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New biocomposite obtained using poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) and microfibrillated cellulose

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ABSTRACT: This research evaluates the effects of filler content and silanization on thermal, morphological and mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH)-based composites. Microfibrillated cellulose (MFC) was obtained by a mechanical treatment of high-pressure homogenization, starting from oat hull fiber, a byproduct of the agri-food sector. MFC reinforced PHBH composites were prepared by melt compounding. SEM and FT-IR analysis showed a good dispersion of the filler in the polymeric matrix, denoting the effectiveness of the surface silanization process. The thermal stability of PHBH composites remains substantially unchanged, and the glass transition temperature marginally increases with the increase of the filler content. Furthermore, silanized MFC shows slightly reinforcing mechanical effects on PHBH composites, such as the increase of 10% of the Young modulus with an increase of the maximum tensile stress as well. This finding has an economical interest since the results showed that MFC, deriving from a byproduct, can be successfully used as filler, decreasing the cost of the bio-based compound leaving substantially unaltered its mechanical and thermal properties. © 2020 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2020**, *137*, 48953.

KEYWORDS: biopolymers and renewable polymers; cellulose and other wood products; extrusion

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INTRODUCTION

Nowadays, in order to face modern environmental issues, bioplastics are getting increasingly attention due to the sustainable development policies and the decreasing reserves of fossil fuel. This can be easily demonstrated by the 17 global goals set by the United Nations in 2015 with the formal name of "Transforming our World: the 2030 Agenda for Sustainable Development".[1]

Even if, so far, the definition of bioplastic has not been clearly fixed, however, it is important to remember the distinction between a bio-based plastic and a biodegradable plastic. The former one is obtained, in whole or partially, from renewable biological resources (i.e., derived from plants or microorganism)[2]; the latter one can be degraded by microorganisms into water, CO_2, and/or methane under specified conditions.[3] Thus, it would be a great achievement to succeed in replacing traditional plastics with both bio-based and biodegradable plastics, in order to decrease carbon footprint, reduce pollution issues and oil depletion.

Polyhydroxyalkanoates (PHAs) are a class of bio-based biodegradable aliphatic polyesters; they have produced increasing interest in recent years, because their physical properties are similar to those of petroleum-based plastics.[4] Many different polymers belong to PHAs: that is, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) is a thermoplastic copolymer synthesized by bacteria and other microorganisms under conditions of nitrogen and oxygen imbalance.[5] The two constituent monomers of PHBH are 3-hydroxybutyrate (3HB) and 3-hydroxyhexanoate (3HH). 3HH content influences the properties of the polymer, such as crystallinity, thermal properties, strength, and crystallization rate.[6] Due to its good biocompatibility and biodegradability, PHBH could be used as an environmentally friendly material. However, the thermomechanical properties and crystallization rate of PHBH are lower if compared to petroleum-based plastics, limiting its extensive use.[7] In order to enhance these properties of the material, many studies trying to modify the polymer with a reinforcing agent, such as glass fibers (Willson *et al.*),[8] porous cellulose (Hosoda *et al.*),[6] cellulose nanocrystals (Zhou *et al.*),[4] cellulose and wood flours (Deepika *et al.*)[9] and fibrillated nanocellulose (Valentini *et al.*)[10] have been conducted.

A particular interest has been reserved to cellulose derivates, due to their biocompatibility, biodegradability, and interesting mechanical properties.[4,6,7,9,11] Nano and micro cellulose derive from the most abundant and natural polymer, cellulose, which can be produced not only from plants, but also from microorganism, such as bacteria,[12] and in this case, it is called bacterial cellulose (BC). Cellulose derivatives are obtained by chemical treatments (e.g. 2,2,6,6-tetramethylpiperidinyloxy, TEMPO-oxidation), mechanical processes (*e.g.* homogenization, grinding, milling), by a combination of these approaches,[13] or also by electrospinning process.[14] In the first case the obtained product is nanocrystalline cellulose (CNC) and, after an acid hydrolysis that breaks down the amorphous region of the cellulose fibrils, the CNC is needle shaped with 150–300 nm in length and 5–10 nm in diameter.[15] Whereas, the product of a mechanical treatment is called nanofibrillated cellulose (NFC) or microfibrillated cellulose (MFC). Both of them have a fibrillar shape with amorphous and crystalline domains. The difference between them is the actual dimensions of the fibrils: in the first case the fibrils have a diameter of 5–60 nm and a length of several micrometers,[16] while in the second case, the fibrils have a diameter of hundreds of nanometers and a length of tens of microns.[17] One of the main issues about compounding cellulose and polymers is obtaining a well-dispersed and distributed filler, without aggregations, and a good adhesion between the hydrophobic matrix and the hydrophilic filler. To achieve this goal, many studies have been carried out and many approaches have been experimented (*e.g.* silanization, grafting “onto”, grafting “from”, esterification, acetylation…).[18] Another important aspect to consider in the compounding of the polymeric matrix and the filler is the method to follow; nowadays most of the researches are focused on the solvent-casting procedure[19] but this technique has the disadvantage of being limited to a laboratory scale.

