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Polyhydroxyalkanoates/Fibrillated Nanocellulose Composites for Additive Manufacturing

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Abstract

Novel poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)(PHBH)/fibrillated nanocellulose biodegradable composites for additive manufacturing were produced and characterized. Fibrillated nanocellulose (NCF) was isolated with high energy ultrasonication and dispersed via solution mixing in the polymer matrix. Composite filaments having a nanofiller concentration of 0.5 wt%, 1 wt% and 3 wt% were then extruded, characterized and used in fused deposition modeling (FDM). Neat PHBH powder was then manually added to prepare a solid mixture at different fibrillated nanocellulose concentrations (from 0.5 to 3 wt%), to be then used to feed an extruder. SEM observations on filaments and 3D printed samples evidenced the good dispersion of fibrillated nanocellulose inside the matrix with the presence of agglomerates at higher NCF contents. The beneficial effects of the fibrillated nanocellulose in terms of stress at break and of elongation at break showed a maximum at a fibrillated nanocellulose content of 0.5 wt%. Moreover, the presence of fibrillated nanocellulose did not affect the thermal degradation behaviour of the materials, and also the glass transition and the melting temperatures were not influenced by NCF addition.

Keywords Polyhydroxyalkanoates · Nanocellulose · 3D printing · Fused deposition modeling · Additive manufacturing

Introduction

The interest in using sustainable materials, coming from renewable resources and/or biodegradable is growing rapidly [1]. In particular, biopolymers can be widely applied in many technological fields like packaging, tissue engineering, agriculture and also in additive manufacturing processes [2]. Nowadays, the majority of the bio-based polymers is obtained from biomasses derived from natural products such as corn, sugar, starch, etc. [3].

Polyhydroxyalkanoates (PHAs) are natural thermoplastics totally synthesized by microorganism as an intracellular storage product under particular growth conditions (abundant

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¹ Department of Industrial Engineering and INSTM Research Unit, University of Trento, Via Sommarive, 9, 38123 Trento, Italy carbon source, limited sources of oxygen, phosphorous or nitrogen) [4]. The carbon is assimilated and processed into hydroxyalkanoate units, polymerized and stored in the cell cytoplasm. The product of the process is a high molecular weight crystalline polyester that is maintained in an amorphous state in vivo [4]. PHAs can be used to make films, foils, for application in the packaging industry and tissue engineering [5].

In order to overcome some disadvantages of PHAs such as the thermosensitivity and the brittleness, block copolymers have been developed introducing different monomeric units. This is the case of poly(3-hydroxybutyrateco-3-hydroxyhexanoate) (PHBH), a random copolymer of 3-hydroxybutyrate and 3-hydroxyhexanoate [4]. PHBH is used in tissue engineering, for the production of medical devices, flexible packaging and in agriculture in the controlled release of insecticides [5].

