

USE OF NANOFIBRILLATED CELLULOSE (NFC) IN THERMOPLASTIC BIOCOMPOSITES FOR ECO-RESPONSIBLE AUTOMOTIVE INTERIOR PARTS

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Abstract

Current environmental changes mandate for immediate actions to be taken by players from all industries. Automotive industry needs to decrease vehicles fuel consumption and, implicitly, their emissions. The main solutions are the weight reduction of vehicles, the introduction of renewable, bio-sourced and of recycled materials in the car parts. In North America, thermoplastics account for ~8 % of the total vehicle weight, i.e. ~155 kg/vehicle. This proportion is expected to increase due to continuous growing of the replacement of metals by fiber reinforced plastics. The utilization of the most common automotive plastics, such as polypropylene (PP) (interior applications) and polyamides (PA) (under-the-hood applications), can be reduced by using cellulosic fibers in their composition, a renewable and abundant natural polymer.

This work presents the use of nanofibrillated cellulose (NFC) in the development of thermoplastic biocomposites for automotive interior parts. NFC, cellulose fibrils belonging to the nanocellulose reinforcement category, are produced from Northern Bleached Softwood Kraft pulp (NBSK) by a chemical-free top-down mechanical refining process which results in fibrils of high strength, purity, aspect ratio, and surface area. NFC fibrils were used in mixtures with NBSK fibers. The effect of NFC amount in NBSK:NFC mixtures, i.e. 100:0, 90:10, 80:20, and 70:30, was explored in PP and PA6 biocomposites containing 20 wt.% NBSK:NFC mixtures. Up to 50% increments in mechanical and thermal properties were observed when the mixture of NBSK:NFC 80:20 was used. This mixture, at different contents, was compounded further in PP, PA6, and polylactic acid (PLA) matrices to obtain new biocomposites. Mechanical and thermal properties of biocomposites presented increments when compared at initial matrices but, also, when compared to composites currently used in car parts. Biocomposites based on PP and PLA were also tested for their recyclability and proved, after at least five cycles of recycling, a preservation of their performance. The biocomposites were used in injection molding to fabricate prototypes for automotive interior applications, and, as well, in the fabrication of filaments for 3D printing and 3D printed objects. These eco-friendly bio-based materials shown great potential to replace the conventional petroleum-based ones currently used in automotive interior parts.

Background

Our modern environmental crises impales for reducing the petroleum-based plastics utilization, for collecting and recycling of outstanding ones, and for increasing the usage of environmentally-friendly biopolymers and biocomposites containing cellulosic fibers with recyclability potentials. The cellulose is the most abundant biopolymer, naturally synthesized as elementary cellulose chains hierarchically organized into nanofibrils, microfibrils, fibers, and

bundles. The energy level and/or types of chemical helpers used in the transformation of wood cellulosic fibers lead to different physical aspects reliant to fiber diameter and length, diameter distribution, length distribution, aspect ratio, crystallinity, and biomass source [1]. The cellulose nanocrystals (CNC) named also nanowiskers, the micro/nanofibrillated cellulose (NFC) and the cellulose nanofibers (CNF) are the most representative products resulting from wood fibers processing. NFC fibrils are defined to be long, flexible, containing both crystalline and amorphous regions [2]. NFC fibrils have a width distribution range of 80 nm - 25 μm , a length distribution range of 100 μm - 2 mm and an aspect ratio up to 1200. They have a relative small mass while their surface area is large, i.e. up to 80 m^2/g , which will have significant advantages when used as reinforcements in thermoplastic polymers [3, 4].

The utilization of polymers reinforced by cellulose such as NFC fibrils will continuously increase to become very significant in the near future. The most studied NFC biocomposites are those based on PP, one of the most used plastic worldwide designated for applications such as automotive interior parts, construction, packaging, and common goods. The generation of micro/nanofibrillated cellulose and its simultaneous blending with PP was studied by kneading a mixture of Kraft pulp and powdered PP via a twin-screw extruder. The kneaded PP / 50 wt.% fibrils biocomposites containing maleic anhydride grafted polypropylene (MAPP) as compatibilizer proved a 2-times increment in tensile modulus, 1.5-times increment in tensile strength, and the heat deflection temperature increased by 53 $^{\circ}\text{C}$ compared to pristine PP [5]. These enhanced properties seemed to prove that the nano/micro fibrils were formed during kneading and were well dispersed in the matrix. PP biocomposites containing up to 5 wt.% nanofibrillated cellulose surface modified with silane were also studied. The best performance was obtained for PP / 3.5 wt.% modified nanofibrillated cellulose. Biocomposite hardness, tensile, and impact strength were evaluated respectively at 7.4 %, 12.6 %, and 86.1 % higher than the neat PP [6]. Hence, surface modification of cellulose fibrils with silanes or MAPP demonstrated to create enhanced interaction between fibrils and polymer matrix. In another study, the microfibrillated cellulose were reacted with tannic acid which rendered hydrophobic the fibrils surfaces. This improved their dispersion in an apolar thermoplastic matrix, such as poly(propylene)-poly(ethylene) copolymer. Despite this good dispersion of cellulose fibrils, some remaining aggregates impaired the impact performance of biocomposites at loadings greater than 1 wt.% [7]. Interesting reviews are available in the literature stating on the adhesion between the cellulose fibrils / fibers and different thermoplastic matrices and are guiding the way to compatibilize them to further obtain biocomposites with optimal performance [8]. The processability of nano/microfibrillated cellulose was investigated with the purpose to state on the effect of applied transformation processes on the thermal stability of NFC fibrils and of their biocomposites [9]. It was demonstrated that the PP biocomposites containing up to 10 wt.% fibrils, under melt blending and injection molding, would not be seriously affected by the high temperature used during processing.

Polyamides are also among the most used thermoplastic worldwide in automotive parts applications. Polyamide 12 (PA12) was used to produce biocomposites by incorporation of cationic treated microfibrillated cellulose by twin screw extrusion and injection molding. The appropriate cationic treatment onto fibrils significantly increased mechanical and thermal properties of obtained biocomposites [10]. CNF nanopapers (obtained from slurries) and PA6 fibers thermoplastic nanocomposites were successfully fabricated by wet-laid hand sheet forming process. The tensile strength and modulus of PA6 / 40 wt.% CNF wet-laid structures seemed to have values of 3- and 8-times higher compared at pristine PA6 [11].

Micro/nanofibrillated cellulose-, nanowiskers- or nanocrystals-reinforced biocomposites based on biodegradable and/or bio-based polymers have also attracted the attention [12]. Polylactic acid (PLA) is a plant-based, compostable, and commercially available biopolymer. During the last years, very valuable reviews were published on the way of preparation, structure,

and properties of PLA - nano/microfibrillated cellulose biocomposites with important focus on the surface modification of fibrils for their dispersion improvement in PLA [13-17]. An useful example is the use of a reactive coupling agent, the PLA-*g*-MA, to increase the adhesion between cellulose fibrils the PLA matrix. PLA biocomposites were prepared through twin-screw extrusion considering 5 wt.% maleated PLA and two levels of cellulose nanofibers, i.e. 3 and 5 wt.%. At 5 wt.% CNF, the impact strength, tensile strength and modulus presented 131%, 138% and 40% increments, respectively, compared to pure PLA [18].

Additive manufacturing (AM) of thermoplastics, also known as 3D printing or fused filament fabrication (FFF), is an effervescent industry which appeals for important innovation of new materials, technology progress, molds and tooling making, and for direct manufacturing of series parts. Due to its novelty, very few studies were done thus far on thermoplastic filaments fabrication based on biocomposites containing NFC and their 3D printing to manufacture objects and parts. 3D printing filaments using PLA containing 30 wt.% NFC were 3D printed and the obtained specimens proved mechanical properties being comparable to neat PLA, i.e. an elongation at break of 12 %, tensile strength of 59.7 MPa, and flexural strength of 50.7 MPa [19]. In another study, the PLA grafted cellulose nanofibers (PLA-*g*-CNFs) was extruded in filaments and 3D printed into parts. The thermal annealing, at a temperature above PLA's glass transition, enhanced the flexural properties of 3D printed specimens [20]. PLA / NFC biocomposite filaments for FFF are promising environmentally friendly solutions for parts design reiteration, prototyping, 3D printing of jigs, tooling and fixtures. When 3D printed in-house and on-demand, these 3D printed objects would drastically simplifies logistics while reducing times and cutting their costs.

This work presents methods of easy-utilization of nanofibrillated cellulose (NFC) in the development of thermoplastic biocomposites for automotive interior parts and 3D printing applications. The NFC fibrils used in this work, have high purity, high aspect ratio and surface area, and were produced from by a top-down mechanical chemical-free refining process [21]. NBSK:NFC 80:20 mixtures were used, in concentrations 10, 20, and 30 wt.%, in PP, PA6, and PLA to compound biocomposites. PP and PLA biocomposites containing NBSK:NFC also demonstrated to be recyclable while PLA biocomposites proved to be easy to use in 3D printing applications. Mechanical and thermal performance of developed biocomposites proved significant increments, similar and even higher than the performance of current used composites while being easy to manufacture and easy to use in more eco-responsible automotive parts.

Experimental Part

Materials

Mixtures of NBSK:NFC were supplied by Performance BioFilaments Inc. (Vancouver, British Columbia, Canada). NFC is manufactured using a proprietary processing technology consisting in a high-consistency refining step. Pulp fibers are fed into the refiner where high shear forces pull them apart resulting in peeling / delaminating to produce nano/microfibrillated cellulose. Nanofibrillated and micro/nano-fibrillated materials can be used as reinforcing agents in thermoset and thermoplastic composites [20, 21], for enhancing internal curing and structural properties in concrete [22, 23], in filtration media, and as rheology modifiers for drilling and industrial fluids. In this work, NFC fibrils were used in mixtures with NBSK fibers in different proportions. NBSK:NFC were in proportion, at 90:10, 80:20, and 70:30, by weight. The physical aspects of pure NFC, NBSK:NFC mixtures, and of pure NBSK fibers are presented in the Figure 1.