This work was focused on the effective possibility of processing and compounding a PHBH matrix with cellulose derivates, microfibrillated oat hull fibers, *via* melt-compounding, using a twin-screw extruder and then an injection molding to create specimens at different filler concentrations. Avoiding the use of solvents, a more “eco-friendly,” industrially and economically viable approach was investigated.[20] To increase the dispersion and distribution of the filler in the matrix, a silanization step was introduced in order to investigate the reinforcing effect of silanized and unsilanized cellulosic filler in PHBH composites, according to their morphological, mechanical, and thermal properties.

EXPERIMENTAL

Materials

Oat hull fibers were provided by GEA Mechanical Equipment (Parma, Italy) as a powder. Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate, PHBH) pellets were purchased from MAIP Group (MAIP SRL, Turin, Italy). Ammonium hydroxide 30% was purchased from Carlo Erba Reagents Co. Ltd (Milano, Italy); ethanol was purchased from J.T. Baker Co. Ltd (Phillipsburg), methyltriethoxysilane (Dynasylan MTES) was purchased from Evonik Industries (Rheinfelden, Germany) and the paraffin oil “Vestlan” was provided by Tizi, S.R.L, (Arezzo, Italy).

Preparation of Microfibrillated Cellulose (MFC) Suspension

The oat hull fiber suspension was processed by GEA Mechanical Equipment (Parma, Italy). In the typical preparation procedure, oat hull fibers were dispersed in water in a concentration of 5 wt % by a mechanical mixer and subsequently by a high-shear mixer (ULTRA-TURRAX) at 10.000 rpm. The suspension was homogenized with a high-pressure process with a NS3006L homogenizer (GEA Mechanical Equipment) at 700 bar for 15 times. The obtained MFC suspension in water was stored at refrigerator temperature.

Silanization

In order to improve the interfacial adhesion between filler and PHBH, a coupling agent is required. For the effective adhesion of MFC and PHBH, MTES is a suitable molecule for increasing chemical compatibility, since it has both polar and nonpolar groups. In Figure 1, chemical modification mechanism of the cellulose by silane coupling agent is schematically represented. The hydroxyl groups (-OH) of the cellulose react with an ethoxy