Among different reinforcing materials available to reinforce bioplastic products, cellulose based materials, fully deriving from renewable organic materials, could represent interesting candidates [6]. Nanocellulose is one of the most interesting reinforcing fillers for producing green nanocomposites due to its properties and the ability to undergo chemical modification. In fact, fibrillated nanocellulose exhibit excellent mechanical properties (the tensile strength can reach 200 MPa [7, 8]), good optical transparency [9, 10] and low thermal expansion coefficient [11]. Moreover, NCF is fully biodegradable and it can be used in a wide variety of applications, including substrate for displays, component for optical instruments and automotive windows [12, 13]. NCF is prepared from cellulose using high-intensity ultrasonication (HIUS) without the use of solvents. HIUS waves cause cavitation producing violent shock waves that can be used to isolate fibrils from cellulose fibers [14]. The production of NCF allows to integrate biopolymers with fillers in order to generate composites with increased mechanical properties and therefore combining the advantages coming from three different directions. For example, Cataldi et al. [15] found that cellulose nanocrystals (CNC) improved the thermo-mechanical behavior of PVOH along with its water resistance and dimensional stability, without impairing its optical features. Moreover, CNC-based nanocomposites resulted to be suitable as coatings for wood protection [16]. Among the different processes utilized to process bioplastics based composites, little attention has been so far devoted to additive manfacturing (AM) technologies. The main advantages of this process are the low operation and maintenance costs, the cheap equipment, the low operation temperature, the small quantity of wastes and the possibility to print a huge variety of polymers. On the other hand the time needed for the fabrication can be quite long, there is the presence of porosity inside the material, and delamination between the layers can occur. Moreover, the quality of the process can be affected by temperature fluctuations during the process [17, 18]. The application of additive manufacturing technology allows the production of objects with complex geometry, not only for prototyping but also for industrial production [17, 18]. In particular, fused deposition modelling (FDM) combines low operation costs with an easy use and the possibility of creating small and complex objects. In the FDM process, a thermoplastic filament is molten and deposited on a substrate layer by layer. The FDM machine is a computer numerically controlled machine, carrying a miniature extruder head nozzle. The operation principle is the presence of a thermoplastic filament that passing through a heated nozzle is molten and extruded on a heated plate where it cools down forming a layer. After that the plate moves down allowing the deposition of a second layer over the first one; this process continues until the final form of the object is reached. There is the possibility to have a second nozzle operating with a second filament used as support material: this part is then removed because it is only a support to the building structure and therefore it can be realized using a less expensive polymer [19]. Despite the advantages of AM technologies, only few papers dealing with the investigation of the physical properties of bioplastic based nanocomposites prepared through FDM can be found in the open literature [15]. Moreover, the reinforcing effect played by fibrillated nanocellulose on PHBH and the application of the additive manufacturing technologies on these composites have been never investigated in literature.

On the basis of these consideration, the aim of this work is the development and the investigation of the most important physical properties of PHBH nanocomposites filled with fibrillated nanocellulose, to be produced through FDM process. In particular, fibrillated nanocellulose was dispersed in the polymer matrix through solution mixing, and then extruded nanocomposites filaments suitable for the subsequent FDM process were produced. The influence of the nanofiller content and of the production method on the mechanical, thermal and rheological properties of the resulting materials was investigated.

Experimental Part

Materials

Polymer granules of PHBH X151A grade, provided by Kaneka Corporation (Osaka, Japan) were used as polymer matrix (melting point 126 °C, density 1.19 g/cm³). This copolymer is mainly applied in packaging films, especially agricultural mulch films and composting bags. Microcrystalline cellulose powder, having a mean particle size of 20 µm and a bulk density of 0.6 g/ml, was provided by Sigma-Aldrich. Both materials were used as received. Fibrillated nanocellulose was prepared starting from microcellulose powder through a ultrasonication process in a similar way as found in literature [11, 20–23]. Microcrystalline cellulose was dispersed in double distilled water with the aid of a magnetic stirrer to obtain a solution with a final composition of 10 wt%. This solution was ultrasonicated for 20 min in an ice bath with a Hielscher UP400S device (Teltow, Germany), equipped with a cylindrical sonotrode of 3 mm in diameter operating at a specific power of 400 W. The solution was kept at 4 °C for one week in order to let the micrometric particles to sediment and the supernantant was collected and freeze at -30 °C. Frozen supernatant was freeze-dryed with a LIO-5PDGT device for at least one week to remove completely the water. At the end of the process, fibrillated nanocellulose was obtained and stored at 4 °C.

Samples Preparation

Preparation of Nanocomposite Filaments

The fibrillated nanocellulose was added by solution mixing to the PHBH in order to obtain films containing fibrillated nanocellulose. PHBH granules were diluted in chloroform and stirred at 45 °C until complete dispersion was reached. Fibrillated nanocellulose was diluted in chloroform, ultrasonicated for 5 min using a Hielscher UP400S device (Teltow, Germany) equipped with a cylindrical sonotrode 3 mm in diameter, operating at a specific power of 400 W and then added to the solution of X151A.

