NANOCELLULOSE AS REINFORCING AGENT FOR BIODEGRADABLE POLYMERS IN 3D PRINTING FUSED DEPOSITION MODELING

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Abstract

The aim of this work is the development of different kind of thermoplastic biodegradable polymer composites reinforced with nanocellulose and to study their applicability in additive manufacturing technology such as Fused Deposition Modeling (FDM). The final goal is the production filaments of poly(lactic acid) (PLA) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) reinforced with nanocellulose suitable to feed commercially available FDM 3D-printing machines and to print small dumbbell specimen. Ultrasonication and freeze-drying were used to isolate nanocellulose starting from micro-cellulose powder. Nanocellulose was homogeneously dispersed in the polymer matrices as observed by electron microscope and improved the resistance to thermal degradation. Mechanical properties of the filaments were enhanced by the presence of the filler, but this positive effect was not shifted to 3D printed samples due to increased viscosity with respect to neat polymer. A new approach to better evaluate the mechanical properties of printed samples based on an apparent density is presented.

1. Introduction

Biodegradable and bio-based polymers have gained great attention since sustainable development policies tend to enlarge with the growing concern for the environment and the decreasing reserve of fossil fuel [1]. Cellulose is the most abundant natural polymer on Earth, which is a virtually inexhaustible source of raw material for the increasing demand for environmentally friendly materials [2]. Cellulose is organized in a hierarchical fashion with nanometric size crystal of organized molecules as building blocks. Nanocellulose exhibits excellent properties, such as, a high specific surface area (ca. 150 m2/g) [3], impressive mechanical properties (its stiffness is estimated to be about 150-250 GPa and its tensile strength can reach 200 MPa[4, 5] and it is fully biodegradable and, interestingly, hastens the biodegradation of green-composite materials[6]. Recently, low cost and environmentally friendly methods were developed to extract nanocellulose from cellulose, one of the most promising is ultrasonication. Wei et al. showed the possibility to obtain nanofibrils of cellulose starting from pulp wood with high energy ultrasonication and their reinforcement capabilities in polyvinyl alcohol film [7].

Biopolymers like polyhydroxyalkanoates (PHAs) or polylactic acid (PLA), continue to attract increasing industrial interest as renewable, biodegradable, biocompatible, and extremely versatile thermoplastics. These materials bring a significant contribution to the sustainable development in view of the wider range of disposal options with minor environmental impact [8]. Nanocellulose has attracted a huge

interest as reinforcing agent for bio-polymers, but the main problem in the development of nanocellulose composites based on thermoplastic polymer is the dispersion and the distribution of this filler inside the matrix. Bio-polyesters with their hydrophobicity nature makes the nanocellulose to organize in bundle due to the presence of intra and inter molecular hydrogen bonds and the hydrophilicity behavior of cellulose, which led to an inefficient strengthening. Different kinds of solution to improve the dispersion and the compatibility between nanocellulose and thermoplastic polymers were followed [9-11].

The new additive manufacturing technologies like 3D printing provide the possibility to produce an object where it is really required, leading to a reduction in CO_2 emissions due to the less transportation needed [12, 13]. The development of sustainable and degradable polymers is the natural step to improve the "green" benefits of 3D printing. The most diffused additive manufacturing technology is based on Fused Deposition Modeling (FDM). FDM is a technique used to build up objects layer by layer with the support of computer aided design. A filament of thermoplastic polymer is extruded through a nozzle at a temperature usually higher than the glass transition temperature or melting temperature of material and deposited layer by layer to form the final object.

In this paper, nanocellulose obtained with ultrasonication was used to prepare 3D printable filaments and later 3D printed specimen were produced to compare the effect of this green filler dispersed in two different matrices, PLA and PHA. Some highlights on the thermal and mechanical properties of the composites were discussed.

2. Materials and Methods

2.1.   Materials

Cellulose microcrystals, CMC, (density 1.56 g·cm^{-3}, mean molecular weight of 90,000 g/mol) prepared through the reaction of cellulose with a water solution of strong mineral acid at boiling temperature, were supplied by Sigma Aldrich (USA). CMC particles consist of elongated flakes with an average length of about 24 µm and a diameter of about 10 µm (average L/D ratio of 2.4). Poly (lactic acid) (PLA 4032D) with a density of 1.24 g/cm^3 and a melting point of 160°C was purchased from Nature Works LLC. Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH), trade name X151A; was provided by Kaneka Corporation (Osaka, Japan). Melt flow index was 3 g/10 min at 165°C under a constant load of 5 kg, density was 1.19 g/cm^3 according to datasheet.

