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Valorization of oat hull fiber from agri-food industrial waste as filler for poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate)

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Abstract:

Oat hull fibers are an agri-food industrial waste used in this research as a filler for a poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) matrix, in order to obtain a fully bio-based polymer-matrix composite material. The compounding process was carried out with a twin-screw extruder, avoiding chemical solvents and employing a technology commonly used by the industrial field. Silanization procedure was run to improve the affinity between the matrix and the filler. Compounds were structurally, microstructurally, mechanically and thermally characterized. Results denote that also at 8 v/v%, oat hull fibers work not only as inert filler, but also they have a slightly improving effect on mechanical properties of neat biopolymer, increasing of almost 12% the Young's modulus, without a loss in tensile elongation at break. Therefore, this research study is a noteworthy approach which reduces the material costs and PHBH volumes, while valorizing waste biomasses.

Keywords:

Oat hull fibers
Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate)
Bio-based and biodegradable compounds
Silanization
Melt compounding

1. Introduction:

Environmental issues, sustainability of human lives, depletion of natural resources and pollution caused by all kind of waste are raising always more interest in the modern global discussion. [1, 2] Scientific research is also focusing on the possible changes for a better and safer future; in particular bio-based and biodegradable materials are attracting more interest for industrial application. [3, 4] A copolymer of polyhydroxyalkanoates (PHAs), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) is starting to be highly investigated due to its biodegradability, versatility, processability and mechanical properties. Considering a possible sector of application of this biopolymer with large production volumes for durable and semi-durable goods, such as household crockery or gardening accessories, the substitution of petroleum-based polymers with eco-friendly and sustainable materials would have a really high and positive impact on the environment. However, this replacement is still hindered by the cost of biopolymers compared to traditional plastic. [5] In order to overcome this limitation, some research studies have been conducted to replace part of the bulk amount of pristine PHA with a filler and, so far, different biowastes have been tested such as wine wastes, [6] rice husk ash, [7, 8] coffee wastes, [9] carnauba fibers, [10] waste wood sawdust fibers [11] and also keratin from poultry feathers. [12] Plant derivatives is another attractive class of materials that seems to be auspicious for their wide mechanical properties and thus range of applications, particularly as bio-based fillers for biopolymers. To date, many research studies have been carried out, focusing on the different reinforcing effect of cellulosic based materials in several polymer matrices, according to their morphology (crystals or fibrils), their dimensions (micro or nano sizes) or their origin (plants or bacteria). [13, 14] To the best knowledge of the authors, only a limited exploration has been conducted to determine the effect of oat hull fibers (OHF) as filler for a polymer matrix. Here, the novelty of this research study is that a fully bio-based composite material was obtained starting from a PHBH matrix, which was chosen as only component rather than a blend of different synthetic and fossil-based polymers. [15–17] A limitation of the former research is that the filler worked properly as a replacement for the polymer matrix, but the mechanical properties of the composite were affected by this. [15, 16, 18] Compared to our prior work, [19] this research investigates even the possibility of saving energy by avoiding the high-pressure homogenization step and using the pristine OHF.

2. Experimental

OHF were provided by GEA Mechanical Equipment (Parma, Italy) as a powder. The fibers were obtained as a waste from the oat processing. The fibers morphology is composed of fibrils many hundreds of microns long and several tens of microns thick; their aspect ratio is about 20. PHBH is a copolymer of 3-hydroxybutyrate (3HB) and 3-hydroxyhexanoate (3HH). The PHBH pellets were kindly provided by MAIP Group (MAIP SRL, Turin, Italy) and the composition ratio is 89 mol% of 3HB and 11 mol% of 3HH. This composition was chosen because it represents the semi-rigid grade of PHBH and it has balanced values of ductility and elastic modulus, broadening the possible application fields. Ammonium hydroxide 30% was purchased from Carlo Erba Reagents Co. Ltd (Milano, Italy), ethanol was purchased from J.T.Baker Co. Ltd (Phillipsburg, United States of America), methyltriethoxysilane (MTES, Dynasylan) was purchased from Evonik Industries (Rheinfelden, Germany) and the paraffinic oil "Vestlan" was provided by Tizi S.R.L. (Arezzo, Italy). MTES was used as coupling agent to improve the affinity between the hydrophobic polymeric matrix and the hydrophilic OHF. The fiber silanization was pursued following some procedures already tested in previous researches, chosen in accordance with the aim of the research: the valorization