PP Pro-fax PD702 (Lyondell Basell Industries, USA), a homopolymer grade with a melt flow rate of 35 g/10 min (230 °C/2.16 kg) for injection molding application was used in this work. High impact PP copolymer Profax SG802N (Lyondell Basell Industries, USA), was also used to produce one biocomposite for comparison purposes. Commercial PP composites (i.e. data from

their Technical Data Sheets) were selected for comparison purposes: PP containing 20 wt.% BioFiller (Agriplas™ BF20H, Lyondell Basell Industries, Wilmington, DE, USA) and PP containing 20 wt.% short glass fibers (Sabic® PP S3620, Sabic Plastics Canada, Long Sault, ON).

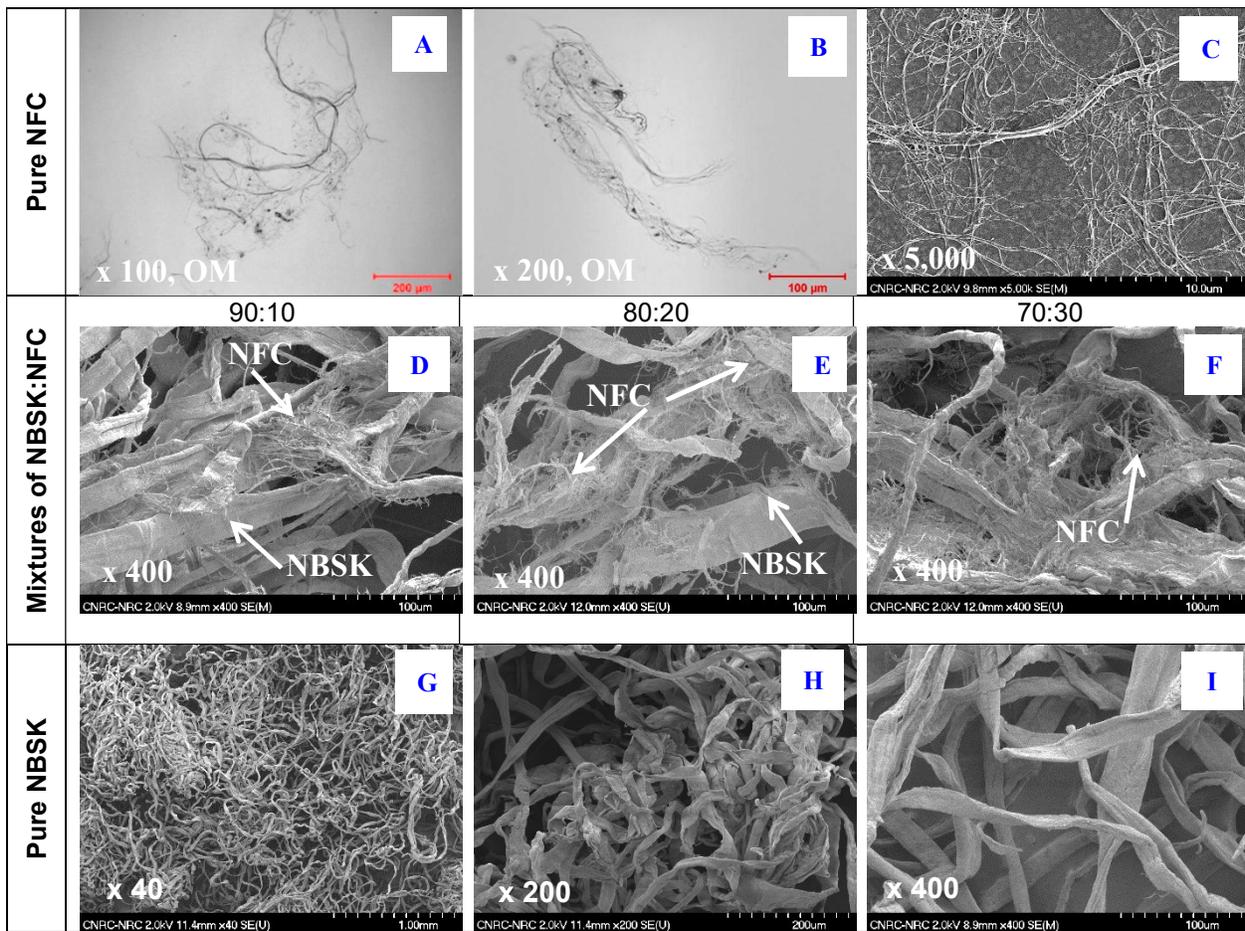


Figure 1: SEM and OM images of pure NFC fibrils (1st row), of NBSK:NFC fibers:fibrils mixtures (2nd row), and of pure NBSK fibers (3rd row)

PA6 grade Ultramid B27 E01 (BASF Polyamides and Intermediates, Freeport, TX, USA), a compounding grade, was used in this work. Its melt volume rate was of 130 cm³/10 min as evaluated by the manufacturer at 275 °C/5 kg. The properties (i.e. data from their Technical Data Sheets) of commercial PA6 composites were selected for comparison purposes: PA6 containing 20 wt.% short glass fibers (Silamid® LSV20) and PA6 containing 30 wt.% short glass fibers (Silamid® LSV30) both from Roonamid A.S., Žilina, Slovakia.

PLA8302D, a semi-crystalline grade (cPLA), with approximately 2 % of D-lactic acid monomer, was supplied by NatureWorks, Minnetonka, MN, USA. Properties of commercial PLA biocomposites (i.e. the data from their Technical Data Sheets) were also used for comparison purposes as follow: PLA / 30 wt.% cellulosic fibers obtained from meadow grass (AgriPlast NFNI 3070/40000 HM, Biowert Industrie GmbH, Brensbach, Germany) and PLA / 25 wt.% bleached long fiber Nordic soft wood pulp (Karelina® PLMS7525, Plasthill Oy, Kontiolahti, Finland).

Specific coupling agents were added as a function of the type of polymer used as matrix. The coupling agent used in PP biocomposites was Admer AT2305A, a maleic anhydride modified homo-PP which was designed to bind the PP to polar materials (Mitsui Chemicals America Inc.,

Rye Brook, NY, USA). It contains three times the normal maleic anhydride grafted in its polymer chain for enhanced adhesion, properties, and efficiency. CesaExtend OMAN698493 (Clariant Additive Masterbatches, USA) was used for its reactivity to play the role of coupling agent in PLA and PA6 based biocomposites. It is an epoxy/styrene/acrylic copolymer, provided in a PLA carrier in masterbatch form. The epoxy groups are believed to bind the carboxyl (-CO-OH) end-groups of PLA chains, the amide groups from PA6 chains to the carboxyl groups from cellulotics.

Processing

Compounding

The extrusion line used to compound the biocomposites was a Coperion 34 mm co-rotating twin-screw extruder (Houston, TX, USA), having 12 mixing zones and L/D ratio of 40. The screw configuration was specially designed by our team to assure an adequate dynamics in the barrel with the purpose to disperse and distribute uniformly the NBSK:NFC in the polymer melts. A die strand, with 6 holes of 2 mm diameter each, was used at the exit of the extrusion line. The temperature profiles were settled considering the melting temperature of each matrix. PA6 and PLA were dried before compounding as per their TDS recommendations. The formulations of compounded biocomposites are presented in the Table I and Table II.

Table I: 1st compounding: formulations of extruded PP and PA6 biocomposites containing un-pelletized 20 wt.% NBSK:NFC mixtures having different contents of NFC, i.e. 0, 10, 20 and 30 wt.%. Coupling agents were used, unless otherwise specified

NBSK:NFC mixture (wt.:%wt.%)			
100:0	90:10	80:20	70:30
In PP matrix			
20 wt.%	20 wt.%	20 wt.%	20 wt.%
-	-	-	20 wt.%, no CA
In PA6 matrix			
20 wt.%	20 wt.%	20 wt.%	20 wt.%
-	-	-	20 wt.%, no CA

Table II: 2nd compounding: formulations of extruded PP, PA6 and PLA biocomposites containing pelletized NBSK:NFC 80:20 mixtures

Mixtures of NBSK:NFC 80:20		
10 wt.%	20 wt.%	30 wt.%
In PP matrix		
+ CA	-	+ CA
	+ CA	
	PP high impact grade + CA	
In PA6 matrix		
+ CA	-	+ CA
	+ CA	
In PLA matrix		
+ CA	-	+ CA
	+ CA	

Injection molding

Biocomposites pellets were dried first and then injection molded using a 34 ton Boy press

(BOY Machines, Exton, PA, USA). The injection barrel and mold temperatures were adapted as a function of melting temperature corresponding to each polymer matrix. Standard specimens were molded according to ASTM D638, ASTM D790, ASTM D256, and ASTM D648 for tensile, flexural, Izod impact, and heat deflection temperature evaluation, respectively.

Recyclability evaluation

The recyclability of PP and PLA biocomposites was evaluated using tensile mechanical testing applied on formulations containing 20 wt.% NBSK:NFC 80:20. The biocomposites were dried, injection-molded, tested, and grinded; this cycle was repeated up to 7 times.