2.2.   Nanocellulose isolation

Nanocellulose (NC) was obtained through mechanical sonication. In particular, 5 g of microcrystalline cellulose provided by Sigma-Aldrich, were dispersed in 0.5 liter of deionized water, stirred for 5 minutes and ultrasonicated at 400 W for 20 minutes using a Hielscher UP400S Ultrasonicator (Teltow, Germany) in an ice bath. The obtained solution was stored at 3 °C for one week to allow the deposition of the micrometric particles remained. The supernatant was then freeze-dried using a 5Pascal LIO-5PDGT freeze-dryer (Trezzano sul Naviglio, Italy) in order to separate the nanocellulose from the water.

2.3.   Sample preparation

2.3.1. Filaments

PLA and PHBH were treated in a similar way to obtain nanocomposite filaments, in this paragraph they were called simply polymer. Polymer was dissolved in chloroform under stirring at 40°C until complete dissolution. Freeze dried nano-cellulose was dispersed in chloroform through ultra-sonication for 5 minutes in ice bath. The two previous solutions were mixed for 4 hours under magnetic stirring and let evaporated at room temperature to obtain masterbatch plates with a final NC content of 10wt%. The obtained plates were grinded in liquid nitrogen and dried at 50°C under vacuum for 24 hours.

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The powder was mixed with neat polymer to obtain the desired concentration of NC. The obtained powder compound was used to feed a *Friul Filiere TCM 500* single screw extruder whose die diameter was 3mm and. The speed of the screw was set at 30 rpm while the temperatures were carefully adjusted for the two polymers to avoid a possible thermal degradation. Temperature profile inside the extruder rise from 100°C in the feed zone to 190°C for PLA and to 150°C for PHBH in the die zone. Under these selected processing conditions, continuous filaments were obtained with various concentration of NC and with a diameter of 1.7 ±0.1 mm suitable to be used in a commercial 3D printer machine based on FDM technology.

2.3.2.   FDM samples

Dumbbell specimens (ISO 527 1BA) were designed in SolidWorks software, exported in a stereo lithography format .stl and uploaded into the Slic3r software where the model was sliced by a cutting algorithm to generate G-code. These 2D sliced layers were then built by the printer layer by layer till the final object was physically formed. Sharebot Next Generation desktop 3D printer, provided by Sharebot Italy, with a nozzle diameter of 0.35 mm was used to print our composite materials. Specimens were printed in the horizontal plane and coded as XZ where X is the direction of filament deposition and Z is the direction of the overlapping layers. Linear infill type with an angle of $\pm 45°$ between layers, layer height of 0.2 mm and a fill percentage of 100% were chosen to obtain the best mechanical properties without the introduction of stress amplifiers inside the parts due to the infill path. PLA composites required an extrusion temperature of 210 °C and a bed temperature of 40 °C to guarantee the adhesion of the object. More complicated was the printing of PHBH, a gradient of temperature during printing was needed to avoid the warping of the specimen, from 200 °C in the first layer to 190 °C in the second one and 180 °C for the subsequent ones. Bed temperature was settled at 75 °C to avoid the crystallization of the material after the extrusion and the generation of thermal stresses that could end in the detachment of the specimen from the printing bed.

2.4.   Experimental techniques

Microstructural observations carried out with a Zeiss Supra 40 high resolution field emission scanning electron microscope (FESEM) with an accelerating voltage of 2.5 kV, after the deposition of a platinum palladium conductive coating. Thermal stability of nanocomposite was investigated through thermogravimetric analysis (TGA), using a TGA Q5000 from TA instrument in a temperature interval between room temperature and 700 °C, at a heating rate of 10 °C/min, under a nitrogen flow of 150 ml/min. The maximum degradation temperature and the residual mass at 700 °C were estimated from the maximum of the peak of mass loss rate curves. Differential scanning calorimetry (DSC) measurements were performed with a Mettler Toledo TC15 calorimeter. Samples of 10 mg were analyzed under a nitrogen flow of 150 ml/ min, from 0 to 220 °C, heating and cooling runs were performed at 10°C/min. The glass transition temperature (T_g) was evaluated as the inflection point of DSC thermographs. The melting temperature (T_m) was estimated in correspondence of the endothermic peak. The enthalpy values were evaluated as the integral of their corresponding peaks: area under exothermic peak to estimate enthalpy of crystallization, and area under endothermic peak to estimate enthalpy of melting. Quasi-static tensile tests allowed to collect data related to both the elastic behavior and the failure properties of the material. They were performed using an Instron 5969 electromechanically testing machine, equipped with a 50 kN cell load, at room temperature with a crosshead speed of 10 mm/min. At least five specimens for each composition were tested to estimate the average values of stress at break (σ_B) and elongation at break (ε_B).