of a waste without further energy and time consuming. The procedure consists in mixing the fibers with an hydroalcoholic solution in acid or basic environment: [20, 21] firstly, a suspension was prepared adding 2.5 g of fibers in 48 mL of water and 74 mL of pure ethanol. Then, 3.6 mL of ammonium hydroxide solution were added to the previous suspension under magnetic stirring. The obtained suspension was placed into a constant-temperature oil bath at 50 °C and equilibrated for 30 min. After the dispersion reached uniform temperature, 1 mL of MTES was added, drop by drop, and stirring continued at 50 °C for 20 h. The same procedure was followed without OHF in order to obtain a reference sample of sol-gel reaction of MTES, which is referred as hydrolyzed MTES. The resulting suspension was washed from the excess of MTES by two subsequent centrifugations and redispersions in ethanol. The obtained precipitate was vacuum dried at 35 °C overnight and then milled by an A 10 basic mill (IKA).

Before any processing, PHBH pellets were oven-dried at 85 °C overnight and then they were manually pre-mixed with oat hull powder and some drops of paraffin oil, for a better adhesion with the pellets. Thereafter, the mixtures were melt compounded using a co-rotating twin-screw extruder (Haake Extruder Rheomex CTW100p). After extrusion, the obtained filament was granulated by a pelletizer (Scheer SGS 25-E4), and then processed to obtain standard tensile test specimens (UNI EN ISO 527-2, type 1 BA) by injection molding (Tecnicaduebi MegaTech H7/18-1).

In this study, two different concentrations were prepared to evaluate the effect of the filler volume content: the first one at 2 v/v% (PHBH/OHF_2) and the second one at 8 v/v% (PHBH/OHF_8). To appraise the effect of the silanization procedure, the sample with the higher amount of cellulose was also prepared with the silanized fiber (PHBH/OHF_SIL_8).

The true density of OHF was calculated by the helium pycnometer Ultrapyc 1200e (Quantachrome Instruments, Boynton Beach, USA). About 1 g of sample was placed in the 10 cm^3 sample cell and the density was measured as the mean of 20 measurements.

The cryofracture surface of injection-molded specimens and the filler morphologies were investigated using a Quanta-200 Environmental Scanning Electron Microscopy (ESEM – Fei Company, Thermo Fischer Scientific). In order to highlight the presence of silicon due to surface functionalization, energy dispersive X-ray spectroscopy (EDS) microanalysis data were acquired by an X-EDS Oxford INCA-350 microanalysis system (Oxford Instruments) on OHF.

In order to prove the successful functionalization, Fourier Trasform-Infrared (FT-IR) spectra of the non-treated and silanized fillers were recorded with a FT-IR Vertex 70 spectrophotometer. Thermal properties were investigated by a Differential Scanning Calorimeter (DSC 2010, TA Instruments), under nitrogen atmosphere, in order to evaluate the glass transition temperature (T_g) and the melting temperature (T_m) of the obtained composites. The crystallinity degree (X_c) of PHBH matrix and compounds was calculated according to the equation previously reported: [22]

$$X_c = \frac{\Delta H_m}{\Delta H_m^0 (1 - w_f)} \times 100$$

where ΔH_m^0 (115 J/g) is the enthalpy of 100% crystalline PHBH, [13] w_f is the mass fraction of filler and ΔH_m is the measured enthalpy of melting. Tensile tests were carried out at a crosshead speed of 2 mm min^{-1} on a tensile testing machine (Universal Testing Machine, TesT GmbH) equipped with a 2 kN load cell, according to UNI EN ISO 527-1. Five specimens were tested for each sample.