Filaments extrusion and FFF printing

Selected biocomposites were extruded in filaments with a diameter of 1.75 ± 0.05 mm. The biocomposites were appropriately dried prior to their transformation into filaments. Filaments having a consistent diameter and ovality were produced using a Brabender extrusion line (Brabender Technologie GMBH & CO, Duisburg, Germany) adequately adapted in our laboratory for filaments fabrication. The filaments were dried again at appropriate temperatures before using them in 3D printing. The parameters used in 3D printing, such as nozzle diameter, layer thickness, printing temperature, plateau temperature, etc. were adapted as a function of each polymer matrix. Specimens for tensile testing were printed using $+45^\circ / -45^\circ$ bead orientation and 0.2 mm layer thickness on a Prusa i3 MK3S 3D printer (Prusa Research a.s., Praha, Czech Republic).

Characterization

Morphology and microstructure

Scanning electron microscopy (SEM) was carried out on surfaces of fractured specimens resulted from Izod impact test. A coating of gold-palladium alloy was applied on observed surfaces prior to their observation. A Hitachi S-4700 SEM (Hitachi, Krefeld, Germany) was used to investigate the dispersion of NBSK:NFC mixtures and their adhesion to polymeric matrices. Optical microscopy (OM) observations were also done on polished surfaces of selected specimens.

Mechanical testing

Tensile testing was done according to ASTM D638 at a velocity of 5 mm / min on standard type I dog-bone specimens. A video extensometer was used to determine the elastic modulus. For flexural properties, according to ASTM D790, a speed of 1.3 mm / min and a span of 48 mm were applied. The Izod impact strength was evaluated according to ASTM D256 using notched specimens and a hammer of 2 kg. Specimens were conditioned as per each standard recommendations before their testing. All reported values are the average of at least five tests.

Melt flow rate

MFRs were evaluated using a plastometer following the ASTM D1238-13. The materials were dried under the vacuum before testing. The tests were done at 230 °C for PP biocomposites and at 275 °C for PA6 biocomposites while the piston weight of 2.16 kg. The mass of material that extrudes from a 2 mm die over time was measured and MFRs were calculated as g / 10 min.

Heat deflection temperature

Heat deflection temperature (HDT) was measured using an Instron Ceast HDT-3-Vicat (Instron, Norwood, MA, USA). ASTM D648 was applied as follows: a bar of rectangular cross section was tested in edgewise position as a simple beam with central load of 0.455 MPa. The

specimen was immersed under load in a heat-transfer medium which temperature increased by 2 °C / min. Values of temperature under flexural load were recorded as the medium temperature where test bars deflected by 0.25 mm.

Coefficient of linear thermal expansion

Coefficients of linear thermal expansion (CLTE) were evaluated for temperature interval from -50 °C to 150 °C according to ASTM E831. Samples of 6 mm x 4 mm x 3.2 mm were tested under nitrogen. The tests were done in a DMA Q400 (TA Instruments, New Castle, DE, USA) and the data was analyzed using a Universal Analysis software.

Results and discussions

Effect of NFC fibrils content in NBSK:NFC mixtures on biocomposites performance

The effect of NFC content in NBSK:NFC mixtures on the performance of biocomposites was evaluated in PP and PA6 matrices. The NBSK:NFC mixtures, in which the NFC fibrils content was 0, 10, 20, and 30 wt.%, were extruded in both matrices at same concentration of 20 wt.%. The NBSK:NFC mixtures were used as received, in a fluffy un-pelletized shape, using a belt feeder with weight-in-loss control. All PP- and PA6- 20 wt.% NBSK:NFC biocomposites were compounded in the presence of CA, while the formulations containing 20 wt.% NBSK:NFC 70:30 were also compounded without CA, as well. All the compounded formulations are presented in the Table I. Figure 2 presents the biocomposites morphologies obtained in optical microscopy on polished surfaces. The first column presents the PP biocomposites (Figure 2 A - D) and the second one the PA6 biocomposites (Figure 2 E - H). From the top to the bottom are presented the optical morphologies of the biocomposites containing NBSK:NFC mixtures having from 0 up to 30 wt.% NFC fibrils contents in the presence of coupling agents, while the morphologies of biocomposites containing 20 wt.% NBSK:NFC 70:30 with no coupling agents are on the last row.

As disclosed already in the Figure 1, the typical NBSK fibers have a length of 2 - 3 mm, a width of 30 - 50 µm, and an aspect ratio of 50 - 100, and NFC fibrils have a length of 100 - 500 µm, a width of 80 - 300 nm, and an aspect ratio of 800-1200. In the Figure 2, all micrographs, are presenting NBSK:NFC mixtures uniformly dispersed and distributed in both matrices, having rather few or no agglomerates. In all images, the presence of bimodal type of reinforcements can be observed. The thicker fibers should be associated to NBSK fibers and the thinner and shorter ones to NFC fibrils. This bimodal distribution of mixtures of NBSK fibers and NFC fibrils can be distinguished also from SEM observations of as-received mixtures presented in Figure 1. Some NBSK:NFC agglomerates can be seen in PP biocomposite micrograph presented on the last row of the Figure 2. The presence of those agglomerates is due, in this unique case, to the absence of the coupling agent. A further contribution at agglomerates presence, is also the high content of NFC, 30 wt.%, in the NBSK:NFC mixture, which, potentially, predisposed to fibrils agglomeration during its manufacturing process. While those agglomerates are very rare in PP biocomposites, it seems that they are not observable in the PA6 biocomposites (Figure 3 H). PA6, through its amide groups, -CO-NH, had a partial affinity to the carboxyl groups, -CO-OH, from cellulose fibrils and fibers. Further, with the purpose to conserve this good dispersion and distribution of fibers/fibrils in the polymer matrices and to avoid the agglomerates presence, the NBSK:NFC mixtures in a proportion of 80:20 were selected to continue the work.

Figure 3 presents morphologies observed in SEM on fractured surfaces resulted from Izod impact test. The micrographs are presented at different magnification with the purpose to capture the most important trends of biocomposite microstructures and fracture aspects related to adhesion between phases. The first column presents the PP biocomposites (Figure 3 A - D) and the second one PA6 biocomposites (Figure 3 E - H). From the top to the bottom are presented the

micrographs of biocomposites containing NBSK:NFC mixtures having from 0 up to 30 wt.% NFC contents in the presence of CAs. The last row presents the SEM morphologies of biocomposites containing 20 wt.% NBSK:NFC 70:30 with no CAs (Figure 3 D and 3 H).

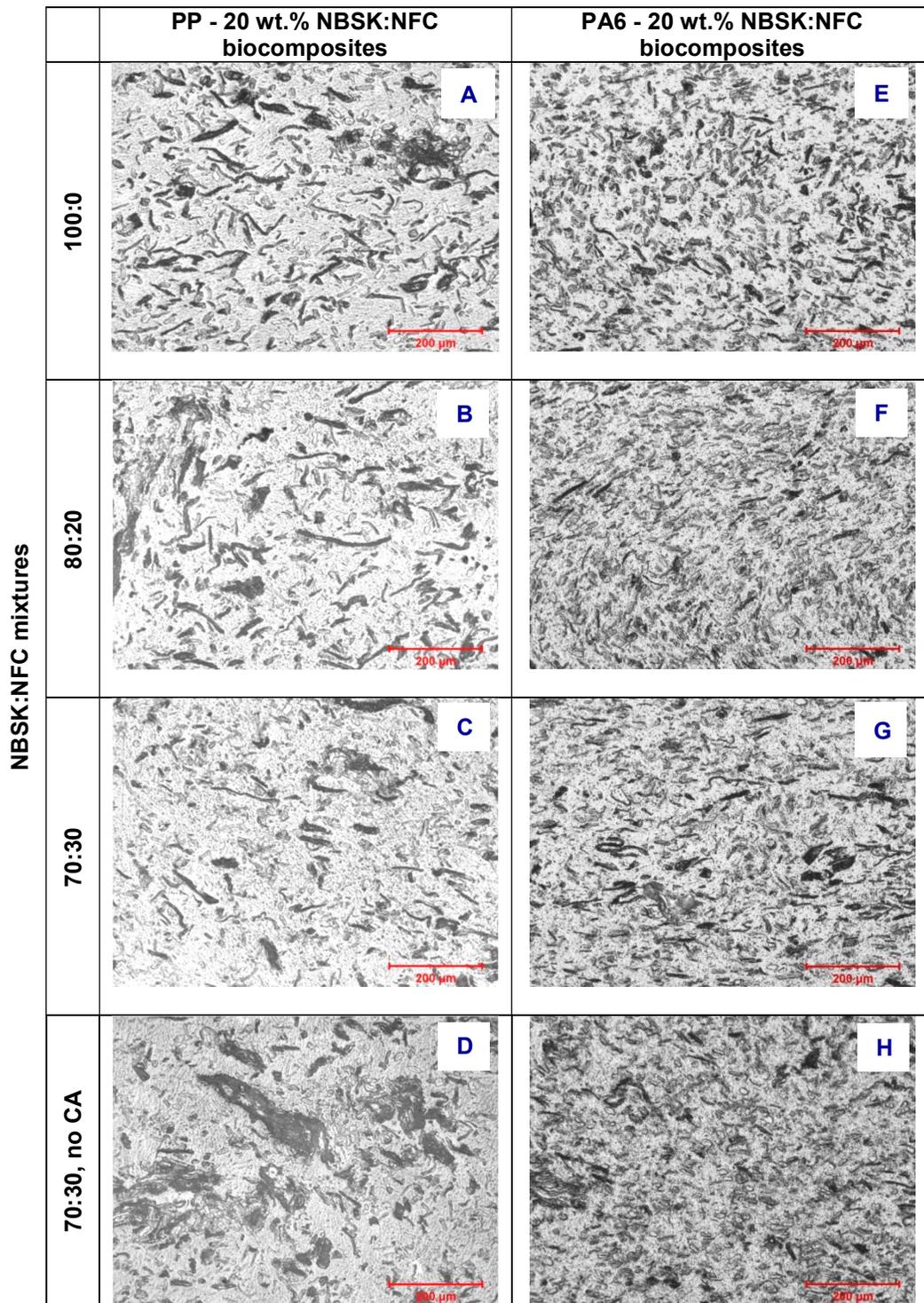


Figure 2: Morphologies observed in OM on polished surfaces of PP and PA6 biocomposites containing 20 wt.% of NBSK:NFC mixtures, at different contents of NFC. All magnifications are x100.