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In order to discern the effect of the increasing amount of nanocellulose from the quality of the printing, that is also related to the amount of filler in the matrix, it became necessary to introduce a new strategy to compare different 3D printed samples. Apart from the variety of defects that could affect a 3D printed component, an intrinsic problem related to this particular manufacturing technique is the presence of porosity that led to a worsening of the mechanical properties. The approach followed in this work is to relate the measured dimensions of the specimen with its apparent density. With the aid of Solidworks ® software, a base area of 520 mm^2 was calculated for dumbbell specimen 1BA with a width in the central part of 5 mm. Volume of the specimen was calculated, according with Eq. 1, multiplying the base area for a correction coefficient, given by the ratio of the measured width (w) with the theoretical one (W) and for the measured thickness (t).

$$Apparent\ volume = \left(\frac{w}{W}\right)^2 * Area * thickness \qquad (1)$$

The apparent density of the specimen was calculated dividing the weight of the dumbbell for the apparent volume Eq. 2.

$$Apparent\ density = \frac{Weight}{Apparent\ Volume} \qquad (2)$$

The ratio between the apparent and the theoretical density, Eq. 3, could be used as a yardstick to compare different sample with different density relating to a material without porosity.

$$R = \frac{apparent\ density}{theoretical\ density} \qquad (3)$$

3. Results and Discussions

Morphological aspects were investigated by FESEM and the images are shown in Figure 1. The average diameter of nanocellulose fibrils resulted of 15 ± 3 nm (see Figure 1a). The distribution of those fibrils inside the polymers was investigated looking at the cryofracture surface of our samples. In Figure 1b, the fracture surface of a filament of PHBH with 1wt% of NC is shown, it's possible to notice a good dispersion of the nanocellulose inside the matrix and a good adhesion between the matrix and the NC.
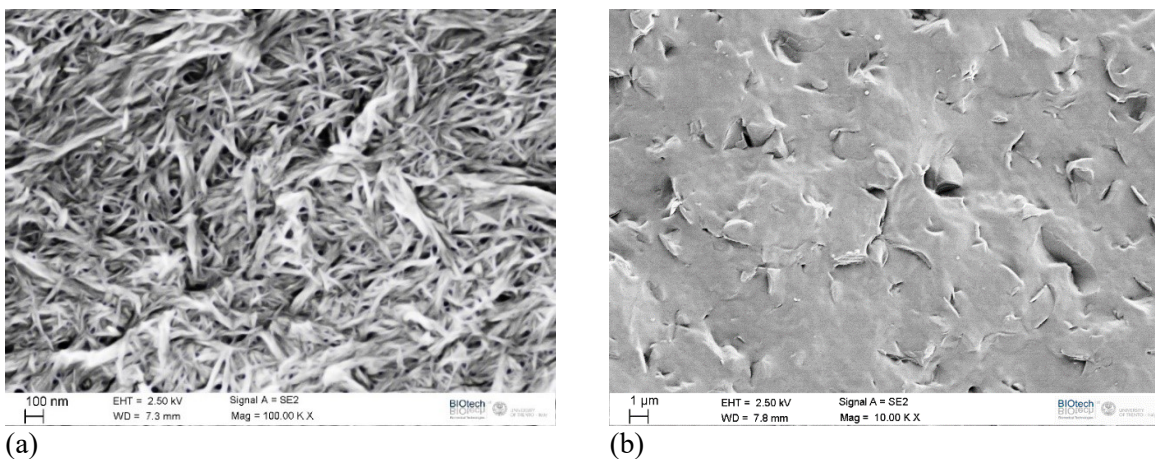

(a)   (b)

Figure 1. Scanning electron microscopy pictures of ultrasonicated nanocellulose before the freeze-drying process (a) and the cryofracture surface of a filament contain 1wt% of nanocellulose (b).

