± 0.5</td>
<td>2.6 ± 0.3</td>
</tr>
<tr>
<td>PCAWF30</td>
<td>3.0 ± 0.1</td>
<td>21.7 ± 0.3</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td>PCAPEF10</td>
<td>2.1 ± 0.1</td>
<td>21.0 ± 0.2</td>
<td>2.9 ± 0.3</td>
</tr>
<tr>
<td>PCAPEF20</td>
<td>2.2 ± 0.1</td>
<td>18.5 ± 1.2</td>
<td>2.3 ± 0.2</td>
</tr>
<tr>
<td>PCAPEF30</td>
<td>2.6 ± 0.1</td>
<td>16.2 ± 0.9</td>
<td>1.5 ± 0.2</td>
</tr>
</tbody>
</table>

P = PHBV, C = CaCO₃, A = ATBC, WF = Wood Fibres, PEF = Pea’s Fibres

Table 3. Impact strength of wood fibres based composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charpy Impact Strength (kJ (m²)⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCA</td>
<td>2.47 ± 0.5</td>
</tr>
<tr>
<td>PCA10PEF</td>
<td>2.81 ± 0.7</td>
</tr>
<tr>
<td>PCA20PEF</td>
<td>3.04 ± 0.6</td>
</tr>
<tr>
<td>PCA30PEF</td>
<td>2.41 ± 0.3</td>
</tr>
<tr>
<td>PCA10WF</td>
<td>2.86 ± 0.8</td>
</tr>
<tr>
<td>PCA20WF</td>
<td>3.75 ± 0.2</td>
</tr>
<tr>
<td>PCA30WF</td>
<td>3.29 ± 0.6</td>
</tr>
</tbody>
</table>

P = PHBV, C = CaCO₃, A = ATBC, WF = Wood Fibres, PEF = Pea’s Fibres

In all the cases, with increasing the fibres content regardless of type fibres used (wood 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 [28-30].

The results of the Charpy’s impact test showed that the composites with natural fibres present valuable values of impact resistance, compatible with packaging applications and best properties are observed for 20% by weight of natural fibre content (Table 3), while for 30% content of fibres there is a lowering of impact strength due to excessive presence of zones with low adhesion between fibres and polymeric matrix.

The marked increase of the impact resistance with increasing fibre loading up to 20% by weight can be attributed to the poor fibre/matrix interaction since the impact failure of a composite occurs by factors such as fibre/matrix debonding, fibre and/or matrix fracture and fibre pull out. Fibre fracture dissipates less energy compared to fibre pull out, and this is common in composites with strong interfacial bonds, while the occurrence of the latter is a sign of a weak bond [31-34]. The applied load transferred by shear to fibres may exceed the fibre/matrix interfacial bond strength and the composites fracture in a brittle mode, which is in agreement with the experimental results, and with observation of SEM image of a specimen based on the polymeric matrix PCA (Figure 3a) compared to a composites with 20% of fibres, PCASF20 (Figure 3b) as reported in Figure 3 showing the specimen (fractured in liquid nitrogen) before and after fracture in the tensile test.

![SEM image of a) PCA polymeric matrix and b) composite with 20% of wood fibres, PCASF20, before and after tensile test.](image)

3.2 Simple evaluation of the fibres-matrix adhesion through Pukanszky model

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 (a). There are various types of models that differ from each other for parameters and types of fiber addressed. Generally, the models reported in literature refer to long fibers, because their presence inside the composite can significantly modify the behavior of the overall material [35-37]. The Pukanszky’s model is developed to predict the behavior of composite materials in which the dispersed phase consists of particulate or short fibers. This model takes into account geometric factors, the quantity of fiber contained within and the adhesion between matrix and filler [27,38]. Pukanszky’s model is the one that
most lends itself to predict the mechanical behavior of short fiber composites of which little information is available.

