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# Polyvinyl alcohol reinforced with crystalline nanocellulose for 3D printing application



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### ABSTRACT

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The aim of this work is to produce fully biodegradable nanocomposite filaments with improved thermo-mechanical properties, to be used in fused deposition modeling (FDM) 3D printing process. At this aim, nanocomposites consisting of poly(vinyl alcohol) (PVOH) containing various amounts (from 2 to 20 wt%) of cellulose nanocrystals (CNC) were produced by solution mixing, grinded and extruded into filaments by a single screw extruder. The obtained nanocomposite filaments were then used to feed a desktop 3D printer.

In both filaments and 3D printed specimens, CNC promoted a progressive enhancement of thermal stability manifested in an increase of the glass transition temperature measured by differential scanning calorimetry. Moreover, both dynamic storage and loss moduli were also increased proportionally to the filler content, and a positive reduction of the creep compliance was observed. For a CNC content of 10 wt% the creep compliance at a given loading time (one hour) decreased in both filament (by 47%) and in 3D printed samples (by 35%) in comparison to neat PVOH. Ultimate mechanical properties of filaments also increased with the introduction of CNC till 10 wt%, with a maximum reinforcement effect observed at 2 wt% of CNC for which an increase of 81% in the values of tensile energy to break and 45% in the stress at break were observed. An enhancement in tensile properties was observed also for 3D printed samples at 5 wt% of CNC for which the stress at break manifested an improvement of 73%. Adhesion between layers in 3D printed parts resulted to play a major role in the fracture behavior.

#### 1. Introduction

Indications have recently emerged on the fact that climate changes could have been caused by the human behavior in the last decades [1–3]. Therefore, actions must be taken to preserve our environment, especially in the field of processing of raw materials and manufacturing. The diffusion of new technologies like additive manufacturing could contribute to reduce human footprint [4]. In fact, the intrinsic nature of this process lead to material saving, no generation of scraps like in subtractive process, where the material is removed to form the final object. Waste materials can be turned in final products with a low amount of energy and chemical treatments [5]. Additive manufacturing give us the possibility of producing an object in any place, in our home, inside the International Space Station, on the ground of another planet [6-8], where this object is really required. This will lead to a reduction in CO2 emissions due to the less transportation needed.

One of the most diffused additive manufacturing technology is based on Fused Deposition Modeling (FDM). FDM is a technique used to build up objects from bottom layers to top layers with the support of computer aided design. The ever-growing diffusion of FDM is due to its benefits over traditional manufacturing such as free design, no need to use molds, ability to obtain complex parts. With FDM it is possible to manufacture light weight parts for the automotive and aerospace industry. The process starts with the conversion of a three-dimensional solid model of an object to a stereo lithographic (STL) format sprocessed by an appropriate software, where STL file is sliced in layers before to be sent to the 3D printer machine. A filament of thermoplastic polymer is extruded through a nozzle at a temperature usually higher than its glass transition or melting temperature and deposited layer by layer to form the final object.

The development of sustainable and degradable polymers and composites is a logical step to improve the "green" benefits of 3D printing.

Poly(vinyl alcohol) (PVOH) is recognized as one of the very few vinyl polymers soluble in water also susceptible of ultimate biodegradation in the presence of suitably acclimated microorganisms. PVOH can be utilized in a broad field of applications, but exhibits a high tendency to water sorption. Nevertheless, it is a highly hygroscopic

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(a)

Fig. 1. AFM (a) and FESEM (b) images of cellulose nanocrystals.

(b)



Fig. 2. SEM pictures of cryo fractured surface of PVOH filaments with the addition of (a) 0 wt%, (b) 5 wt%, (c) 10 wt% and (d) 20 wt% of CNC.

polymer and this feature may impair its mechanical performances thus limiting its use for some intended applications [9].

Nanocrystalline cellulose, CNC, is one of the most interesting reinforcing fillers for producing green nanocomposites due to its properties and the ability to undergo chemical modification. It can be used in a wide variety of applications, such as foams, adhesives and protective coatings [10–14]. Nanocellulose exhibits excellent properties, such as, a high specific surface area (ca.  $150 \text{ m}^2/\text{g}$ ) [15], impressive mechanical properties (its stiffness is estimated to be about 150-250 GPa and its tensile strength can reach 200 MPa [16,17]) and good optical transparency [18]. Moreover, CNC is fully biodegradable and, interestingly, hastens the biodegradation of green-composite materials [19]. CNC, was found to improve the thermo-mechanical behavior of PVOH along with its water resistance and dimensional stability without impairing its optical features [20,21].