3. Results and discussion

3.1 Effect of silanization

Fig. 1(a) shows the two powders, respectively of pristine fibers and silanized ones, dispersed in water. It is easy to qualitatively evaluate the treatment effect onto OHF: before silanization OHF are easily wettable, while after silanization (OHF_SIL) they stay afloat and do not even get wet, showing an explicitly hydrophobic behavior. Fig. 1(b) and (c) report the SEM images of neat OHF before (b) and after (c) silanization. The OHF morphology is composed of long fibrils with a length (L) of several hundreds of microns and a width (d) of some tens of microns. Their aspect ratio (L/d) is about 20. However, the sample shape is quite heterogeneous, and some particles have different geometry and smaller aspect ratio. The comparison of fig. 1(b) and (c) illustrates that the silanization process does not affect the morphology of the filler. EDS spectrometry was used for qualitative evaluation of the surface compositions of treated and untreated fibers; fig. 1(d) and (e) illustrate the obtained results regarding the elemental composition. The untreated oat hull fibers spectrum only shows peaks corresponding to C and O, fig. 1(d). In the spectrum of the silanized OHF, an additional peak was observed, corresponding to Si, fig. 1(e).

Fig.1(f) shows the FT-IR spectra of pristine MTES (named MTES), reaction products of MTES after hydrolysis and condensation (named MTES_hydrolized), neat OHF and silanized OHF_SIL. The comparison between MTES and MTES_hydrolized are reported to evaluate the spectroscopic features of hydrolysis and condensation reaction products of MTES, which are supposed to be found also onto OHF_SIL. On both spectra, the characteristic peak at 2971 cm^{-1} is attributed to the asymmetric stretching of -CH$_3$, [20] in the −OCH$_2$CH$_3$ and -Si-CH$_3$ groups of MTES, [22] while the peaks at 2923 and 2881 cm^{-1} are ascribed respectively to the asymmetric and symmetric stretching of -CH$_2$ of the ethoxy group. [23] After sol-gel reaction the peaks at 2923 cm^{-1} and 2881 cm^{-1} disappeared. This clearly indicates that no more ethoxy group are bound to Si. In MTES spectrum the peaks at 1167 cm^{-1}, 955 cm^{-1}, 818 cm^{-1}, and 777 cm^{-1} are attributed to the characteristic IR absorption of Si–OCH$_2$CH$_3$ bond. In hydrolyzed MTES spectrum, the intensities of these peaks decrease considerably after sol-gel reaction, [24] as a consequence of the ethoxy groups hydrolysis. Comparing the untreated OHF and the OHF_SIL spectra, hydrolyzed MTES typical peaks are observed only on the latter spectrum, denoting the actual condensation of the coupling agent on the OHF surface, any auto-condensation product of silane was removed by the washing procedure. These peaks are at 2971 cm^{-1}, 1271 cm^{-1} and 766 cm^{-1}, corresponding to the asymmetric stretching of -CH$_3$, the bending of -CH$_3$ and the stretching of Si-O-Si. [23, 25] Assuming that the -OH groups represent the anchor points of the alkoxysilanes during the silanization process, the OHF degree of silanization was quantitatively evaluated, from FT-IR spectra, by calculating the decrease in -OH peak areas, in the range 3700 ÷ 3000 cm^{-1}, before and after the functionalization. Spectra were normalized to the peak intensity at 1032 cm^{-1}, referred to C–O–C stretching mode of skeletal vibration of pyranose ring. [26, 27] The results showed that in OHF_SIL spectrum the –OH peak area decreased of about 33%, indicating that about one third of the -OH groups were replaced by -O-Si-CH3 groups during the silanization process.

3.2 Composites characterization

The presence of OHF in the composite material is detected by structures extended out of the fracture surface in fig. 2 (b) and (c). These structures are not observed in the neat sample (fig. 2(a)). Fig. 2 (c) clearly shows the effect of silanization, highlighting a good adhesion between the PHBH and OHF. This is attributable to a better chemical affinity of the apolar condensed Si-CH$_3$ groups

onto fibers surface. Whereas untreated fibers, in fig. 2 (b), seem to exhibit weaker interfacial compatibility with the polymeric matrix.