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TGA was performed to investigate the thermal behavior of the filaments of neat polymer and its nanocomposites inside the nozzle of the 3D printer, where higher temperature is needed to assure a good quality of the printed samples. In Figure 2, the TGA thermograms for PHBH (Fig 2a) and PLA (Fig 2b) are reported. Each of these two polymers presented a single degradation step that starts at 253°C for PHBH and at 318°C for PLA according to the temperature that correspond at a 5wt% loss in weight. The introduction of nanocellulose in the matrix had a positive effect on the thermal degradation shifting the curves towards higher temperatures. In particular, with a 3 wt% on NC, the degradation starting temperature increased to 266°C and 330°C for PHBH and PLA, respectively.
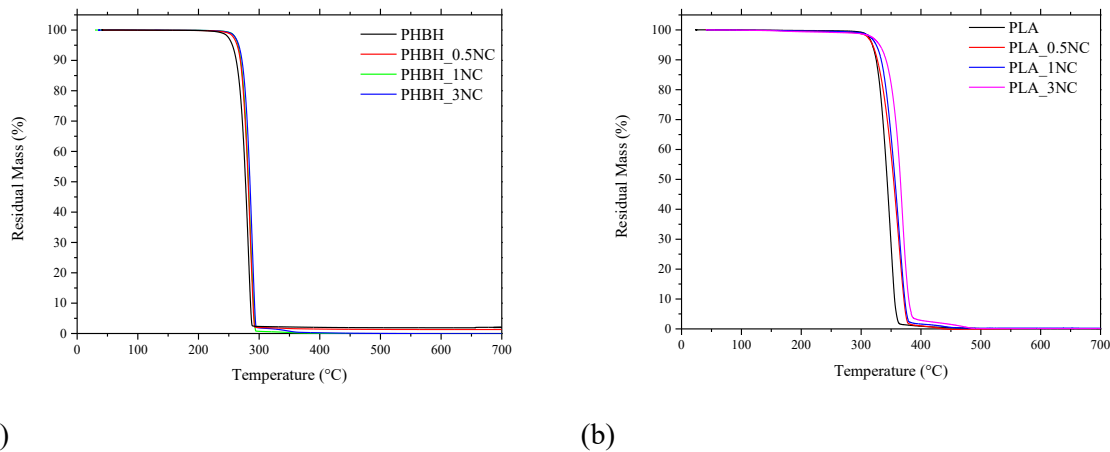

(a)   (b)

Figure 2. Thermogravimetric curves for neat and nanocomposite filament of PHBH (a) and PLA (b).

DSC measurements on filaments were carried out to understand how the thermal properties of the materials are affected by the presence of nanocellulose and to identify some key parameters for the next step of 3D printing. As it can be noticed from Figure 3, the introduction of nanocellulose did not interfere with the glass transition and the melting temperature of PHBH (Fig. 3a) and PLA (Fig. 3b). The ability of the material to crystallize was influenced by the presence of NC, increasing the amount of NC inside the matrix resulted in smaller crystallization peaks. The crystallization temperature of PHBH was very close to room temperature and particularly attention had to be given during the 3D printing to avoid the warping and the detachment of the object from the building plate cause by stresses related to the phase change of the material.
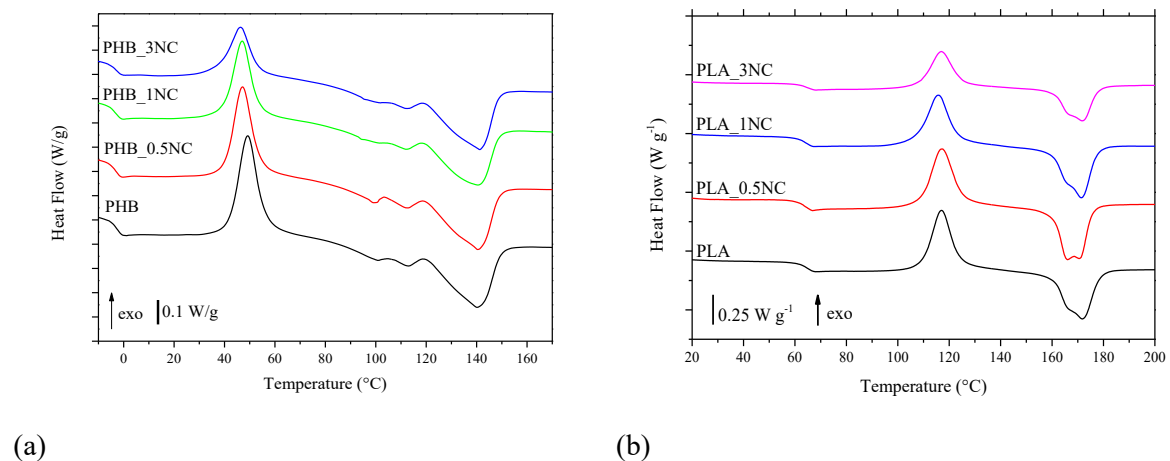

(a)   (b)

Figure 3. Differential scanning calorimetry curves for nanocomposite made of nanocellulose and PHBH (a) and PLA (b).