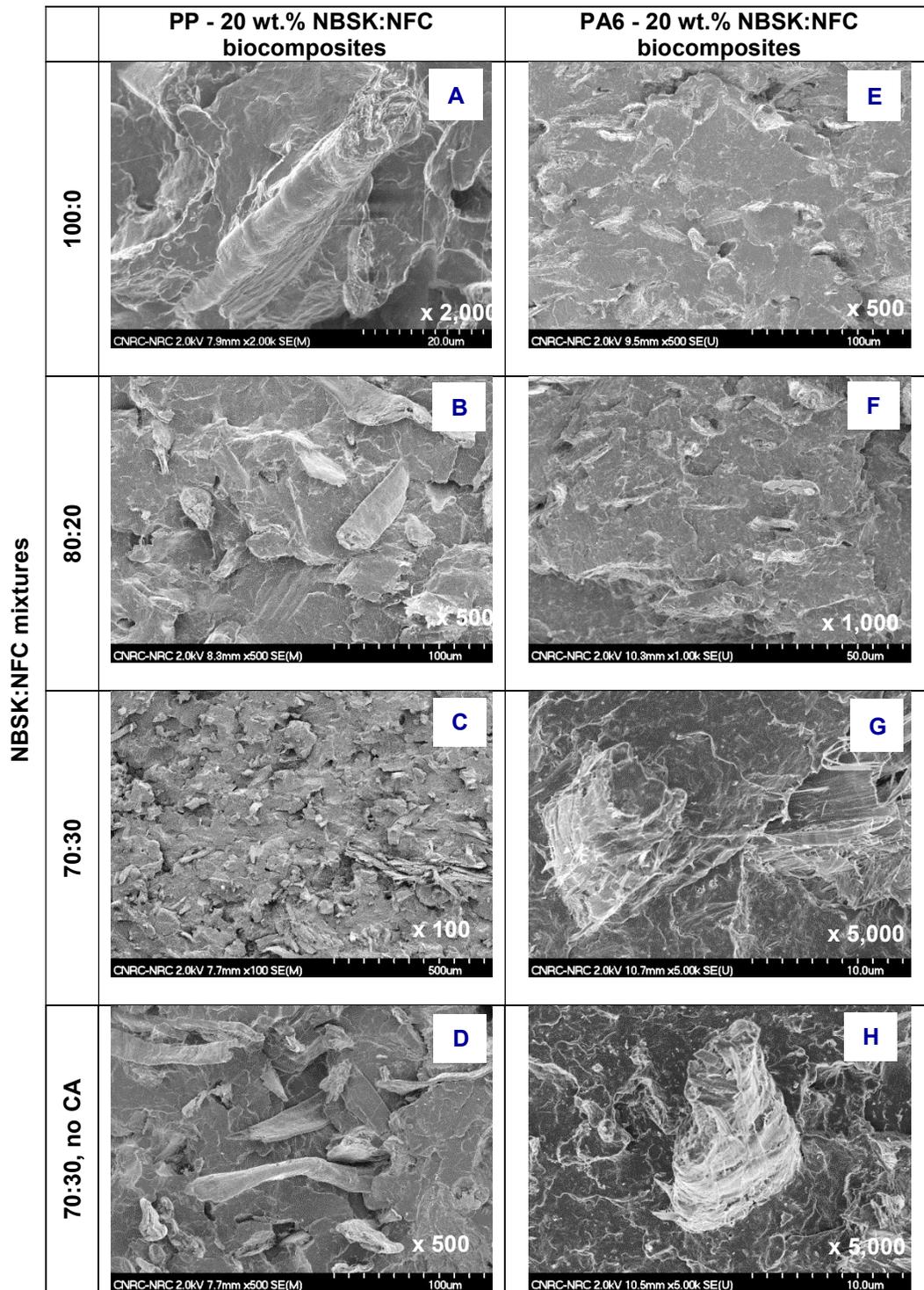


Figure 3: SEM morphology observed on fractured surfaces of PP and PA6 biocomposites containing 20 wt.% of NBSK:NFC mixtures, at different contents of NFC.

From the micrographs presented on rows 1, 2 and 3 in Figure 3, beyond the nice dispersion and distribution observed also previously in the Figure 2, it can be recognized that the matrices

and the cellulose presents an important affinity. In the case of PP - 20 wt.% NBSK:NFC 100:0 - 5 wt.% CA (Figure 3 A), it can be observed that the cellulosic fiber of a diameter of 3 - 4 μm is covered by the PP matrix. From the Figures 3 A to 3 C and Figures 3 E to 3 G an evident adhesion between fibers and matrices can be observed and is justified by a no fibers pull-out. The fracture was produced throughout the cellulose fiber itself as unveiled in the Figure 3 G. Contrary, low affinity can be observed in the micrographs presented on the 4th row (Figure 3 D and 3 H). The PP - 20 wt.% NBSK:NFC 70:30, in the absence of CA, has fractured mostly at cellulose-matrix interface because of their lack of adhesion. Therefore, biocomposites morphological microstructures observed from the SEM micrographs reinforce the existence of an excellent dispersion and distribution observed previously in the Figure 2 but, also, of a good adhesion PP-cellulose and PA6-cellulose reached in the presence of corresponding CA.

Table III: Performance (and standard deviations) of PP biocomposites at different contents of NFC fibrils in NBSK:NFC mixtures.

Name	TS (MPa)	TM (MPa)	FS (MPa)	FM (MPa)	IS (kJ/m ²)	HDT (°C)
PP pristine	29.4 (0.3)	1410 (143)	42.8 (0.5)	1089 (143)	2.4	90.2 (2.1)
Biocomposites with 20 wt.% NBSK:NFC						
100:0, CA	35.6 (0.2)	2707 (95)	61.3 (0.6)	2276 (20)	1.9 (0.1)	137.8 (0.5)
90:10, CA	38.4 (0.5)	2827 (53)	65.5 (0.7)	2487 (30)	2.0 (0.1)	145.1 (1.2)
80:20, CA	37.1 (0.3)	2815 (88)	62.1 (0.8)	2196 (118)	1.9 (0.2)	141.2 (0.6)
70:30, CA	35.9 (0.6)	2711 (79)	62.2 (0.8)	2340 (46)	1.9 (0.1)	143.5 (0.1)
70:30, no CA	32.8 (1.0)	2904 (49)	58.5 (0.5)	2408 (44)	2.5 (0.2)	147.8 (1.8)
Commercial references						
*PP - 20 % biofiller	27.5	NA	NA	2300	3.4	125.0
*PP - 20 % short glass fibers	33.0	2600	NA	2500	38.0	NA

* Numerical values of commercial references are from TDS data provided by their manufacturers (NA= data not available from TDS)

Table III discloses mechanical and thermal performance of PP - 20 wt.% NBSK:NFC biocomposites compared to the ones of pristine PP (top) and of commercial biocomposites based on PP (bottom). At the addition of 20 wt.% NBSK:NFC 100:0 in PP, the tensile strength (TS) increased by 21 % while, when only 10 % of NBSK was replaced by NFC fibrils, the TS increased further by 31 % compared to PP. The difference in this TS increment, at the same total concentration of cellulose in PP, was due to the reinforcement effect of NFC fibrils themselves. At a content of 10 wt.% in the NBSK:NFC mixture and at only 2 wt.% from the total weight of the biocomposite, the NFC alone helped to boost the TS by 10 %. Same TS increment effect was also observed at 20 wt.% NFC in NBSK:NFC mixture (i.e. 4 wt.% in biocomposites), effect which slightly declined at 30 wt.% NFC in NBSK:NFC mixture (i.e. 6 wt.% in biocomposites). This declining of TS should be explained by the presence of some fibers-fibrils agglomerates, as already observed in the morphological microstructures presented in the Figure 2. TS of those biocomposites, in the presence of CA, presented an increase of 22 % compared to PP, and in the absence of CA, the TS increased only by 12 %. Therefore, the loss in tensile strength is due to the lack of CA cumulated to a content of NFC higher than 4 wt.% in biocomposites. The PP-NBSK:NFC biocomposites presented about 2-fold increment in tensile modulus (TM) compared to PP, i.e. a boost from 1400 MPa for pure PP up to 2700-2900 MPa. The same trends can be observed for the flexural properties. The flexural strength (FS) and flexural modulus (FM) increased with increasing NFC content in the mixtures, i.e. up to 53 % (from 42.8 MPa for PP to 62-65 MPa for biocomposites) and up to 128 % (from 1089 MPa from PP to 2200-2500 MPa for

biocomposites), respectively. Again, a declining of the FS is observed for PP-NBSK:NFC 70:30 and also in the absence of CA. The Izod impact strength (IS) of PP biocomposites remained around the value of pristine PP. Notable increments were observed in terms of HDT. The HDT of pristine PP, 90 °C, was upgraded to 138 - 149 °C, which means a boost of 53 - 69 %. The minimum recommended HDT for PP composites to be used in automotive interior applications is 90 °C, therefore the PP - NBSK:NFC biocomposites from this work seem to be suitable for this type of application. What's more, the tensile, flexural, and thermal performance of PP - NBSK:NFC biocomposites are higher than those of commercial references, with the exception of IS for PP - 20 % glass fibers composites.