The aim of this work is the enhancement of the stiffness, dimensional stability and thermal properties of PVOH thanks to the introduction of CNC preserving its high biodegradability in order to expand the field of applications of this green polymer. The final goal is the production of PVOH-CNC filaments suitable to feed commercially available FDM 3D-printing machines.



Fig. 3. Fracture surface after tensile test of 3D printed samples of (a) neat PVOH, and nanocomposites with (b) 2 wt%, (c) 5 wt%, and (d) 10 wt% of nanocellulose.



Fig. 4. Melt flow index as a function of CNC content.

### 2. Materials and methods

#### 2.1. Materials

Thermoplastic poly vinyl alcohol PVOH was used in this study as matrix for the composite, commercial extrusion grade PVOH, Mowiflex TC 232 was provided by Kuraray Co, Ltd. Melt flow index (MFI) (190 °C, 21.6 kg) is 39 ± 8 g per 10 min, glass transition temperature Tg = 34 °C, melt temperature Tm = 178 °C [20], mass density of Mowiflex TC 232 was reported to be  $\rho = 1.27$  g/cm<sup>3</sup> [9].

Cellulose microcrystals, CMC, (specific gravity =  $1.56 \text{ g cm}^{-3}$ ,

mean molecular weight 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  $\mu$ m and a diameter of about 10  $\mu$ m (average L/D ratio of 2.4) CMC (Sigma Aldrich, USA). CMC were used as a starting material for the preparation of CNC as described in the next paragraph.

#### 2.2. Nanocellulose isolation

Cellulose nanocrystals in water solution were prepared from microcellulose through hydrolysis in sulfuric acid according to the method described by Bondeson-Oksman and Cranston-Gray [22,23]. Microcellulose (MCC) was added into a solution of 64 wt% sulfuric acid to obtain a MCC/acid concentration of 0.10 g/ml. The solution was vigorous stirred for 120 min in a mechanical mixer at a temperature of 45 °C. The reaction was stopped by adding distilled water in a volume excess ratio of 10. The acid was removed by two centrifuge cycles at 6000 rpm for 15 min each. The pH of the suspension was neutralized through dialysis using cellulose membranes with a cut-off limit of 3.5 kDa. The suspension was then sonicated for 5 min in a Hielscher 400S sonicator equipped with a sonotrode of a diameter of 3 mm. The obtained aqueous suspension of crystalline nanocellulose was kept at 4 °C until further use. As evidenced by observations with atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM), rod-like particles with a length from 200 nm to 500 nm and a diameter of around 5-10 nm were produced (Fig. 1).



Fig. 5. Thermogravimetric curves (a) and derivative thermogravimetric curves for neat PVOH and nanocomposites filaments.

 Table 1

 Glass transition temperature, melting temperature and crystallinity content for polyvinyl alcohol and relative nanocomposite from DSC results.

5 5		1		
Sample	T <sub>g</sub> first heating (°C)	T <sub>g</sub> second heating (°C)	T <sub>m</sub> peak (°C)	Crystallinity content (%)
f_PVOH	24.6	33.7	178.9	20.9
f_PVOH_CNC-02	26.4	41.6	180.5	19.6
f_PVOH_CNC-05	25.8	41.1	181.4	17.0
f_PVOH_CNC-10	21.7	42.1	180.1	16.9
f_PVOH_CNC-20	16.8	55.9	177.4	29.2
3D_PVOH	25.6	34.0	180.2	26.5
3D_PVOH_CNC-02	26.4	41.9	180.7	16.1
3D_PVOH_CNC-05	25.2	47.9	181.2	15.5
3D_PVOH_CNC-10	25.8	47.9	182.0	14.6

#### 2.3. Preparation of 3D printable filaments

PVOH and PVOH/CNC composite were prepared by solution casting. PVOH pellets were dissolved under magnetic stirring in distilled water at 80 °C for 2 h to obtain a 6 wt% solution. A solution of 1.4 wt% of PVOH/CNC was prepared by mechanically mixing with a homogenizer (Dispermat<sup>\*</sup> FI SIP) for 5 min at 2000 rpm and sonication for 3 min using a 14 mm tip at 30% of the maximum power. The obtained solutions were degassed before poured into silicon molds at 50 °C for 72 h. The CNC content in nanocomposites was varied from 0 to 20 wt%. Finally, plates were obtained with an average thickness of 0.45  $\pm$  0.05 mm and high transparency level.