After 3 h of stirring at 45 °C the obtained solution was sonicated at 25 °C for 5 min using a Labsonic LBS 1-H10 ultrasonic bath (Trezzano sul Naviglio, Italy) and then poured in a Petri dish. The drying was done at room temperature for one night and then in oven at 50 °C for 3 h, in order to obtain nanocomposites having a nanofiller concentration of 0.5%, 1% and 3%, to be used as masterbatch. These films were stored at -30 °C and then grinded. Neat PHBH powder was then manually added to prepare a solid mixture at different fibrillated nanocellulose concentrations (from 0.5 to 3 wt%), to be then used to feed an extruder. Nanocomposite filaments were then produced through a single-screw extruder provided by FriulFiliere (Buoja, Italy), equipped with a screw having a length to diameter ratio equal to 25 and a diameter of 14 mm. A screw speed of 30 rpm and a temperature profile of 105/105/125/150 °C were adopted. In this way, neat PHBH and relative nanocomposite filaments (filler content 0.5, 1 and 3 wt%) with a diameter of 1.72 mm \pm 0.07 mm were produced. In Table 1 the list of the prepared samples is reported.

3D Printed Samples Preparation

Starting from the extruded filaments, dumb-bell specimens of neat polymer and composites were printed using the same working conditions. For the 3D printing a Sharebot NG 3D printer (Sharebot, Italy) was used. The printer was equipped with a heated plate whose temperature was set to 75 °C in order to avoid crystallization during the printing and therefore warping phenomena and the detachment of the object from the plate. A temperature profile of 200/190/180 °C over the different layers (first layer, second layer, rest of the process) was adopted. The specimens were dumb-bell shaped (1BA) according to ISO 527 and they were printed in the horizontal plane. A linear infill type with an angle of $\pm 45^{\circ}$

Table 1 List of the prepared samples

PHBH content (wt%)	Fibrillated nano- cellulose content (wt%)	Filaments	3D printed samples
100	0	F_PHBH	3D_PHBH
99.5	0.5	F_PHBH_NC05	3D_PHBH_NC05
99	1	F_PHBH_NC1	3D_PHBH_NC1
97	3	F_PHBH_NC3	3D_PHBH_NC3

between layers and a fill percentage of 100% were used. In Table 1 the list of the prepared samples is reported.

Experimental Methodologies

The cryofractured surfaces (perpendicular to the specimen axis) of filaments and 3D printed samples were observed through a Zeiss Supra 40 field emission scanning electron microscope (FESEM), operating at an acceleration voltage of 2.5 kV. The samples were metallized through the deposition of a thin coating of electrically conductive platinum palladium over the sample's surfaces inside a vacuum chamber.

Differential scanning calorimetry (DSC) measurements were performed both on filaments and on 3D printed samples with a Mettler DSC30 calorimeter under a nitrogen flow of 10 ml/min. A first heating from -30 to 200 °C was followed by a cooling stage from 200 to -30 °C and all the thermal ramps were conducted at 10 °C/min. The temperatures associated to the glass transition (T_g), the melting (T_m) and crystallization (T_c) of the polymer matrix were thus determined. The crystallinity degree (X_{c1}) was computed as the ratio between the melting enthalpy of the samples during the first heating scan and the reference value of the fully crystalline PHBH (according to literature we used the value for PHB that is equal to 146 J/g [24]). Moreover, also crystallinity degree during the cooling scan (X_{c2}) was evaluated.

Thermogravimetric analysis (TGA) was performed through a TGAQ500 thermobalance under a nitrogen flow of 10 ml/min in a temperature interval between 30 and 700 °C, at a heating rate of 10 °C/min. The temperature associated to a mass loss of 5% (T_{on}) and the decomposition temperature (T_{peak}), i.e., the temperature related to the maximum mass loss rate, were determined.

The viscoelastic properties were evaluated through a dynamic mechanical thermal analysis (DMTA) using a DMAQ800 in a temperature interval between -50 and 100 °C, with a frequency of 1 Hz and a heating rate of 3 °C/min. The temperature associated to a decrease of the storage modulus equal to 5% was identified as the glass transition temperature (T_g).