Table IV: Performance (and standard deviations) of PA6 biocomposites at different contents of NFC fibrils in NBSK:NFC mixtures.

Name	TS (MPa)	TM (MPa)	FS (MPa)	FM (MPa)	IS (kJ/m ²)	HDT (°C)
PA6 pristine	70.4 (1.3)	2657 (73)	120.5 (3.2)	2730 (98)	1.8 (0.5)	163.5 (7.7)
Biocomposites with 20 wt.% NBSK:NFC						
100:0, CA	83.0 (2.3)	4722 (119)	142.9 (2.2)	4429 (24)	2.4 (0.1)	196.4 (0.8)
90:10, CA	90.6 (0.9)	5730 (104)	148.3 (1.3)	5090 (94)	2.4 (0.1)	198.7 3.9)
80:20, CA	89.5 (2.4)	5757 (107)	143.5 (9.8)	5175 (84)	2.5 (0.1)	206.2 (3.3)
70:30, CA	86.5 (1.7)	5528 (109)	144.4 (4.3)	4861 (51)	2.6 (0.2)	201.4 (3.0)
70:30, no CA	81.6 (1.8)	5520 (177)	140.6 (9.6)	5400 (64)	2.3 (0.1)	209.5 (2.9)
Commercial references						
*PA6 - 20 % short glass fibers	70.0	2900	NA	2300	22.0	200.0
*PA6 - 30 % short glass fibers	90.0	5000	NA	3500	25.0	205.0

* Numerical values of commercial references are from TDS data provided by the manufacturer (NA= data not available from TDS)

The evolution of mechanical and thermal performance of PA6 - 20 wt.% NBSK:NFC biocomposites with the increasing of NFC content, along with the properties of pristine PA6 (top) and of commercial biocomposites based on PA6 (bottom) and are presented in Table IV. The TS and FS of pristine PA6 were increased from 70.4 and from 120.5 MPa up to 90 MPa and to 148 MPa, respectively. As for PP biocomposites, a slight deterioration in TS and FS can be observed for PA6 - NBSK: NFC 70:30, with and without CA. This seems to indicate the effectiveness of the selected CA. The most effective NBSK:NFC combination is 80:20. The TM and FM of PA6-NBSK:NFC biocomposites greatly increased, while the IS remained similar to the one of pristine PA6. PA6 biocomposites containing 20 wt.% NBSK:NFC 90:10, 20 wt.% NBSK:NFC 80:20, and 20 wt.% NBSK:NFC 70:30 presented all at least similar tensile, flexural, and thermal performance as commercial references, i.e. PA6 - 20 % short glass fibers and PA6 - 30 % short glass fibers. Hence, PA6 biocomposites from this work seem to be very appropriate for the manufacturing of injection molded parts, including for automotive interiors due to HDT values as high as 200 - 210 °C. The higher IS of the commercial PA6 composites compared to the PA6 biocomposites is due to the high rigidity of the glass fibers reinforcements compared at cellulosic fibers / fibrils that are much more flexible.

Figure 4 shows physical aspects of extruded pellets and injected parts of PP - NBSK:NFC and of PA6 - NBSK:NFC. PP biocomposites were extruded at 190 °C, while PA6 biocomposites at 235 °C. Usually, the injection molding has to take place at a temperature slightly higher than the one used in compounding step to assure the required fluidity to fill-in the tool cavity. Thus, the injection barrel temperature for PP biocomposites was set at 200 °C and for PA6 biocomposites

at 245 °C. An important parameter which determines the exploitation or not of a composites in injection molding process is its melt flow rate (MFR). The MFR of pristine PP, evaluated at 29.7 g / 10 min, was decreased at the addition of 20 wt.% NBSK:NFC down to 2.6 g / 10 min while the MFR of pristine PA6, evaluated at 48.5 g / 10 min, decreased down to 6.2 g / 10 min. These values are very similar to commercial reference composites, i.e. 8 g / 10 min for the commercial PP - 20 % short glass fibers and 1.5 g / 10 min for the commercial PA6 - 20 % short glass fibers. Our PP and PA6 biocomposites present MFR in the same range and proved that they can be easily exploited in injection molding applications.



Figure 4: Physical aspects of extruded pellets and injected parts of PP - 20 wt.% NBSK:NFC (top) and PA6 - 20 wt.% NBSK:NFC biocomposites (bottom)

Effect of the concentration of NBSK:NFC 80:20 on biocomposite performance

Mixture of NBSK:NFC 80:20 was used to compound biocomposites based on PP, PA6, and PLA considering its content in each matrix at 10, 20 and 30 wt.% and appropriate coupling agents (CA). In the case of PP - 20 wt.% NBSK:NFC 80:20, a biocomposite was also compounded based on a high impact grade of PP copolymer (see Table II). For this second step of compounding, the mixture NBSK:NFC 80:20 was used in a pelletized shape to facilitate its feeding using a gravimetric feeder.

Figure 5 presents SEM microstructures of biocomposites containing pelletized NBSK:NFC 80:20 mixtures based on PP (1st column), PA6 (2nd column), and PLA (3rd column). The micrographs were obtained on fractured surfaces of injected specimens corresponding to formulations without CA on the 1st row, with CA on 2nd row, and on 3rd row for the formulations containing 30 wt.% pelletized mixture and CA. In the Figure 5 A, D, G it can be observed that the cellulosic fibers/fibrils were pulled out from the PP, PA6, and PLA matrices and this is due to the lack from the formulations of respective CA, therefore due to a low compatibility between polymers and cellulose. In the presence of CA, the morphological aspects shown in the Figure 5 B, E, and H, demonstrate a good adhesion between cellulose and polymer matrices reflected by fractures evolving throughout the weakest pathways, i.e. through the cellulosic fibers themselves (Figure 5

B and E). The most important increment in the affinity can be observed in the case of PLA - 20 wt.% NBSK:NFC 80:20 biocomposites (Figure 5 H) in the presence of CA. In this case, no pull out of fibers/fibrils was observed, the fibers are completely covered by the PLA matrix. Similar trends in biocomposite microstructures can be observed in the presence of CA for biocomposites containing 30 wt.% NBSK:NFC 80:20 (Figure 5 C, F, and I).

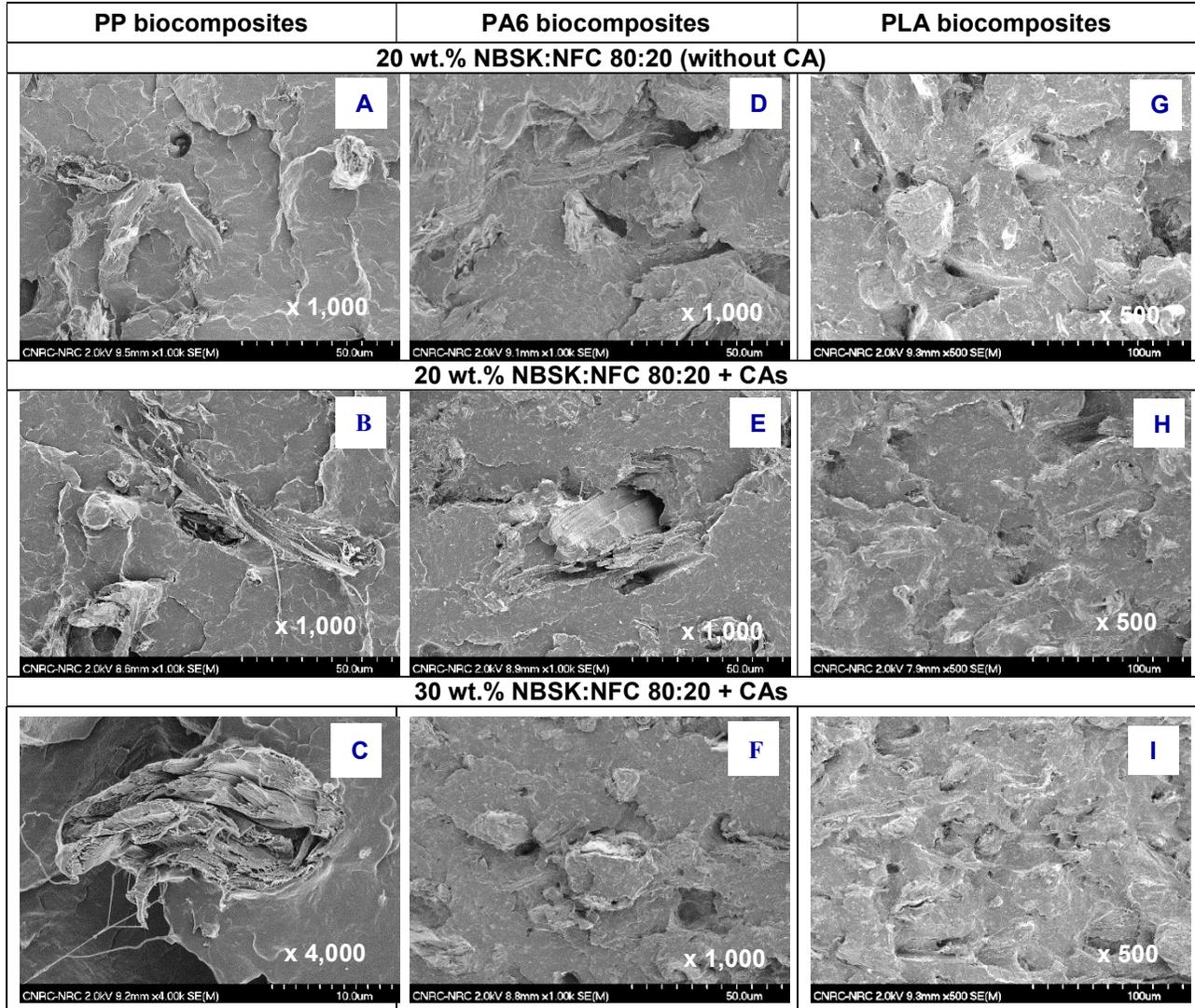


Figure 5: SEM morphologies obtained on fractured surfaces resulted from Izod impact tests of PP biocomposites (1st column), PA6 biocomposites (2nd column), and PLA biocomposites (3rd column)