These plates were reduced to fine particles with a Piovan RN166/1 grinder and dried at 50 °C for 24 h. The so obtained powder was used to feed a single screw extruder (Estru 13, Friul Filiere SpA, Udine, Italy) with a screw diameter of 14 mm and a die diameter of 3 mm. Temperature inside the extruder increased from 145 °C in the feeding zone to 175 °C in the die zone. Under these selected processing conditions, continuous filaments were obtained with various concentration of CNC and with a diameter of 1.7  $\pm$  0.1 mm suitable to be used in a commercial 3D printer machine based on FDM technology.

#### 2.4. 3D printing by fused deposition modeling

Parallelepiped and dumbbell (ISO 527 1BA) specimens were designed using a CAD software, exported in a rapid prototyping format and uploaded to the Slic3r software where the model was sliced by a slicing 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 printing area of 200 mm  $\times$  200 mm  $\times$  200 mm and 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 and a fill percentage of 100% were chosen to obtain the best mechanical properties. Other parameters were a layer height of 0.2 mm, a nozzle temperature of 230 °C, a bed temperature of 40 °C, and a deposition rate of 40 mm/s.

All samples were coded indicating filament (f) or 3D printed (3D), the matrix, the filler and its content (i.e. f\_PVOH\_CNC-05 indicates a filament of PVOH with 5 wt% of nanocellulose).

#### 2.5. Testing techniques

Before testing, filaments and 3D printed samples were conditioned at 23  $^{\circ}$ C and 55% of relative humidity in a chamber with a super-saturated solution of Mg(NO3)2-6H2O until a constant weight was reached.

Morphology of nanocellulose from water suspension was analyzed by Atomic Force Microscope (AFM) technique. AFM measurements were performed with a NT-MDT, Solver Pro instrument in semi-contact mode. A droplet of aqueous CNC suspension was allowed to dry on a silicon surface and a tip of 22 nm of curvature and 10 N/m was used to scan the specimen.

Microstructural observations of CNC filler and of cryo-fractured surfaces of the neat matrix and the corresponding CNC composites were carried out by a Zeiss Supra 40 high resolution field emission scanning electron microscope (FESEM) with an accelerating voltage of 3 kV, after deposition of a platinum palladium conductive thin coating.

Melt flow index (MFI) measurements were performed according to ASTM D1238 standard, by a Kayeness Company, model 4003DE capillary rheometer, at a temperature of 190  $^{\circ}$ C with an applied load of 5 kg.

Differential scanning calorimetry (DSC) measurements were performed by a Mettler Toledo TC15 calorimeter. Samples of about 12 mg were analyzed under a nitrogen flow of 150 ml/min, applying a first heating run from 0 to 220 °C linked to a cooling run from 220 °C to 0 °C followed by a second heating run until 220 °C. All 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. The crystallinity content ( $X_c$ ) of PVOH-CNC was calculated using Eq. (1):





Fig. 6. E' (a), E" (b) and tan delta (c) curves for PVOH filaments at different concentration of CNC.

$$\Delta X_{\rm c} = \frac{\Delta H_{\rm m}}{\Delta H_{\rm r} (1 - X_{\rm CNC})} x100 \tag{1}$$

A T T

Where,  $\Delta H_m$  is the enthalpy of melting,  $\Delta H_r$  is the reference enthalpy of fusion of 100% crystalline PVOH (taken equal to 161 J/g [24]), and  $X_{CNC}$  is the weight fraction of nanocellulose.