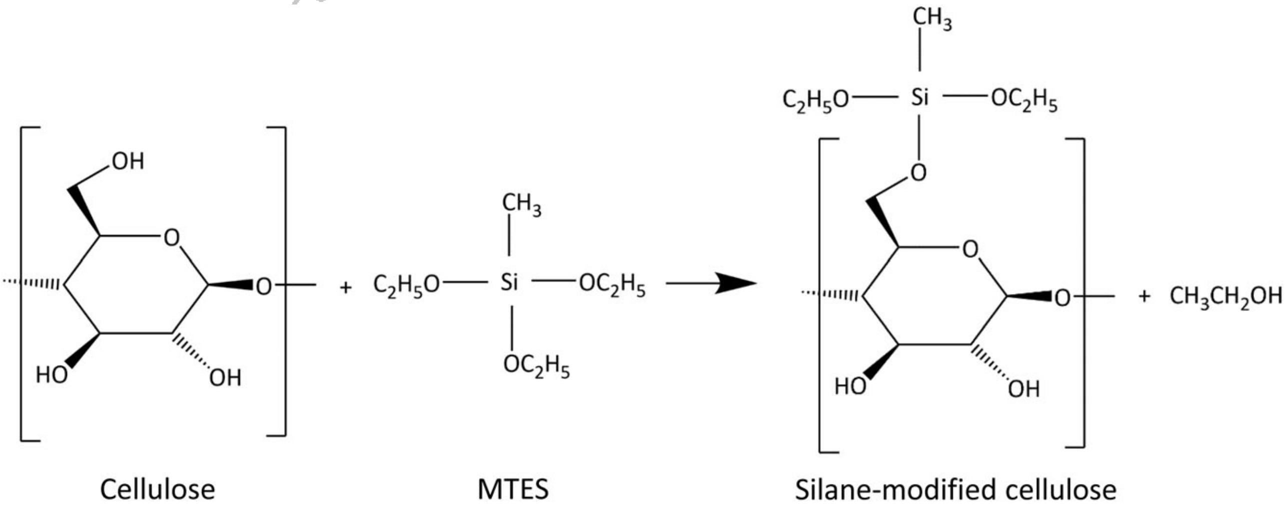

Figure 1. Modification mechanism of cellulose by means of silane coupling agent.

group of MTES. With this condensation reaction, the silane coupling agent is chemically bonded to the external surface of cellulose. The presence of the methyl group in the silane molecule modifies the surface chemistry of cellulose and it should promote the compatibility with PHBH matrix.

The fiber silanization was obtained as follow[21]: in a typical formulation 2,9 mL of ammonium hydroxide solution (conc. 30 wt % in water) was added to 40 mL of MFC suspension (conc. 5 wt % in water) and to 57,1 mL of pure ethanol under magnetic stirring. Then, the suspension was placed into a constant-temperature oil bath at 50 °C and equilibrated for 30 min. After the dispersion reached uniform temperature, 0.8 mL of MTES were added, drop by drop, and stirring continued at 50 °C for 20 h. 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).

Compounding of PHBH and Microfibrillated Cellulose (MFC)

Before any processing, PHBH pellets were oven-dried at 85 °C overnight, while MFC powder was vacuum-dried at 35 °C overnight.

In the beginning, the PHBH pellets and the filler powder were mechanically mixed. In order to obtain a better adhesion of the filler upon the pellets, some drops of paraffin oil (VESTLAN) were used. Thereafter, the mixtures were melt compounded using a corotating twin-screw extruder (HAAKE EXTRUDER RHOEMEX CTW100p) operating at a rotational speed of 15 rpm and with a temperature profile varying from 145 °C at the feed zone to 160 °C at the metering zone. After extrusion, the obtained filament was granulated by a pelletizer (SCHEER SGS 25-E4), and then molded to obtain standard tensile test specimens (UNI EN ISO 527-2, type 1 BA) by injection molding (TECNICADUEBI MegaTech H7/18–1). For the last process, these conditions were used: hopper temperature 120 °C, screw-barrel temperature 135 °C, die temperature 130 °C, injection pressure 120 bar, holding pressure 20 bar, holding time 3 s, and cooling time 7,5 s.

In this study, different composites were prepared, varying the MFC content. The sample codes and the composite compositions are summarized in Table I. To evaluate the effect of the functionalization procedure, the sample with the higher amount of MFC was also prepared with the as-received MFC.

Table I. Composition of PHBH/Cellulose Composites

Composite code	PHBH content (wt%)	MFC content (wt%)	Silanized MFC content (wt%)
PHBH	100	0	0
PHBH_MFC_10	90	10	0
PHBH_MFC_Sil_3	97	0	3
PHBH_MFC_Sil_10	90	0	10

Materials Characterization

In order to obtain a better knowledge of the material microstructure and of the interaction between fibers and PHBH matrix, the fracture surface of injection-molded specimens and the filler morphologies were investigated using a Nova NanoSEM 450 Field Emission Gun-Scanning Electron Microscopy (FEG-SEM) (FEI Company). Each specimen was mounted on carbon tape and sputter-coated with gold. Regarding the morphology of the fracture surface, a fragile fracture was obtained breaking the samples after immersion in liquid nitrogen. The presence of silicon in samples, after silanization, was investigated by energy dispersive X-ray spectroscopy (EDS) microanalysis system, using an X-EDS QUANTAX-200 (Bruker), integrated in the FEG-SEM.

Fourier trasform-infra red (FT-IR) spectra of the silanized fillers were recorded with a FT-IR Vertex 70 spectrophotometer (Bruker), in order to investigate the chemical structure of the obtained powders and to evaluate the efficacy of the silanization process.