Table V gathers mechanical and thermal performance of PP, PA6, and PLA biocomposites obtained in the 2nd round of compounding. TS of PP biocomposites, compounded with pelletized NBSK:NFC 80:20 mixtures, increased with the cellulosic content from 29.4 MPa (for pristine PP) up to 39.8 MPa (at 30 wt.% pelletized NBSK:NFC 80:20), i.e. by 35 %. PP containing 20 wt.% pelletized NBSK:NFC 80:20 mixture presents a TS of 34.5 MPa, which is slightly lower than the 37.1 MPa of PP biocomposites compounded with unpelletized mixtures (see Table III). This is a very minor difference. It can be said that during the pelletizing step the attrition of NBSK:NFC 80:20 fibers was negligible while the reinforcement effect of NFC fibrils in polymer matrix was preserved. Very similar effects can be observed for FS of biocomposite obtained with pelletized

vs. unpelletized fibers. TM and FM increased also with increasing the cellulosic content. In the case when PP matrix was replaced by a high impact PP grade, the tensile and flexural performance were slightly decreased but remained equivalent to PP. The explanation consists on low TS of pure PP high impact copolymer compared to PP homopolymer matrix. But, the IS was almost doubled. In terms of HDT, increments from 90.2 °C up to as high as 144 °C were observed at increasing NBSK:NFC 80:20 content. These PP biocomposites containing pelletized NBSK:NFC mixtures have similar and, in some cases, higher mechanical and thermal performance compared to references PP - 20% biofiller and PP - 20% glass fibers.

Table V: Performance (and standard deviations) of PP, PA6, and PLA biocomposites at different contents NBSK:NFC 80:20 fiber mixtures

Name	TS (MPa)	TM (MPa)	ε (%)	FS (MPa)	FM (MPa)	IS (kJ/m ²)	HDT (°C)
Biocomposites PP / pelletized NBSK:NFC 80:20							
PP pristine	29.4 (0.3)	1410 (143)	11.5 (0.9)	42.8 (0.5)	1089 (33)	2.2 (0.6)	90.2 (2.1)
PP high impact*	20	NA	4.0	NA	1080	11.0	81
+ 10 wt.% + CA	31.9 (0.6)	1476 (94)	18.1 (2.3)	54.1 (0.9)	1550 (44)	2.0 (0.2)	126.5 (6.3)
+ 20 wt.%	33.5 (0.9)	1889 (80)	12.2 (0.8)	57.2 (0.5)	1741 (83)	2.7 (0.4)	126.7 (8.9)
+ 20 wt.% + CA	34.5 (1.0)	1842 (73)	13.4 (1.2)	60.6 (0.8)	1871 (80)	3.0 (0.4)	137.0 (7.9)
+ 20 wt.% + CA PP high impact	27.3 (0.5)	1936 (77)	14.7 (0.4)	48.7 (0.4)	1735 (71)	5.3 (0.4)	132.9 (8.1)
+ 30 wt.% + CA	39.8 (0.7)	2476 (36)	12.1 (0.7)	70.3 (0.5)	2235 (26)	3.1 (0.2)	144.0 (1.1)
+20% BioFiller, commercial*	27.5	NA	3	NA	2300	3.4	125
+20% Glass fibre, commercial*	33.0	2600	7	NA	2500	38	110
Biocomposites PA6 / pelletized NBSK:NFC 80:20							
PA6 pristine	70.4 (1.3)	2657 (73)	15.0 (4.8)	120.5 (3.2)	2730 (98)	1.9 (0.5)	150.7 (21.1)
+ 10 wt.% + CA	72.6 (0.9)	3856 (104)	15.8 (5.1)	124.7 (4.2)	3500 (93)	2.6 (0.4)	164.4 (10.0)
+ 20 wt.%	76.2 (1.6)	4139 (50)	7.2 (0.4)	117.2 (2.6)	4368 (77)	2.2 (0.2)	204.3 (4.5)
+ 20 wt.% + CA	78.0 (0.5)	4404 (60)	6.3 (0.3)	126.9 (8.8)	4324 (64)	3.2 (0.2)	200.2 (4.3)
+ 30 wt.% + CA	80.4 (3.2)	5750 (64)	4.7 (0.6)	134.0 (1.9)	5654 (74)	2.3 (0.2)	206.7 (4.6)
+20% Glass fibre, commercial*	70	2900	NA	NA	2300	NA	200
+30% Glass fibre, commercial*	90	5000	NA	NA	3500	NA	205
Biocomposites PLA / pelletized NBSK:NFC 80:20							
PLA pristine	55.3 (0.8)	3052 (72)	4.0	83.0	3800	2.6 (0.4)	57.0
+ 10 wt.% + CA	66.1 (1.5)	4311 (123)	6.2 (0.3)	117.6 (2.4)	4197 (57)	2.7 (0.1)	92.5 (15.5)
+ 20 wt.%	65.7 (1.8)	5001 (31)	4.7 (0.3)	108.3 (3.0)	4859 (18)	2.4 (0.1)	133.5 (16.5)
+ 20 wt.% + CA	67.5 (2.4)	5031 (33)	5.4 (0.2)	116.4 (3.3)	4996 (71)	2.7 (0.1)	NE
+ 30 wt.% + CA	72.4 (0.7)	6026 (79)	4.7 (0.1)	120.1 (8.3)	5724 (75)	2.5 (0.3)	NE
+25% soft wood pulp, commercial*	70.3	NA	2.5	110.0	5100	15.0*	NA
+30% cellulotics, commercial*	34.1	3850	1.4	64.9	4150	2.8*	NA

* Values taken from the TDS supplied by material manufacturers; NA = Not Available data

The biocomposites based on PA6 and pelletized NBSK:NFC 80:20 mixtures displayed also an augmentation in TS, from 70.4 MPa up to 80.4 MPa, and in FS from 120.5 MPa up to 134 MPa, with the increase of cellulosic content up to 30 wt.%. These TS values are from 7 to 10 % lower than those obtained for the PA6 biocomposites containing unpelletized mixtures, but these slightly lower values remained very limited. TM and FM were enhanced proportionally with the

pelletized fibers addition and, at 30 wt.% NBSK:NFC 80:20, the TM and FM were doubled compared at pristine PA6. HDT values were evaluated at 200 - 207 °C, as previously observed for the PA6 biocomposites containing unpelletized fibers. Overall, PA6 containing pelletized NBSK:NFC 80:20 fibers present mechanical and thermal properties at least equal compared to the commercial PA6 - 20% glass fibers composites used as reference.

PLA - NBSK:NFC 80:20 biocomposites presented a 31% increase in TS. i.e. from 55.3 MPa (for pristine PLA) up to 72.4 MPa (for PLA with 30 wt.% pelletized mixtures). Similar, the FS was increased from 83 MPa (pristine PLA) to as high as 120 MPa for a content of 30 wt.% NBSK:NFC 80:20 in PLA. This represents a noteworthy increase of 46 %. TM and FM were almost doubled, while the low elongation at break of PLA, its innate weakness, was surprisingly increased. The low HDT of PLA, also a drawback of this biopolymer, was highly improved. The PLA's HDT of 57 °C was increased at 92.5 °C at the addition of 10 wt.% pelletized NBSK:NFC 80:20 and, to as high as 133.5 °C when 20 wt.% NBSK:NFC 80:20 was used. When compared to the commercial PLA biocomposites, i.e. the PLA - 25% soft wood pulp and the PLA - 30% cellulotics (not disclosed by the manufacturer), our PLA biocomposites containing NBSK:NFC 80:20 mixtures present similar tensile and flexural performance, while having much more important thermal resistance.

CLTE was evaluated for PP - and PA6 - NBSK:NFC 80:20 biocomposites. CLTE is a material property which characterizes its ability to expand under the effect of temperature elevation. It expresses how much a composite part considered for automotive interior applications might remain dimensionally stable under temperature variations. Figure 6 presents the dimensional changes observed for PP, PA6 and their biocomposites with temperature increase from -50 °C up to 125 °C. The pristine PP sample, when heated from -50 °C, to -40 °C, to 25 °C, and further up to 100 °C, presented changes in dimensions due to its thermal expansion of 1.87, to 35.6 and up to 99.8 µm. For the same increase in temperature, the PP - 10 wt.% NBSK:NFC 80:20 sample presented thermal expansions of 0.99, 25.6, and 63.7 µm, so less than PP. For the biocomposite containing 20 wt.% NBSK:NFC 80:20 mixture, the thermal expansion was much less important, i.e. of 0.53, 18.4 and 37.2 µm. Similar trends are observed for pristine PA6, PA6 - 10 wt.% NBSK:NFC 80:20 and for PA6 - 20 wt.% NBSK:NFC 80:20. By evidence, NBSK:NFC mixtures presence in PP and PA6 significantly reduced the thermal expansions of biocomposites.