Pukanszky’s model was applied to composites prepared with respectively wood fibres and pea’s fibres. Many models have been proposed in the specific literature to predict the yield stress of composites. Pukanszky’s model [27] describes the effects of the volume filler fraction ($\phi_f$) and the interfacial interaction on tensile yield stress of particulate filled polymers (Eq. 1):

$$\sigma_c = \sigma_m \frac{1 - \phi_f}{1 + 2.5 \phi_f} \exp(B\phi_f)$$  \hspace{1cm} (Eq. 1)

Parameter B is an interaction parameter that considers the capacity of stress transmission among the various components. This value gives an estimate of the interaction between the fiber and the matrix and in particular of the adhesion between the fibers and the matrix. The terms $\sigma_c$ and $\sigma_m$ are yield stresses of the composites and matrix, respectively. The term $\exp (B\phi_f)$ indicates the interaction, while the term $(1-\phi_f) (1+2.5\phi_f)^{-1}$ indicates the effective decrease of useful cross section due to filler introduction. Interfacial interaction depends on B parameter, that is correlated to the thickness of the interphase, and the strength of the interaction is shown in the Eq. 2.

$$B = \left(1 + A_f \rho_f \right) \ln \frac{\sigma_c}{\sigma_m}$$  \hspace{1cm} (Eq. 2)

Where $A_f$, $\rho_f$, $l$, $\sigma_c$, $\sigma_m$ are the specific surface area, density of the filler, thickness of the interphase and strength of interaction, respectively. Parameter B can be easily calculated by knowing the yield stress of the composites filled with different volume percentages of particle fillers.

We can write Eq. 1 in linear form and plotting the natural logarithm of Pukanszky’s reduced (adimensional) tensile strength against volume fraction should result in a linear correlation, the slope of which is proportional to the interaction parameter B (Eq. 3).

$$\ln(\sigma_{red}) = \ln \left(\frac{\sigma_c(1 + 2.5\phi_f)}{\sigma_m(1 - \phi_f)}\right) = (B\phi_f)$$  \hspace{1cm} (Eq. 3)

The Pukanszky’s model is a good starting point for predicting the behavior of filler-reinforced composites, useful when there is little information regarding the fibers used.

The model has been applied to the following polymers showed in Tables 4 and Table 5. From the graphs shown in Figures 4 for wood fibres, and in Figure 5 for pea’s fibres it is possible to derive the angular coefficient of the straight line representing the parameter B of the Pukanszky’s model, this index gives a measure of the adhesion between the matrix and the fibre.

Table 4. Values of Pukanszky’s model parameters for wood fibres

<table>
<thead>
<tr>
<th>Sample</th>
<th>$p$ [g/cm³]</th>
<th>%vf</th>
<th>$\sigma_m$ (MPa)</th>
<th>$\sigma_c$ (MPa)</th>
<th>$l$ (mm)</th>
<th>$\phi_f$</th>
<th>$\eta_f$</th>
<th>D (mm)</th>
<th>$\alpha$</th>
<th>ln red</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCAWF10</td>
<td>0.46</td>
<td>0.23</td>
<td>27.87</td>
<td>20.59</td>
<td>0.25</td>
<td>0.230</td>
<td>0.20</td>
<td>0.025</td>
<td>10</td>
<td>0.41</td>
</tr>
<tr>
<td>PCAWF20</td>
<td>0.46</td>
<td>0.40</td>
<td>27.87</td>
<td>21.63</td>
<td>0.25</td>
<td>0.402</td>
<td>0.20</td>
<td>0.025</td>
<td>10</td>
<td>0.96</td>
</tr>
<tr>
<td>PCAWF30</td>
<td>0.46</td>
<td>0.53</td>
<td>27.87</td>
<td>20.35</td>
<td>0.25</td>
<td>0.536</td>
<td>0.20</td>
<td>0.025</td>
<td>10</td>
<td>1.30</td>
</tr>
</tbody>
</table>

$P$ = PHBV, $C$ = CaCO$_3$, $A$ = ATBC, $WF$ = Wood Fibres

Figure 4. Plotting and calculation of B parameters for composites with wood fibres