Thermal stability of filaments and 3D printed composites was investigated through thermogravimetric analysis (TGA), using a TGA Q5000 device from TA instrument in a temperature interval between 25 and 700 °C, at a heating rate of 10 °C/min, under a nitrogen flow of 150 ml/min. The weighing accuracy of the machine is  $\pm$  0.1% and the weighing precision is  $\pm$  0.01%. The onset temperature (i.e., the temperature associated to a mass loss of 5%) and the residual mass at 700 °C were evaluated. The maximum degradation temperature was estimated from the maximum of the peak of mass loss rate curves.

Dynamic mechanical thermal analysis (DMTA) measurements were performed by using a DMA Q800 device (TA Instruments, New Castle, USA) under tensile configuration. Strips (15 mm long and 5 mm wide) obtained by 3D-printing and filaments (15 mm long) were tested in a temperature range between -10 °C and 150 °C at a heating rate of 3 °C/ min and a frequency of 1 Hz to determine the temperature dependence of the storage modulus (E'), loss modulus (E'') and loss tangent (tan\delta).

Creep tests were carried out by a DMA Q800 device under a constant tensile stress ( $\sigma_0 = 10\%$  of the stress at break,  $\sigma_B$ , of the neat matrices) at 30 °C for a total time of 3600 s. The creep compliance D(t), calculated as the ratio between the time dependent deformation  $\epsilon(t)$  and the applied stress, was evaluated.

Quasi-static tensile tests were carried out by means of an universal tensile testing machine Instron 4502, equipped with a load cell of 1 kN

at a crosshead speed of 10 mm/min. An long-travel extensiometer (Instron mod. 2603-080/656) was used to monitor the deformation during the tensile tests. At least five specimens for each formulation were tested to determine the elastic modulus E, the strength  $\sigma_B$  and the strain at break  $\epsilon_B$ . Additionally, by the integration of the area under the stress-strain curves, the tensile energy to break, (TEB) corresponding to the total energy absorbed per unit volume up to fracture was determined.

#### 3. Results and discussions

#### 3.1. Morphology

Morphological aspects of the cryo-fractured sections of pure PVOH and CNC nanocomposite filaments were investigated by FESEM and the images are shown in Fig. 2. For the neat PVOH matrix (Fig. 2a) a smooth and uniform surface can be observed, while for PVOH-CNC composites (Fig. 2b–d) a high degree of surface corrugation, proportionally to the filler content, can be noticed.

CNC nanoparticles appear homogeneously and evenly dispersed. No appreciable aggregation has occurred during the extrusion process, apart for the sample with 20 wt% of CNC where a certain filler agglomeration can be noticed. In the latter case, the fracture surface turns from a smooth flat surface to a corrugated one due to the stress concentration of these aggregates leading to a localized early brittle rupture [25,26].

In Fig. 3, the fracture surfaces of 3D printed samples after tensile test are presented. The effect of nanocellulose incorporation on the morphology of printed structure and in the fracture behavior can be





Fig. 7. E' (a), E" (b) and tan delta (c) curves for PVOH 3D printed samples at different concentration of CNC.

clearly observed. The aspect ratio of printed filaments inside the sample decreases with the amount of CNC. Filaments change from an oval cross section to a circular one, this could be due to an increase of the viscosity. Samples printed with the neat polymer show a good spread of the filament and a good adhesion between layers resulting in a smooth fracture surface. Nanocomposite 3Dprinted specimens show a weaved fracture surface and an incomplete joint between the layers. The activation of new fracture mechanisms could be the cause of an enhancement in the stress at break with the increase of CNC as reported in Paragraph 3.4.

#### 3.2. Thermal properties

Fig. 4 represents MFI of neat PVOH and nanocomposite filaments at different concentrations of CNC. The results reveal the influence of addition of CNCs on the viscosity of the nanocomposites filaments. MFI decreases drastically as the nanofiller content increases. This behavior is obviously due to the strong interaction of nanocellulose with the PVOH matrix. MFI of filaments containing 20 wt% of CNC is not reported since it was not determiend due to the high viscosity. Therefore, 3D printing was not possible for this composition.