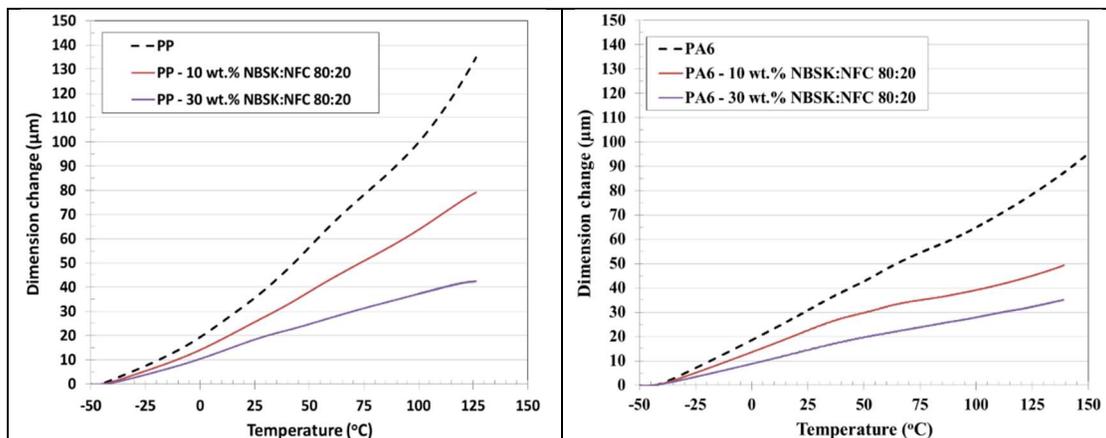


Figure 6: CLTE curves for pristine polymers and their biocomposites with 10 and 30 wt.% NBSK:NFC 80:20 fibers for PP (1st plot) and for PA6 (2nd plot)

PP - , PA6 - and PLA - NBSK:NFC 80:20 biocomposites proved to be mechanically and thermally performant and, therefore, very appropriate for injection molding of parts for many

automotive interior applications. Beyond their good performance, other advantage is the use of the NBSK:NFC cellulosic mixtures in a pelletized form. The cellulosic pellets are easy to handle at industrial scale and also have a lower cost for transportation than for the fluffy, low bulk density, unpelletized cellulosic fibers.

The recyclability of biocomposites was evaluated for two selected biocomposites, i.e. the PP - 20 wt.% NBSK:NFC 80:20 and PLA - 20 wt.% NBSK:NFC 80:20, both containing CA. For PP biocomposite, the physical aspects of injected specimens and their tensile performance after each recycling cycle are presented in the Figure 7. It can be observed that the color of the specimens R1 to R7 slightly changed during recycling from light brown to medium brown. This is due probably to a slight thermal degradation of NBSK:NFC fibers in a repetitive injection molding process which took place 7 times at 200 °C. The TS of the biocomposite slightly declined after each recycling step applied. The declining of the TS was limited, from 37 down to 32.3 MPa while TM was maintained at 1.850 ± 100 MPa as well as the elongation at break which was maintained at around 13 %. Despite the minor change in color, it can be stated that the PP - 20 wt.% NBSK:NFC 80:20 can tolerate at least 7 recycling steps of recycling without undergoing a deterioration of their performance.

Figure 8 - 1st column presents the evolution of color aspect of pure PLA injected specimens during the 5 recycling cycles along with their tensile properties. The pristine PLA became darker, its TS slightly decreased from 67.8 down to 65.6 MPa and TM decreased from 3,743 down to 3,481 MPa. It seems that pristine PLA slightly degraded during this repetitive grinding - injection molding. Surprisingly, the color of PLA biocomposite presented in the Figure 8 - 2nd column did not change after the 5 grinding - injection molding steps. Moreover, from specimens R1 to R5, the TS was preserved at around 70 MPa and the TM at around $5,100 \pm 100$ MPa. This conservation of tensile properties of PLA biocomposites after 5 recycling steps was unexpected and can be justified, among other factors, by the presence of the CA and by the degree of purity of NBSK:NFC fibers/fibrils. The CA, an epoxy/styrene/acrylic copolymer provided in a PLA carrier, acts in the polyester regrind to reverse the adverse effects of heat and moisture. During each injection molding step, at 200 °C, the so far possibly unreacted epoxy groups probably continued to react to carboxyl (-CO-OH) end-groups of PLA and from NFC fibrils helping the preservation of the molecular weight of PLA and preserving the fibers from thermal degradation. In conclusion, PP and PLA biocomposites containing NBSK:NFC cellulosic mixtures can be recycled without losing their properties.



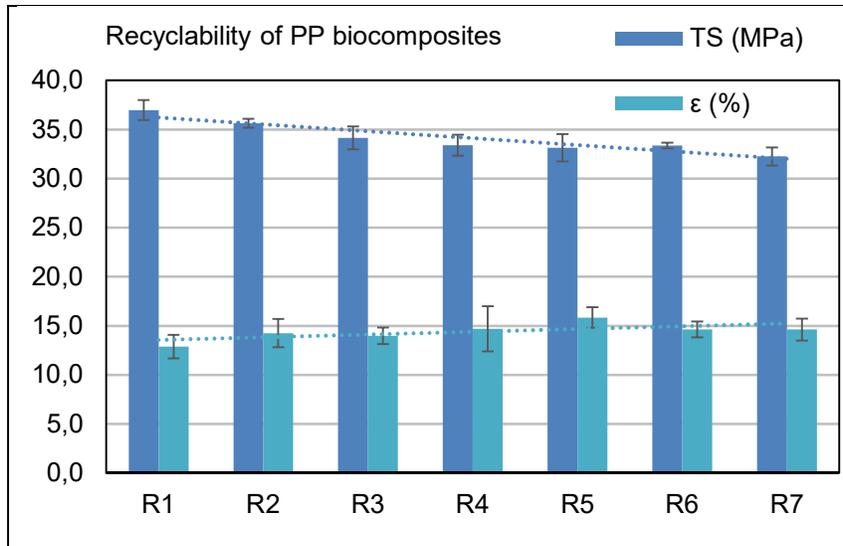


Figure 7: Behavior of PP - 20 wt.% NBSK:NFC 80:20 - CA biocomposites during the recycling; color changes (top) and tensile performance (bottom) during the 7 recycling steps.

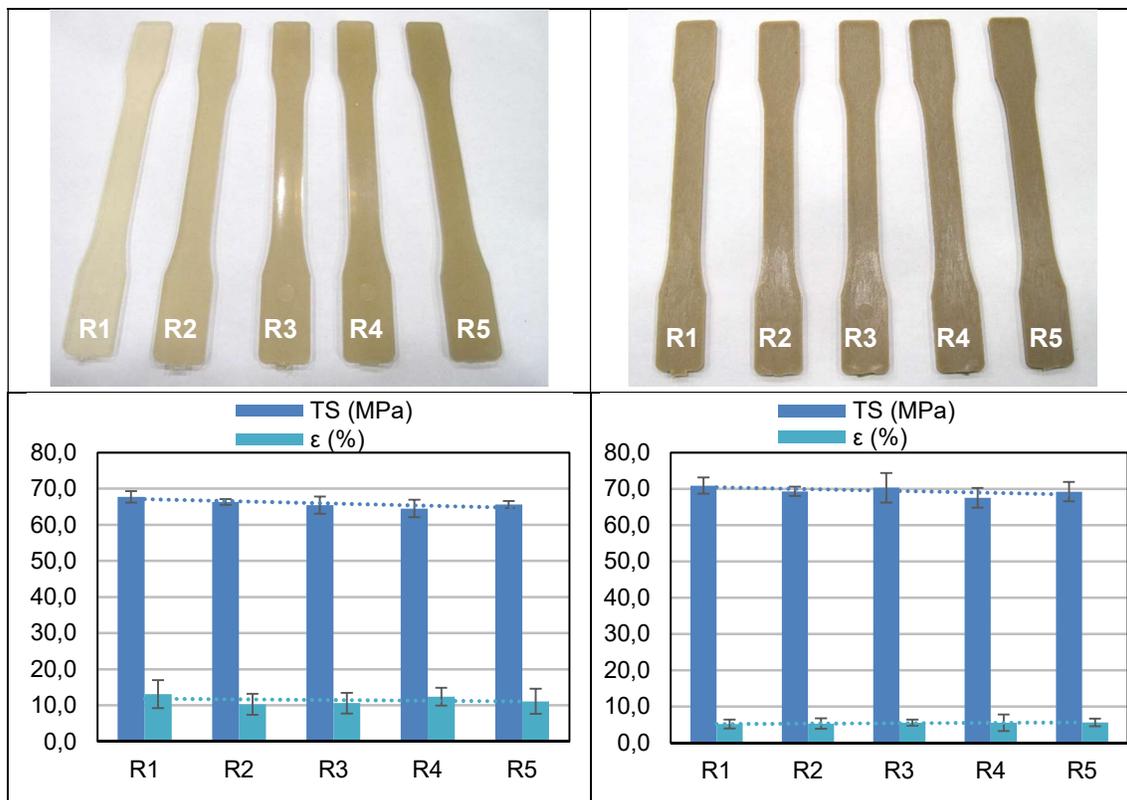


Figure 8: Behavior of pure PLA (1st column) and of PLA - 20 wt.% NBSK:NFC 80:20 - CA biocomposites (second column) during the 5 steps of recycling; color changes (top) and tensile performance (bottom)

3D printing of biocomposites containing NBSK:NFC 80:20 mixtures

An interesting application of thermoplastic biocomposites is the extrusion of filaments and

their 3D printing using Fused Filaments Fabrication technology (FFF or additive manufacturing). In this work, PP - and PA6 - 10 wt.% NBSK:NFC 80:20 biocomposites were extruded in filaments of 1.75 mm with a constant ovality. The aspects of the composite pellets and filaments, and of the 3D printed specimens obtained using the PP biocomposites (1st row) and PA6 biocomposites (2nd row) are shown in the Figure 8. Figure 9 presents a comparison of mechanical performance of injection-molded and 3D printed specimens obtained from PP and PA6 biocomposites containing 10 wt.% NBSK:NFC 80:20 mixtures. The performance of the injected pristine polymers and 3D printed parts using commercial filaments are also included for comparison purposes. The TS of 3D printed PP - 10 wt.% NBSK:NFC 80:20 is lower than the injection-molded counterpart and the injected pristine PP as well. Similar trend can be observed for the 3D printed specimen based on PA6 - 10 wt.% NBSK:NFC 80:20 biocomposite.