Figure 5. Plotting and calculation of B parameters for composites with peas fibres
Table 5. Values of Pukanszky’s model parameters for pea’s fibres

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \rho )(^{[g (cm^3)^{-1}]} )</th>
<th>%vf</th>
<th>( \sigma_{in} ) (MPa)</th>
<th>( \sigma_{r} ) (MPa)</th>
<th>l (mm)</th>
<th>( \theta_{f} )</th>
<th>( \theta_{p} )</th>
<th>D (mm)</th>
<th>a</th>
<th>ln red</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCAPEF10</td>
<td>0.5</td>
<td>0.21</td>
<td>27.87</td>
<td>21.00</td>
<td>0.25</td>
<td>0.317</td>
<td>0.20</td>
<td>0.025</td>
<td>10</td>
<td>0.40</td>
</tr>
<tr>
<td>PCAPEF20</td>
<td>0.5</td>
<td>0.38</td>
<td>27.87</td>
<td>18.48</td>
<td>0.25</td>
<td>0.510</td>
<td>0.20</td>
<td>0.025</td>
<td>10</td>
<td>0.75</td>
</tr>
<tr>
<td>PCAPEF30</td>
<td>0.5</td>
<td>0.51</td>
<td>27.87</td>
<td>16.24</td>
<td>0.25</td>
<td>0.641</td>
<td>0.20</td>
<td>0.025</td>
<td>10</td>
<td>1.02</td>
</tr>
</tbody>
</table>

\( B \) = Parameter obtained for each fibre (Table 6) used confirmed in accordance with mechanical properties that there is no good adhesion between matrix and fibres, confirming increase of elastic modulus associated with loss of tensile strength, but there is a medium intensity adhesion between fibres and polymer matrix, justifying still valuable impact resistance.

**4. Conclusion**

Composites based on PHA, in presence of ATBC as plasticizer, and calcium carbonate as inorganic filler, with wood or peas fibres, as biobased fillers, showed a good process ability up to 30% of fibre content. Elastic modulus increased, while tensile strength and elongation at break decreased with increasing fibres loading, due to medium-low adhesion between fibres and polymeric matrix, and in the case of pea’s fibres to the shape and size of the peas residue more similar to a filler than to a fibre. The mechanical properties of the composites resulted, anyway valuable for applications in rigid food packaging, tableware etc. or single use agriculture items such as pots. Pukanszky’s model predicts with a good accuracy the tensile behaviour of the composites showing a medium intensity adhesion between fibres and polymer matrix in both cases analysed, in agreement with the trend of mechanical properties observed for increased fibres content. The present composites allow the valorisation of food residue such as peas fibres, left over of peas by-products treatment after protein extraction, for the production of sustainable composites. This results in benefits in terms of cost reduction, due to saving of expensive polymeric matrix, and improved sustainability due to promoted degradability and use of consistent fraction (up to 30% by weight) of a residue from food production (pea, pea’s proteins), in agreement with a circular bio economy approach.

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**6. Conflict of interest**

The authors confirm that this article content has no conflict of interest.

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چکیده

زیچندسازه‌های (Biocomposite) بر پایه فیبرهای طبیعی و پلی‌هیدروکسی آلکانواکسی آلکانواکسی‌های حاصل از فرآورده‌های جانبی تجدیدپذیر از فرآورده‌های جانبی تجدیدپذیر پاتریشیا سینلی، نورما مالنگی، ویتو جیجانته، آنجلا مونتاواری، ماریزیا سجیانی، ماریا بئاتریس کلنتی، سیمونا برونکو، آندریا لازری، پاتریشیا سینلی، نورما مالنگی، ویتو جیجانته، آنجلا مونتاواری، ماریزیا سجیانی، ماریا بئاتریس کلنتی، سیمونا برونکو، آندریا لازری

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قبولهای جانبی مواد‌های خاص

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