The tensile properties under quasi-static conditions of filaments and 3D printed samples were measured at 23 °C through an Instron 4502 tensile machine. In the case of 3D printed samples ISO 527 type 1BA specimens were tested. Tests for the determination of the elastic modulus (E) were carried out at 0.25 mm/min, setting a maximum deformation of 1%. The strain was monitored by using an Instron model 2620-601 resistance extensometer, having a gauge length 12.5 mm. The elastic modulus was measured as secant modulus between strain levels of 0.05% and 0.25%. Tensile tests at break were performed without extensometer at a crosshead speed of 10 mm/min; the stress at yield (σ_y); the stress at break (σ_b), the deformation at break (ϵ_b) and the tensile energy to break (TEB) were determined. For all the tensile tests, five specimens were tested for each sample.

In order to evaluate the theoretical values of the mechanical properties referring to a material without porosity, a factor R, i.e. the ratio between the real and the theoretical density, was introduced and the mechanical properties were normalized by using this factor. The apparent density was compared with the theoretical one (i.e., the density of the material with 0% of porosity) for each printed specimen. The apparent density, as shown in Eq. (1) is the ratio between the weight of the specimen and the volume.

$$Apparent \ density = \frac{weight}{volume} \tag{1}$$

The volume was evaluated using the Eq. (2), where *w* is the width of the specimen, b_1 is the width at center (5 ± 0.5 mm), *A* is the area (520 mm²) and *t* is the thickness.

$$Volume = \left(\frac{w}{b_1}\right)^2 \cdot A \cdot t^2 \tag{2}$$

The R-factor, as shown in Eq. (3), is the ratio between the apparent density and the theoretical density of the sample.

$$R = \frac{apparent \ density}{theoretical \ density} \tag{3}$$

Results and Discussion

Nanocomposites Filaments

SEM observations were carried out to understand the morphological characteristics of the prepared samples and to assess the dispersion degree of the fibrillated nanocellulose in the PHBH matrix. SEM micrographs of filaments containing different percentages of fibrillated nanocellulose are reported in Figure 1a-d. Observing the F_PHBH_NC05 sample, it is possible to notice the presence of fibrillated nanocellulose homogeneously distributed within the matrix, with a mean length of 1.8 µm and a thickness of 22.6 nm. Increasing the filler amount up to 3 wt%, the formation of aggregates can be observed. Moreover, a rather good fillermatrix interfacial adhesion can be observed over the whole range of investigated compositions. The investigation of the thermal degradation behaviour of the prepared materials could be important to assess their potential in some industrial application, in which elevated temperatures are involved. Therefore, thermogravimetric tests were carried out.

From the TGA thermograms (not reported for the sake of brevity) it is clear that all the samples are characterized by a single degradation step. In Table 2 the most important results of TGA tests are summarized. A significant mass



Fig. 1 SEM micrographs on the cryofractured surfaces of filaments: a F_PHBH, 20,000 ×; b F_PHBH_NC05, 20,000 ×; c F_PHBH_NC1, 20,000 ×; d F_PHBH_NC3, 20,000 ×

Table 2 Results of TGA tests on nanocomposite filar	nents
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Sample	T_{on} (°C)	T _{peak} (°C)
F_PHBH	253.0	288.0
F_PHBH_NC05	260.0	286.7
F_PHBH_NC1	265.2	284.5
F_PHBH_NC3	266.4	288.0

loss starts around 260 °C, while the maximum mass loss rate occurs after 285 °C. From Table 2 it is evident that the temperature associated to the onset of the degradation (T_{on}) is slightly increased upon nanofiller addition, while T_{peak} is practically not affected by the NCF addition. A similar behaviour has been found in a previous work [15].

In order to investigate the effect of the NCF introduction on the thermal properties of the prepared composites, also DSC tests were thus carried out. Representative DSC thermograms collected during the first heating scan and cooling scan are respectively reported in Fig. 2a, b, while the most important results are summarized in Table 3.

It can be noticed that the glass transition temperature (T_g) is only slightly affected by the the NCF introduction. Also the melting (T_m) and the crystallization temperature (T_c) of the materials, respectively collected during the first heating and the cooling stage, are not significantly affected by the presence of nanofiller. On the other hand, it could be observed that the crystallinity degree evaluated during the cooling scan (X_{c2}) increases with the NCF amount. As already reported in other papers on polymer nanocomposites [25], this means that NCF acts as a nucleating agent promoting a crystallinity increase of the PHBH matrix.