The thermal properties of the samples 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 was calculated by the following equation[22]:

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

where ΔH_m^0 (= 146 J/g) is the enthalpy of 100% crystalline PHB,[9] 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 on a tensile testing machine (Universal Testing Machine, TesT GmbH, Erkrath, Germany) equipped with a 2 kN load cell, according to UNI EN ISO 527-1. Five specimens (1BA type according to ISO 527) were tested for each sample.

Finally, dynamic mechanical analysis was performed with a single cantilever clamp, in temperature ramp/frequency sweep mode using a DMA Q800 (TA Instruments) with heating rate of 3 °C/min. All the samples, $40 \times 5 \times 2$ mm^3 (length × width × thickness), were scanned over a temperature range from −20 to 120 °C, applying a strain of 0.1%, under frequency of 1 Hz. All samples were equilibrated for 10 min at −20 °C before starting the analysis, in order to homogenize the temperature in the measuring head.

RESULTS AND DISCUSSION

Effect of Silanization on MFC

The process of silanization of the microfibrillated cellulose was initially investigated by FEG-SEM analysis. The images of the untreated and silanized microfibrils are presented in Figure 2(a,b) and (c,d), respectively, and show the fiber dimension, their microstructure and the effect of the silanization process upon cellulose microfibrils. In the homogenized MFC, Figure 2(a,b), the fibrils have a length of some tens of microns and a width of approximately 10 μm. It is important to note that the sample

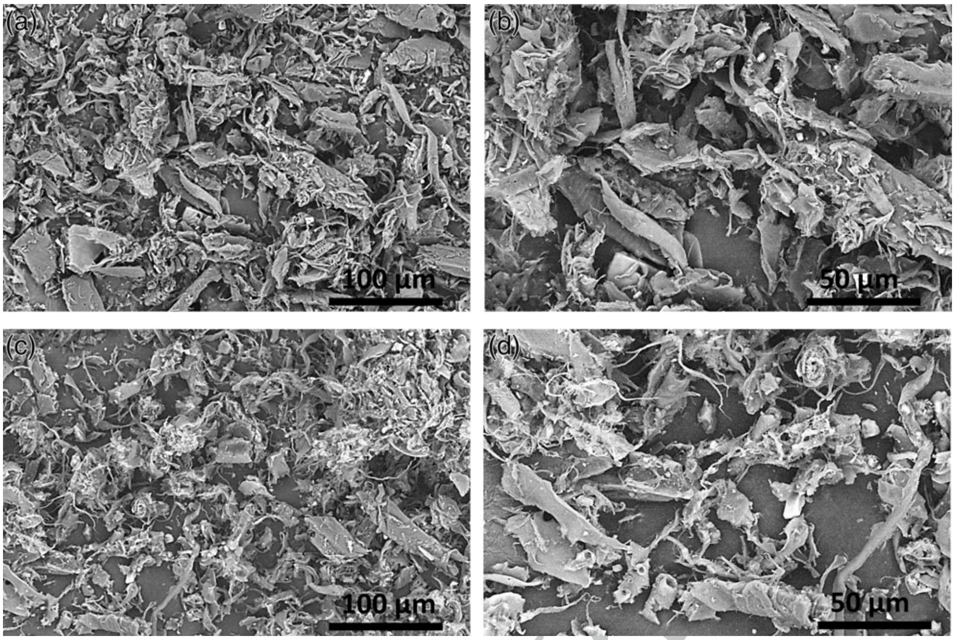

Figure 2. SEM images of: (a, b) MFC and (c, d) silanized MFC morphologies.

appears morphologically quite heterogeneous, considering also the plates and the aggregates, probably due to the oven drying process. The mean aspect ratio (L/d) of the micro-fibrils is about 100. The silanization process does not affect neither the dimension nor the morphology of the sample, as observed in Figure 2 (c,d).

To confirm the efficiency of the silanization procedure, untreated MFC, silanized MFC and PHBH compounds are examined by EDX spectrometry. Figure 3 illustrates the obtained results. The unmodified MFC spectrum and the PHBH matrix spectrum [Figure 3(a,c)] only show peaks corresponding to photon energies of $K_{\alpha 1}$ emission lines of C and O, near 0,277 and 0,525 keV, respectively. In the spectrum of the silanized MFC and PHBH/MFC_Sil samples [Figure 3(b,d)], an additional peak near 1,74 keV was observed, corresponding to photon energies of silicon emission lines $K_{\alpha 1}$ and $K_{\alpha 2}$, confirming the condensation of silicate groups on the MFC surface.