The effect of CNC on thermal stability of PVOH and its composites was evaluated through thermogravimetric analysis (TGA). In Fig. 5, TGA curves and derivative (DTG) curves for filaments of neat PVOH and nanocomposites are presented. An initial mass loss can be noticed which is common to all composition and related to the evaporation of absorbed water. In the curve of the neat polymer we can clearly distinguish two different steps in the degradation kinetics. From 250 °C to 400 °C dehydration reactions and formation of volatile products are the main causes of mass loss. The peak for neat PVOH at 320 °C is shifted to higher temperatures, 360 °C–370 °C, with the increase of filler content, enhancing the thermal stability of the composites as compared with the neat PVOH. At the highest concentration of CNC a new peak appears at 270 °C, resulting in a mass loss of 20%. In accordance with literature information [27], this effect could be attributed to the more heterogeneous distribution of CNC nanoparticles at a filler content of 20 wt%. At temperatures higher than 400 °C the decomposition of carbonaceous species occurs [28] with a peak in the derivative thermogravimetric curves located at about 440 °C for all the composition. This behavior is positive for the subsequent processing step of 3D printing for which high nozzle temperatures are needed to ensure a good quality of the final products.

Thermal properties of the PVOH and PVOH-CNC composites were determined using differential scanning calorimetry DSC. The glass transition temperature, the melting temperature and degree of crystallinity obtained from the DSC are reported in Table 1.

The collected DSC thermo-grams reveal some striking similarities between the thermal behavior of all 3D printed samples and nanocomposites filaments during the heating and cooling stages. The introduction of nanocellulose in the matrix increases the thermal stability of the material as we can see from the rising values of the glass transition temperature during the second scan. No effects are observed on the melting behavior of the composites and the crystallinity fraction decrease as the nanofiller content increases in good agreement with the findings or Roohani et al. [29].





Fig. 8. Creep compliance curves for filaments (a), 3D-printed samples (b), and relative creep compliance value at 3600 s (c).

 Table 2

 Mechanical properties of filaments and 3D printed components.

	E <sub>10%ε</sub> (MPa)	σ <sub>B</sub> (MPa)	$\epsilon_{\rm B} \ (mm/mm)$	TEB (MJ/m <sup>3</sup> )
f_PVOH	$5.60 \pm 0.26$	$17.84 \pm 1.01$	$2.18 \pm 0.21$	$23.34 \pm 3.61$
f_PVOH_CNC-02	$6.79 \pm 0.49$	$25.85 \pm 3.21$	$2.63 \pm 0.16$	$42.21 \pm 3.15$
f_PVOH_CNC-05	$9.17 \pm 0.26$	$20.09 \pm 2.49$	$2.05 \pm 0.38$	$28.55 \pm 8.67$
f_PVOH_CNC-10	$11.61 \pm 0.70$	$21.77 \pm 3.82$	$1.77 \pm 0.37$	$28.86 \pm 8.23$
f_PVOH_CNC-20	$16.63 \pm 0.81$	$20.94 \pm 2.83$	$0.56 \pm 0.19$	$11.08 \pm 4.66$
3D_PVOH	$2.88 \pm 0.15$	$11.19 \pm 0.58$	$2.93 \pm 0.06$	$25.45 \pm 3.62$
3D_PVOH_CNC-02	$4.25 \pm 0.19$	$11.69 \pm 0.67$	$2.63 \pm 0.05$	$20.00 \pm 0.65$
3D_PVOH_CNC-05	$4.98 \pm 0.26$	$19.32 \pm 0.69$	$2.55 \pm 0.06$	$25.64 \pm 6.02$
3D_PVOH_CNC-10	$5.71 \pm 0.21$	$15.46 \pm 0.55$	$2.36~\pm~0.16$	$24.06 \pm 3.84$

#### 3.3. Thermo-mechanical properties

DMTA thermograms of filaments with various concentration of CNC are reported in Fig. 6. A progressive enhancement of both the storage (E') and the loss (E") moduli of the filaments can be observed as the filler loading increases. It is worthwhile to note that at room temperature an increase of E' and E" of 380% and of 320% was respectively reached at the highest concentration of CNC of 20 wt%, while an increase of respectively 280% for E' and 250% for E" was observed for a 10 wt% CNC content. Tanð values decrease with the amount of CNC until 30 °C. After this temperature a switch in the trend with the increase of the values with the increase of filler content can be observed. This effect could be explained with the fact that crystalline nanocellulose has a more relevant action on the elastic components than on the viscoelastic behavior of neat PVOH at low temperature while this effect is switched at higher temperatures. The increase of CNC content has

only a marginal effect on the transition temperature as revealed by the slightly increase in the temperature of tan  $\delta$  peak.