DMTA analysis was carried out on filaments in order to understand the role played by NCF on the viscoelastic behaviour of the nanocomposites. From the storage modulus (E') curves reported in Fig. 3a it can be observed that, above the (T_g) of the matrix, the F_PHBH_NCC05 presents the highest storage modulus, while E' values of F_PHBH_NC1 and F_PHBH_NC3 are systematically lower than those of the neat PHBH sample. From the numerical results reported in Table 4, it is evident that the relative difference between E' values of the nanocomposite and neat PHBH filaments increases at low temperatures while, in accordance with DSC tests, T_g is not influenced by NCF introduction. Loss modulus (E") and loss tangent curves (tan δ), respectively shown in Fig. 3b and c, confirm the trends already observed for storage modulus.

Representative tensile stress–strain curves of neat PHBH and relative nanocomposites are reported in Fig. 4, while the most important results are summarized in Table 5. A significant increment of the elastic modulus (+ 40% with respect to the neat PHBH), limited to the sample containing 0.5% of fibrillated nanocellulose, can be detected. The



Fig. 2 DSC on nanocomposite filaments: \mathbf{a} first heating scan; \mathbf{b} cooling scan

Table 3 Results of DSC tests on nanocomposite filaments

Sample	$T_{g}(^{\circ}C)$	T _m (°C)	X _{c1} (%)	$T_{c}(^{\circ}C)$	X _{c2} (%)
F_PHBH	3.8	139.4	25.9	44.6	4.9
F_PHBH_NC05	- 0.2	138.6	24.6	47.4	10.1
F_PHBH_NC1	0.1	139.7	27.9	43.8	10.5
F_PHBH_NC3	2.0	137.7	26.8	46.1	14.0

F_PHBH_NC05 sample shows also the highest yield stress and tensile energy to break. For higher NCF contents, elastic modulus has a little drop, even it is higher than that of the neat PHBH. The stress at yield and the stress at break for NCF loading of 1 wt% and 3 wt% are very similar to that of the neat matrix. It could be also important to underline that the values of strain at break are not dramatically reduced by the nanofiller. It could be therefore concluded that for NCF



Fig. 3 DMTA tests on nanocomposite filaments: a storage modulus; b loss modulus; c loss tangent

content higher than 0.5 wt% filler aggregation detected in SEM images (see Fig. 1) limits the NCF reinforcing

Table 4 Results of DMTA tests on nanocomposite filaments

Sample	Storage modulus at – 20°C (GPa)	Storage modulus at 25°C (GPa)	$T_{g}(^{\circ}C)$
F_PHBH	5.03	1.69	2.1
F_PHBH_NC05	4.99	1.85	1.0
F_PHBH_NC1	4.24	1.54	3.6
F_PHBH_NC3	3.21	1.31	3.7

capability, but the presence of some aggregated structures does not compromise the ductility of the materials.

3D Printed Samples

Neat PHBH and nanocomposites filaments were printed using a FDM machine, in order to investigate the possibility to industrially exploit this technology also for fully biodegradable nanocomposite materials. The possibility of carrying out the printing process on this polymer was assessed, and also the good quality of the printed objects was verified. It should be noticed that, with respect to other polymers, working with PHBH containing fibrillated nanocellulose required low operating speed, because of the limited flowability of the material. It could be also important to underline that viscosity measurements on neat 3D printed samples, performed in order to evaluate the molecular weight of the samples and to verify possible thermo-mechanical degradation during the processing, revealed that no decrease of molecular weight due to the printing process occurred. The results of these measurements were not reported for the sake of brevity.

SEM analysis was carried out in order to understand the morphological features of the printed samples and to assess the dispersion degree of fibrillated nanocellulose. In Fig. 5a-d SEM micrographs of the cryofractured surfaces of 3D printed samples containing different amounts of fibrillated nanocellulose are reported. As it could be expected, the surface of the neat PHBH sample is corrugated, because of the plasticization phenomena that occurred during the breaking operations. Observing the 3D PHBH NC05 sample, it is possible to notice the presence of fibrillated nanocellulose aggregates homogeneously distributed within the matrix, with a mean length of 0.9 µm and a thickness of about 160 nm. Even in this case, increasing the filler amount up to 3 wt%, the formation of aggregates can be observed. From a qualitative point of view, it can be concluded that the observed morphology is not so different from that of the corresponding filaments, but the printing process promotes an increase of the NCF aggregation tendency. Moreover, at elevated filler amounts (i.e., 3 wt%) a partial filler-matrix debonding can be detected, with the presence of some voids in the interfacial regions. From the results of TGA tests