Additionally, FT-IR spectroscopy was used to follow and evaluate the MTES hydrolysis and subsequently the condensation on MFC. Figure 4 shows the FT-IR spectra of MFC, MTES coupling agent, hydrolyzed MTES coupling agent and silanized MFC. The spectroscopic variations in the silane after hydrolysis and polycondensation reactions can be observed, comparing the FT-IR spectrum of pure MTES and the one obtained after the sol–gel reaction. The characteristic IR band at 2971 cm^{-1} is attributed to the asymmetric stretching of CH_3, deriving from ethoxy (-OCH_2CH_3) and methyl-silyl (-Si-CH_3) groups of MTES, and it is present on both spectra. In the MTES spectrum, there are other two different peaks at 2923 and 2881 cm^{-1}, corresponding, respectively, to the asymmetric and symmetric stretching of CH_2, from ethoxy group.[23] These last two peaks are no more visible in the condensed MTES, since after sol–gel reaction methylene groups in the ethoxy functionalities are removed as ethanol. In the condensed MTES, the peak at 2971 cm^{-1} is still evident, due to the silyl group, and the weak peak at 2911 cm^{-1} appears, corresponding to the symmetric stretching of CH_3. Moreover the characteristic bending vibration of the methyl group was identified at 1267 cm^{-1}.[24,25] The bands at 1167, 955, 818, and 777 cm^{-1} were attributed to the absorption of Si–O–CH_2CH_3 in MTES, whose intensities decrease considerably after sol–gel reaction.[25] Additionally, another proof of the successful silanization is the presence of the characteristic peaks of Si-O-Si with a broad signal at 1100 cm^{-1} and a sharp signal at 766 cm^{-1}.[23,24] Comparing the FTIR spectrum of MFC_silanized with the spectrum of pristine MFC, three typical peaks can be noticed and they are present only on the MFC_silanized spectrum, denoting the actual condensation of the coupling agent on the MFC surface. These peaks are at 2971 cm^{-1}, at 1271 and at 766 cm^{-1}, corresponding to the asymmetric stretching of -CH_3, the bending of -CH_3 and the stretching of Si-O-Si.[23,24] It is clear from these peaks, which are not evident in the neat MFC spectrum, that the silanization process occurred. In the MFC_silanized spectrum, the superimposition of the peaks, due to the aliphatic silane functionalization (Si-CH_3), on the MFC spectrum can be observed. Beside these peaks, other typical absorptions of cellulose can be observed in both spectra: the broad band at 3350 cm^{-1} due to the —OH stretching and the peaks at 1031 and 895 cm^{-1}, corresponding to the C—O stretching and the CH bending.[26]

Composite Characterization

The microstructure of the composites and the interaction between fibers and PHBH matrix are examined by SEM-FEG microscopy. In Figure 5, the microstructures of neat PHBH sample [Figure 5(a,b)] and the composites [Figure 5(c-f)] are compared. The presence of MFC in the composites is detected by structures extended out of the fracture surface that are not observed in the neat sample [Figure 5(a,b)].