The same trend was found also for 3D printed samples whose DMTA thermograms are reported in Fig. 7. In comparison to filaments, lower values in storage and loss moduli are reached, but the increase in the E' and E" values at 23 °C are more or less the same with an increment of 290% and 250% respectively with the 10% of CNC. Lower values are expected due to the presence of voids and porosity intrinsic to the manufacturing process.

In Fig. 8 the isothermal creep compliance curves for filaments (a) and 3D printed samples (b) are presented. A proportional reduction of the creep compliance with the increase of filler content confirms an improvement of the dimensional stability (Fig. 8c). A decrease of the creep compliance at 3600 s of 47% for filaments and 35% for 3D printed samples can be observed.



Fig. 9. Representative curves for filament (a) and 3D printed samples (b).

#### 3.4. Mechanical properties

The effect of CNC on the elastic modulus (E), tensile strength ( $\sigma_B$ ) and strain at break ( $\varepsilon_B$ ) of neat PVOH and PVOH nanocomposite filaments and 3D-printed specimens are summarized in Table 2. The representative stress-strain curves of examined nanocomposites in form of filaments and 3D printed specimens are reported in Fig. 9.

Both filaments and 3D printed samples manifest an increase in the elastic modulus proportional to the amount of nanofiller. Therefore, despite a decrease in crystallinity content was found with DSC analysis, the stiffening effect played by CNC is prevailing.

Ultimate mechanical properties (stress and tensile energy to break) are improved due to the strong interaction between the matrix and the filler as confirmed by SEM analysis. The maximum reinforcement effect was found for filaments at 2 wt% of nanocellulose for which an increase of 81% in the values of TEB and 45% in the stress at break can be observed. An enhancement in tensile properties was observed for 3D printed samples at 5 wt% of CNC where the stress at break shows an increase of 73%. The poor ultimate properties observed for filament at 20 wt% of CNC could be related to the agglomeration of filler inside the matrix.

Interlayer and intralayer debonding in 3D printed samples (Fig. 3) play an important role in determining their fracture behaviour, and possibly explain why the increase of mechanical properties of filament with 2 wt% of CNC is not transferred to 3D printed samples with the same amount of filler.

#### 4. Conclusions

The goal of this work was to produce 3D printed nanocomposites based on poly (vinyl alcohol) (PVOH) and crystalline nanocellulose (CNC). Crystalline nanocellulose was obtained from microcellulose with a hydrolysis treatment with sulfuric acid. Filaments, suitable to feed a desktop 3D printer, were prepared extruding nanocomposite materials obtained by solution casting with a single screw extruder. Different composition, from 2 wt% to 10 wt% of CNC in PVOH, were successfully printed despite the high viscosity of the molten filaments. Electron microscopy revealed that nanocellulose was dispersed well in PVOH both in filament and in 3D printed parts. Microstructure of printed sample seems to be highly affected by the viscosity of the material resulting in a non-completely densification when CNC is introduced in the material. The TGA performed to investigate the thermal stability of the produced materials showed that the introduction of CNC increase the thermal stability of neat PVOH shifting the dTG peak from 320 °C to 370 °C at 10 wt% of CNC. An improve in thermal stability is confirmed also by DSC which evidenced an increase of the Tg of 3D printed parts from 34 °C to 48 °C, while the melting temperature remains practically

unchanged. DMTA tests showed that CNC was able to improve the storage and loss modulus of PVOH in the temperature range analyzed. In particular, E' and E" values of 3D printed samples at 23 °C increase by 290% and 250% respectively with the 10% of CNC. A decrease in creep compliance corresponding to an increase in dimensional stability was observed with the increase of amount of filler confirm another time the positive behavior on thermal stability. Crystalline nanocellulose was able to limit the rubber-like behavior of polyvinyl alcohol. For both filament and 3D printed specimens, tensile tests highlighted an improvement of the stiffness after the introduction of the CNC. The good adhesion between CNC and PVOH increases the toughness of 3D printed material although the lower densification achieved. Stress at break for 3D printed samples increase by 73% when 5 wt% of CNC is added in the matrix and filament at 2 wt% of nanocellulose shows an increase of 81% in the values of TEB and 45% in the stress at break.

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