Fig. 4 Representative stress-strain curves from quasi-static tensile tests on nanocomposite filaments

reported in Table 6 it is clear that the thermal degradation behaviour is similar for all the prepared samples, as it starts around 260 °C and reaches the maximum mass loss rate at around 285 °C (even in this case, all the samples are characterized by a single degradation step). It can be therefore concluded that the degradation behaviour of the 3D printed materials is not substantially affected by NCF additivation.

From the results of DSC analysis, summarized in Table 7, it can be noticed that the trends are very similar to those detected on nanocomposite filaments. In fact, the T_g of the neat filament is around 0 °C and it does not substantially change upon NCF introduction, and also melting temperature (T_m), collected during the first heating scan, is not modified by the presence of nanofiller. Like in nanocomposite filaments, also in 3D printed samples the presence of NCF at a concentration of 3 wt% leads to an increase of the crystallization temperature (T_c) in the cooling scan, probably because of the nucleating effect played

Sample	E [MPa]	$\sigma_{\rm y}({ m MPa})$	$\epsilon_{y}(\%)$	$\sigma_{\rm b}$ (MPa)	$\epsilon_{\rm b}(\%)$	TEB (J/mm ²)
F_PHBH	897 ± 157	21.6 ± 0.4	7.3 ± 0.9	14.8 ± 4.2	10.4 ± 3.0	1.6 ± 0.5
F_PHBH_NC05	1259 ± 221	23.1 ± 1.0	8.0 ± 0.6	16.8 ± 3.5	9.5 ± 1.1	1.6 ± 0.2
F_PHBH_NC1	1051 ± 269	21.7 ± 1.7	8.6 ± 0.8	15.7 ± 1.5	10.9 <u>+</u> 0.9	1.6 ± 0.3
F_PHBH_NC3	1014 ± 214	19.6 ± 1.1	8.1 ± 1.4	15.9 ± 2.1	10.2 ± 2.3	1.4 ± 0.4

Fig. 5 SEM micrographs on the cryofractured surfaces of 3D printed samples: **a** 3D_PHBH, 10,000 ×; **b** 3D_PHBH_NC05, 10,000 ×; **c** 3D_PHBH_NC1, 10,000 ×; **d** 3D_PHBH_NC3, 10,000 ×

Table 5Tensile properties ofthe nanocomposite filaments(with the associated standard

deviation values)



Table 6 Results of TGA tests on 3D printed samples

Sample	T_{on} (°C)	T _{peak} (°C)
3D_PHBH	257.3	287.0
3D_PHBH_NC05	254.7	283.2
3D_PHBH_NC1	258.1	284.3
3D_PHBH_NC3	264.6	286.2

Table 7 Results of DSC tests on 3D printed samples

Sample	$T_g(^{\circ}C)$	$T_m (^{\circ}C)$	$X_{c1}(\%)$	$T_{c}(^{\circ}C)$	$X_{c2}(\%)$
3D_PHBH	0.1	141.8	26.9	42.7	2.3
3D_PHBH_NC05	- 1.2	142.6	28.8	46.9	5.2
3D_PHBH_NC1	0.1	141.5	25.6	42.1	5.2
3D_PHBH_NC3	0.8	141.8	25.0	42.4	15.2

by the nanofiller. Also in this case the materials are able to crystallize at around 50 °C during the second heating stage.