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The effect of NC on the elastic modulus, tensile strength and strain at break of neat polymers and nanocomposite filaments and 3D-printed specimens are summarized in Table 1 and Table 2 respectively. Both filaments and 3D printed samples manifested an increase in the elastic modulus with the addition of the nanofiller, the higher values were found for a concentration around 0.5 and 1 wt% reflecting a good dispersion of the nanofibrils in the matrix. Therefore, despite a decrease in crystallinity content was found with DSC analysis, the stiffening effect played by NC prevailed. Ultimate mechanical properties of the filaments were improved due to the solid interaction between the matrix and the filler as confirmed by SEM analysis. The reinforcing effect saw in the filaments was not found in 3D printed specimens, probably caused by a worse quality in the 3D printed object due the increase in the viscosity of the material with the increase of the amount of filler.

Table 1. Mechanical properties of filaments.

	Elastic Modulus (MPa)	Stress at break (MPa)	Strain at break (%)
PHBH	897±157	14.8±4.2	10.4±3.0
PHBH_0.5NC	1259±221	16.8±3.5	9.5±1.1
PHBH_1NC	1051±269	15.7±1.5	10.9±0.9
PHBH_3NC	1014±214	15.9±2.1	10.2±2.3
PLA	3224±986	56.9±4.0	4.8±1.5
PLA_0.5NC	3575±1176	56.3±2.7	4.7±2.2
PLA_1NC	3918±1022	55.4±1.3	4.5±1.9
PLA_3NC	3576±914	52.8±5.2	4.0±0.6

Table 2. Mechanical properties of 3D printed samples.

	Elastic Modulus (MPa)	Stress at break (MPa)	Strain at break (%)
PHBH	931±150	12.6±2.6	10.7±1.8
PHBH_0.5NC	807±74	14.0±1.7	12.2±1.8
PHBH_1NC	770±44	13.5±0.9	9.5±1.0
PHBH_3NC	681±112	9.3±2.0	9.3±1.5
PLA	2505±248	39.8±4.9	4.2±0.6
PLA_0.5NC	1590±743	21.9±14.1	3.9±0.5
PLA_1NC	2045±671	28.4±13.1	4.5±1.0
PLA_3NC	1651±424	23.7±8.7	4.1±6.1

As mentioned before, the quality of the printed samples decreased with the increase of filler content and it was confirmed by the decrease of the parameter R as shown in Figure 4.
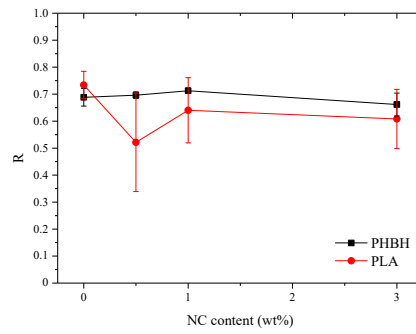
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Figure 4. Density over theoretical density (R) of 3D specimen in function of the filler content.