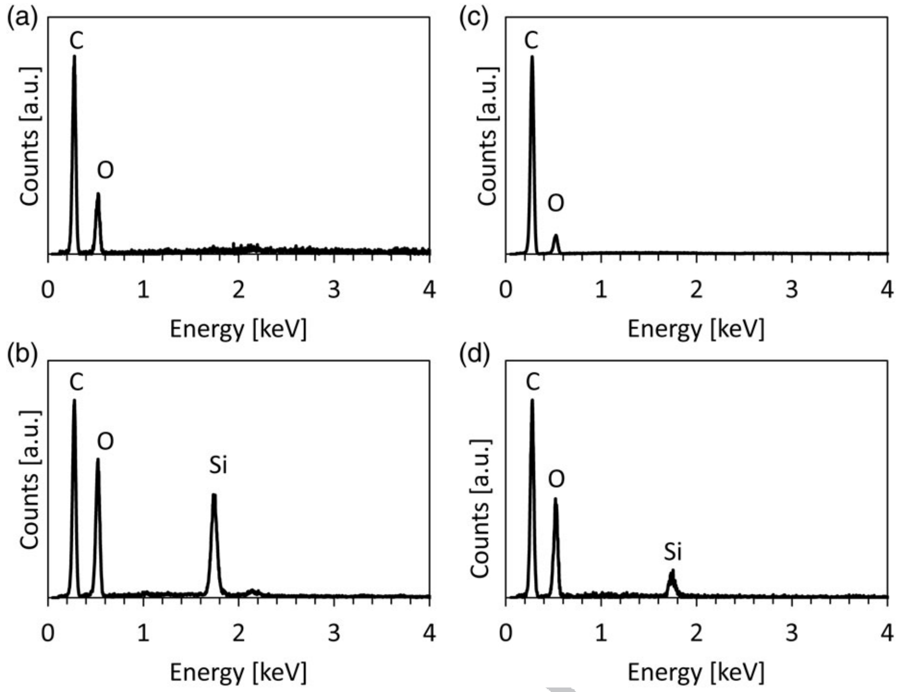

Figure 3. EDX measurements: (a) MFC; (b) silanized_MFC; (c) PHBH; (d) PHBH_MFC_Sil_10.

Silanized cellulose microfibers seem to exhibit a better interfacial compatibility with the polymeric matrix than no treated fibers. The effect of silanization is highlighted by the absence of empty spaces between the PHBH and the silanized MFC fibers [Figure 5 (e,f)], observed in the untreated samples [Figure 5(c,d)].This condition could determine an increase in the mechanical properties of the composite, obtained with silanized cellulose.

The results of mechanical characterization, summarized in Table II, confirm remarks emerged from SEG-FEG analysis.

Based on literature data, MFC has a Young modulus in the range of 29–36 GPa.[27] Due to its higher modulus respect to PHBH, the addition of MFC to PHBH lead to increase the Young modulus of PHBH composites.

This increment is more pronounced using silanized fibers. Moreover increasing silanized MFC content, Young modulus of PHBH/MFC composites gradually raises up to 1861 ± 77 MPa, with a growth of 8,5% compared to the neat PHBH.

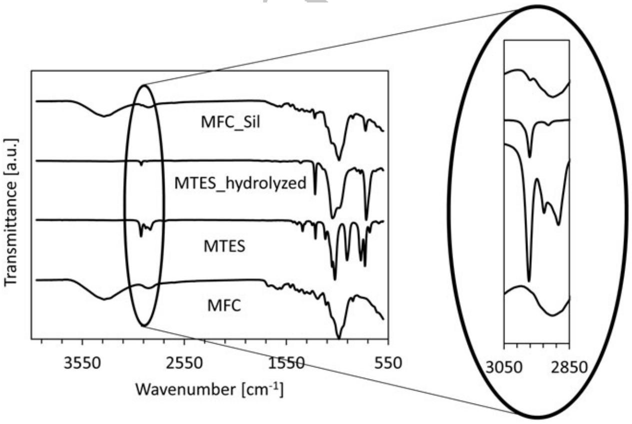

Figure 4. FT-IR spectra of MFC, MTES, MTES_hydrolzyed, and MFC_silanized.

This behavior is accompanied by a slight increase of the tensile strength from 23,1 ± 1,6 MPa to 24,5 ± 0,9 MPa, corresponding to an increase of 6%. The strength increment with respect to the pristine matrix can be considered as a further indirect evidence of the good adhesion between silanized MFC and matrix (REF). At higher filler concentration, a small decrease of the elongation at break occurs, from 3,7 ± 0,4% to 3,2 ± 0,3%, as a result of the greater stiffness of the material.

The thermal properties of neat PHBH and PHBH/MFC composites are analyzed by DSC and are summarized in Table III. All thermal properties are only slightly affected by the addition of the filler to PHBH matrix. The glass transition temperature, T_g, of the polymer can be considered not influenced by the filler addition and its content.[28]

The melting temperature, T_m, is slightly higher for the composites compared to the neat polymer. These results are consistent with already published data[4,10] and can be ascribed to the reduced flexibility of the PHBH chains, due to the filler presence.

Finally, also the crystallization degree is only slightly affected by the MCF presence indicating that the filler does not significantly influenced the crystallization process.