For as concerns the mechanical performances of the 3D-printed samples, in Fig. 6 representative stress-strain curves of neat PHBH and relative nanocomposites are shown, while the most important results are summarized



Fig. 6 Representative stress-strain curves from quasi-static tensile tests of 3D printed samples

in Table 8. No increment of the elastic modulus, due to the presence of fibrillated nanocellulose, can be detected, and nanofiller additivation results in a reduction of the stiffness of the samples. Also in this case it is possible to notice that the sample containing 0.5% of fibrillated nanocellulose shows the highest yield stress, stress at break and tensile energy to break values. The reinforcing effect due to the presence of the filler seems, thus, to be limited to a concentration of 0.5%. Probably, at higher filler loadings, nanofiller aggregation and interfacial debonding detected in Fig. 5 limits the reinforcing capability of the samples. However, similarly to what observed for nanocomposite filaments, the ductility of the materials is not heavily impaired by NCF aggregation, and ϵ_b of nanocomposites is very similar to that of the neat PHBH. It is important to underline that the tensile properties obtained from the mechanical tests on 3D printed materials and reported in Table 8 do not take into account the presence of macropores within the printed structure.

In Table 9 the mechanical properties normalized by the R-factor (E^* , σ_y^* , σ_b^*) are reported and the results of the density measurements in terms of theoretical density, apparent density and R-factor are summarized. It is clear that the R-factor is very similar for all the tested compositions and this confirms the results already discussed in terms of mechanical properties. The sample containing 0.5% of fibrillated nanocellulose shows the best behaviour in terms of yield stress and stress at break and the nanofiller additivation results in a reduction of the stiffness of the samples. Finally, the similarity of the R-factor values, can be an evidence of the good quality of the printed objects and of the optimization of the printing process for these kind of materials.

Conclusion

In this work, novel PHBH/fibrillated nanocellulose biodegradable composites for additive manufacturing were produced and characterized. Filaments, suitable to feed a desktop 3D printer, were prepared extruding nanocomposite materials obtained by solution mixing with a single screw extruder. Different composition, from 0.5 to 3 wt% of NCF

Table 8Tensile propertiesof the 3D printed samples(with the associated standarddeviation values)

Sample	E (MPa)	σ_y (MPa)	$\epsilon_{y}(\%)$	$\sigma_{\rm b}({ m MPa})$	$\epsilon_{\rm b}(\%)$	TEB (J/mm ²)
3D_PHBH	931 ± 150	15.9 ± 0.8	8.8 ± 1.8	12.6 ± 2.6	10.7 ± 1.8	1.2 ± 0.1
3D_PHBH_NC05	807 ± 74	18.0 ± 0.6	9.0 ± 0.7	14.0 ± 1.7	12.2 ± 1.8	1.7 ± 0.3
3D_PHBH_NC1	770 ± 44	14.9 ± 0.7	7.7 ± 0.5	13.5 ± 0.9	9.5 ± 1.0	1.1 ± 0.1
3D_PHBH_NC3	681 ± 112	11.7 ± 1.5	7.0 ± 0.7	9.3 ± 2.0	9.3 ± 1.5	0.8 ± 0.1

Table 9Density, R-factorand normalized mechanicalproperties of the 3D printedsamples (with the associatedstandard deviation values)

Sample	Theoretical density (g/l)	Apparent density (g/l)	R-factor	E* (MPa)	σ_y^* (MPa)	σ_{b}^{*} (MPa)
3D_PHBH	1.196	0.823	0.688	1349 ± 185	23.1 ± 1.5	18.4 ± 3.8
3D_PHBH_NC05	1.193	0.831	0.696	1159 ± 110	26.3 ± 0.9	20.2 ± 2.6
3D_PHBH_NC1	1.190	0.848	0.713	1081 ± 59	21.0 ± 0.9	19.0 ± 1.1
3D_PHBH_NC3	1.178	0.779	0.662	1027 ± 130	17.6 ± 1.1	14.0 ± 2.2

The mechanical properties $(E^*, \sigma_v^*, \sigma_b^*)$ are normalized by the R-factor

in PHBH were successfully printed. SEM observations on filaments and 3D printed samples evidenced the good dispersion of fibrillated nanocellulose inside the matrix with presence of agglomerates at higher NCF contents. The TGA performed to investigate the thermal stability of the produced materials showed that the introduction of NCF does not affect the degradation behaviour of the material. The addition of fibrillated nanocellulose improved the mechanical strength under quasi-static conditions; the stress at break and the elongation at break reached a maximum for a NCF content of 0.5 wt%.

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