In Figure 5, it is possible to appreciate how the mechanical properties of 3D printed specimens depend on the internal porosity. In particular, the lower mechanical properties for PLA_0.5NC are mainly attributable to the low density of the specimen. To overcome this problem, an approach based on the density of 3D printed specimen was taken in account. A first attempt was done fitting the data with a straight line passing through the origin, the slope of this line indicated the value for R equal to 1, in other words the value for a material without porosity. With this approach it was possible to relate the elastic modulus and the stress at break of PLA_0.5NC with the R of the neat PLA sample with values of 2183 MPa and 33.2 MPa respectively. These extrapolated values felt in between the neat PLA and PLA_1NC.
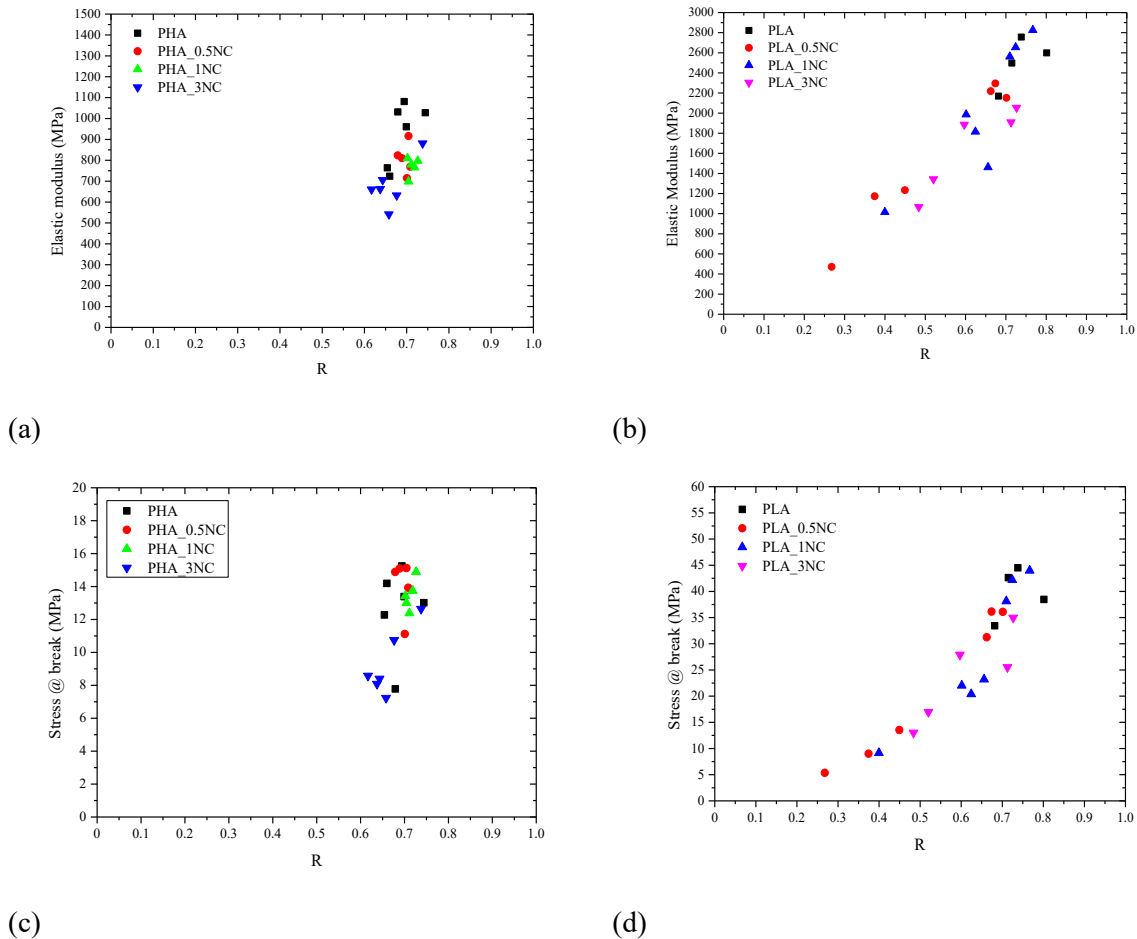

(a)

(b)

(c)

(d)

Figure 5. Mechanical properties of 3D printed specimen made of PHBH (a, c) and PLA (b, d) in function of R factor.

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4. Conclusion

The goal of this work was to produce full biodegradable 3D printed nanocomposites based on bio-polyesters (PLA, PHBH) and nanocellulose. Nanocellulose was obtained from microcellulose with a ultrasonication treatment to disrupt the arranged structure. Filaments, suitable to feed a desktop 3D printer, were prepared extruding nanocomposite materials obtained by solution casting with a single screw extruder. Nanocomposite with different composition, up to 3 wt% of NC, were successfully printed despite the increased viscosity of the molten filaments. Scanning electron microscopy revealed that nanocellulose was homogenously dispersed inside both PLA and PHBH polymers. The TGA performed to investigate the thermal stability of the produced materials showed that the introduction of NC increased the thermal stability of neat polymers. Tensile tests highlighted an improvement of the stiffness and the stress at break after the introduction of the NC in the filament samples. 3D printed material presented a porosity of about 30%. It was verified that a lower densification was reached by the materials containing NC due to an increase in the viscosity. Mechanical properties of 3D printed specimen were correlated with their density and it was possible to extrapolate the mechanical properties and compare them with different samples.

5. References

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