To get a deeper evaluation of the reinforcement effect of MFC, dynamic mechanical analysis is performed as well. The obtained results are aligned with the mechanical properties evaluated by the tensile test.

Figure 6(a) illustrates the temperature dependence of the storage modulus, E', of neat PHBH and PHBH/MFC composites. E' of neat PHBH at temperature below T_g is essentially constant with a

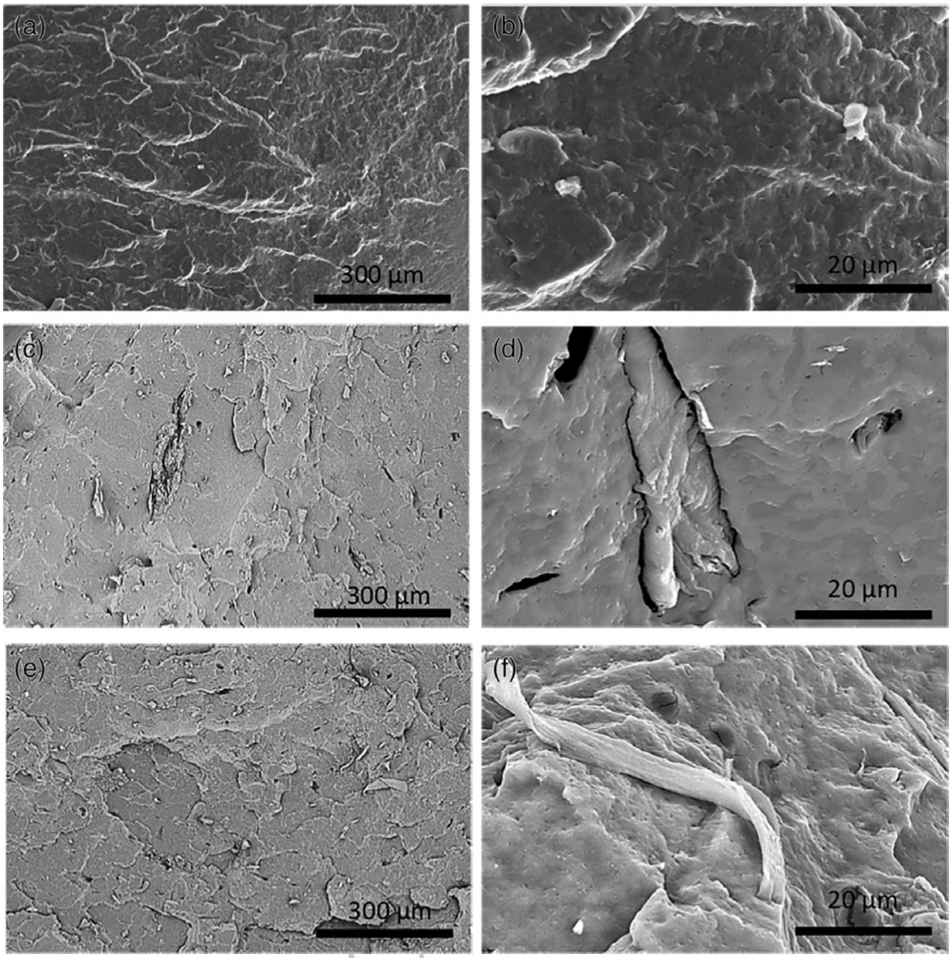

Figure 5. SEM images showing fracture surface of PHBH/MFC composites: (a) and (b) neat PHBH; (c) and (d) PHBH_MFC_10; (e) and (f) PHBH_MFC_Sil_10.

Table II. Tensile Properties of PHBH and PHBH/MFC Composites

Sample	Young modulus, E (MPa)	Tensile strength, σ_M (MPa)	Tensile strain at break, ε_B (%)
PHBH	1715 ± 71	23.1 ± 1.6	3.7 ± 0.4
PHBH_MFC_Sil_3	1776 ± 132	24.2 ± 1.2	3.8 ± 0.4
PHBH_MFC_Sil_10	1861 ± 77	24.5 ± 0.9	3.2 ± 0.3
PHBH_MFC_10	1813 ± 133	26.1 ± 0.6	2.7 ± 0.4