Mechanical properties of neat PHBH and PHBH/OHF composites are shown in fig. 3. Adding oat hull fibers to PHBH the Young's modulus of PHBH composites increased. With increasing filler content, Young's modulus of composites was gradually raised from 1700 ± 70 MPa to 1900 ± 50 MPa, with a growth of 11.5%. Silanized and neat OHF show moderate reinforcing effect in PHBH composites, with variations within the standard deviation of tensile strength of PHBH composites.

Comparing the values of PHBH/OHF_8 and PHBH/OHF_SIL_8, we can conclude that silanization enhances the Young's modulus values of 3%, and tensile elongation at break decreases of almost 14,5%. The better surface interaction between matrix and filler, due to improved chemical compatibility, leads to a higher stiffness of the composite. The lower tensile elongation at break is a consequence of the higher system stiffness. [28] These results are aligned with those obtained in previous research studies, with similar systems [26, 29] and with different polymer matrices and fillers. [30–32] Inorganic fillers give a more evident increase in elastic modulus and decrease in elongation at break of the final composites. This is due to the higher Young's modulus of conventional inorganic fillers such as glass fibers (80 GPa) [33] and silica nanoparticles (80 GPa) [34] compared to the one of OHF, which is one order of magnitude lower. [35]

The obtained ultimate tensile strength values are also similar to those presented in a previous work and do not vary significantly. [36]

Thermal transitions and degree of crystallinity of neat PHBH and PHBH/OHF composites were analyzed by DSC. The main thermal properties are summarized in table 1.

All thermal properties and the crystallization processes are only marginally affected by the addition of OHF to PHBH and by the silanization process, and a clear correlation between thermal properties and filler content cannot be identified. These results are in line with the ones showed in previous researches, where no significant variations of thermal behavior of PHBH can be observed as a function of cellulose based filler content. [37, 38]

4. Conclusions

This work demonstrated that OHF can be positively used as filler for biopolymer matrix without affecting negatively neither the thermal nor the mechanical properties. On the contrary, the results evidenced a slightly improvement of the latter ones, with an increase of almost 12% of Young's modulus, without a loss in tensile elongation at break for PHBH/OHF_8.

The FT-IR and SEM findings add evidences indicating that the silanization procedure occurred positively, not modifying the fiber morphology and enhancing the fiber adhesion with the matrix. Nevertheless, the effect of functionalization upon mechanical properties is not so pronounced: at the same filler content, there is an increase of Young's modulus against a decrease of elongation at break and a maintenance of ultimate tensile strength. For this reason, the results suggest that oat hull fibers can also be used as received, without any other functionalization, in order to decrease the time and the cost of processing.

Despite no major improvements in composite properties were observed, the proposed approach is equally a worthy valorization of an agri-food industrial waste, the disposal costs of which would have to be borne if a new function for it could not be found. Besides, the use of OHF as a filler allowed the reduction of amount of biopolymer matrix, consequently reducing the price of the final item. These results allow to conclude that the obtained results have scientific, technological and economic interests and this new biocomposite opens up significant industrial opportunities for the production of environmentally friendly devices, thus supporting the replacement of conventional plastics.

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Fig. 1 OHF dispersibility in water before and after the silanization process (a); SEM images showing powder of OHF (b) and OHF_SIL (c); EDS spectra of OHF (d) and OHF_SIL (e) samples; FT-IR spectra of MTES, MTES_hydrolyzed, OHF and OHF_SIL (f)

Fig. 2 SEM images showing cryofractured surface of PHBH/OHF composites: (a) neat PHBH, (b) PHBH/OHF_8, (c) PHBH/OHF_SIL_8

Fig. 3 Tensile properties of PHBH/OHF composites: Young's modulus (E), ultimate tensile strength (σ_u) and tensile elongation at break (ε_b)