Table III. Thermal Properties PHBH/MFC Composites

	Glass transition temperature	Melting temperature	Enthalpy of melting	Degree of crystallinity
Sample	T_g (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PHBH	5,9	141,2	43,9	30,0
PHBH_MFC_Sil_3	6,8	147,0	49,5	34,9
PHBH_MFC_Sil_10	6,8	145,0	41,3	31,5
PHBH_MFC_10	6,4	143,5	42,4	32,3

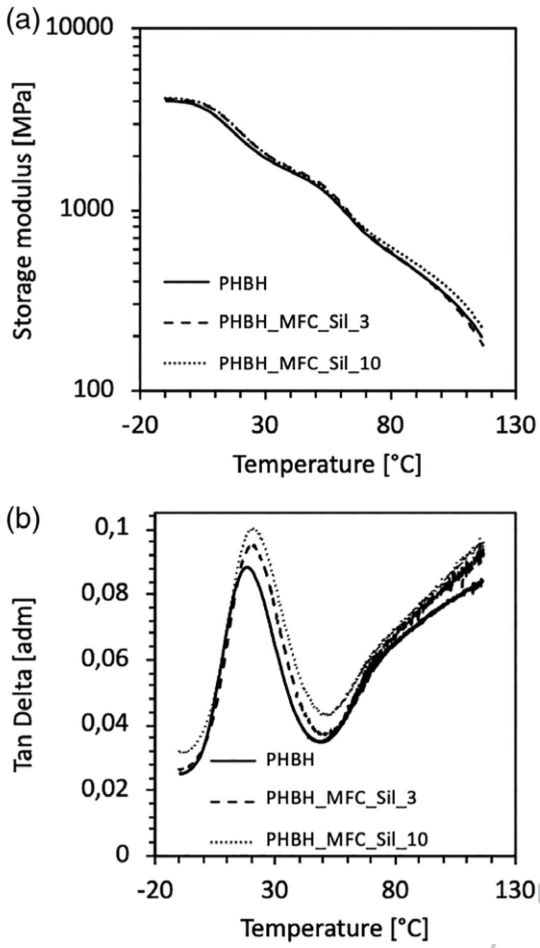

Figure 6. Storage modulus (a) and tan (b) of neat PHBH and PHBH/MFC_Sil composites.

value of ≈ 4 GPa. The incorporation of MFC, at 10 wt%, increased very slightly E' in the rubbery region, suggesting that MFC gives stiffness to the composites.[29] The E' increase of the composites can be related to an improved compatibility between the filler and the polymeric matrix, promoted by the surface modification of the MFC.[30]

Figure 6(b) shows the temperature dependence of the loss factor (tan δ) of neat PHBH and PHBH/MFC composites.

The microfibril addition to the polymeric matrix modifies the number of the mobile chains during the glass transition and the effect depends on the interfacial area and the strength of polymer-filler interactions. Thus, the change in tan δ peak height indicates the variations in the volume of constrained chains.[31,32] Therefore, the introduction of MFC increased the volume of constrained chains and restricted the PHBH chain mobility due to effective interfacial interactions.[33]

Definitely, evaluating with the DMA analysis, the glass transition temperature (T_g) of the PHBH/MFC composites depends on the MFC content of the composite: increasing the amount of the filler, the T_g becomes slightly higher, shifting from 18 to 21 °C.

CONCLUSIONS

The aim of this research was to investigate the realization and subsequently the characterization of a composite material totally bio-based, consisting of a PHBH matrix filled with micro-fibrillated cellulose (MFC) obtained from oat hull fibers, a byproduct of the agri-food sector, after a chemical-free process of high-pressure homogenization.

The composite material is particularly interesting because the followed approach allows to use a byproduct, much cheaper than PHBH, as a filler, saving the biopolymer and reducing the costs of the final product, without not only changing its mechanical and thermal properties, but also slightly improving them.

Particular attention was paid to the effect of the amount of filler and the silanization treatment. The amount of filler slightly improves tensile strength, Young modulus, and glass transition temperature. Silanization has an improving effect on Young modulus, glass transition temperature, and melting temperature.

The applications of this compounded material might be different: specifically, it may replace traditional petroleum-based plastics used for the production of durable and semidurable goods such as for household items and crockeries or gardening accessories.

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Graphical abstract

New biocomposite obtained using poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) and microfibrillated cellulose

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