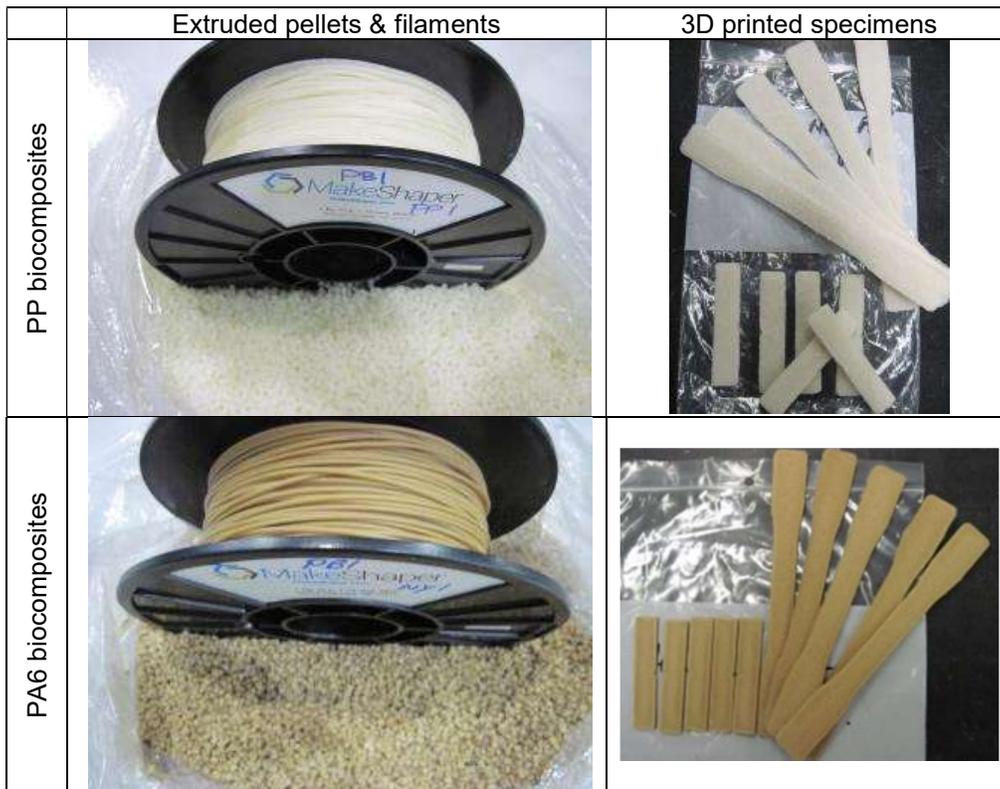


Figure 9: Filaments and 3D printed specimens obtained from biocomposites containing 10 wt.% NBSK:NFC 80:20 based on PP (top) and PA6 (bottom)

Lower performance of 3D printed specimens versus injection molded ones is a common observed phenomena for all types of thermoplastics used in FFF [22]. This can be explained by a scarce cohesion between successive layers and the nature of discontinuities created during the biocomposite filament laying down process which leads to the development of mechanical anisotropies in 3D printed specimens. The relative easy to use FFF technology is unluckily counterbalanced by those drawbacks. Despite this, the 3D printed part based on PA6 biocomposites presented similar properties compared to the part 3D printed using the commercial PA6 filament (Figure 10, purple bars). In terms of IS, the PP and PA6 biocomposites part presented similar performance compared to the injected one.

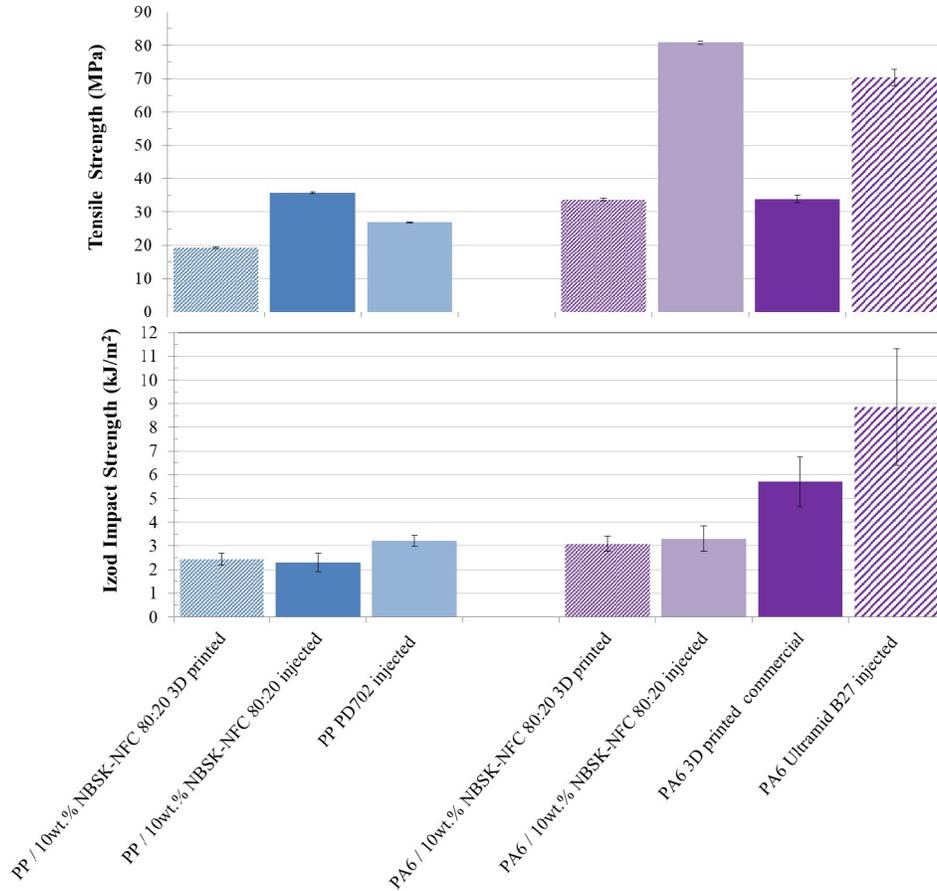


Figure 10: Tensile strength (top) and Izod impact strength (bottom) comparison of pristine polymer, biocomposite specimens resulted from 3D printing and from injection molding for PP (blue bars) and for PA6 (purple bars)

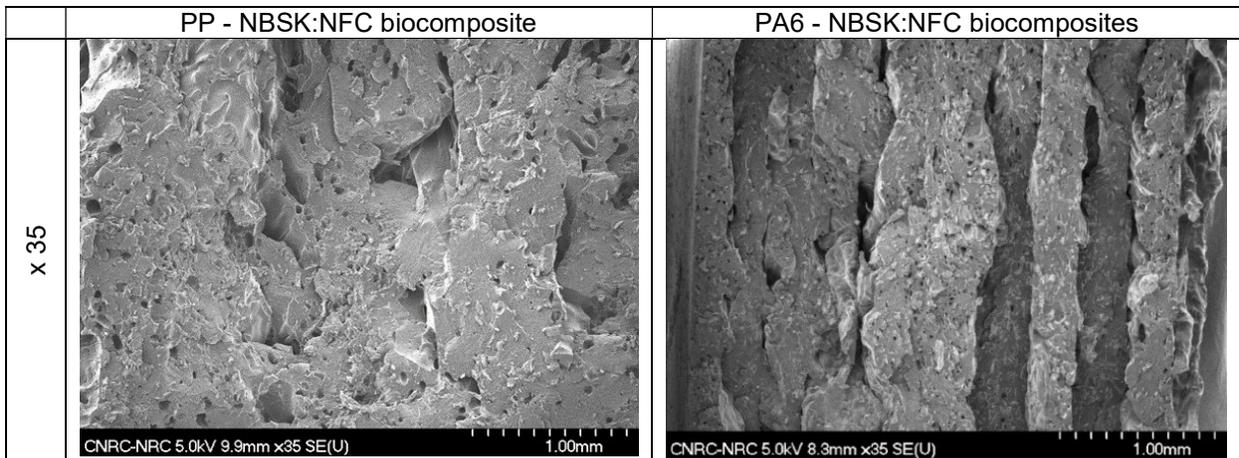


Figure 11: SEM morphology of 3D printed parts based on PP and PA6 biocomposites observed on fractured surfaces of specimens in Izod impact tests

Figure 11 presents the microstructure, as observed by SEM, of 3D printed parts based on PP and PA6 biocomposites containing 10 wt. % NBSK:NFC 80:20. These morphologies show varying degrees of layer-to-layer adhesion and interlayer voids which played the role of points of

weakness during the mechanical testing, points from where the sample fractures were started. Improvements of additive manufacturing parameters (infill, geometry, temperature etc. adjustments) has to be done to further improve the performance of biocomposites 3D printed parts. Even though, the PP and PA6 biocomposites developed with NBSK:NFC mixtures proved their feasibility of being easy to use in filaments extrusion and in the 3D printing, to fabricate complex geometries for design reiteration, prototyping, fixtures, jigs etc. with low material and labor cost, less process complexity, and less overall cost compared to the conventional technologies.

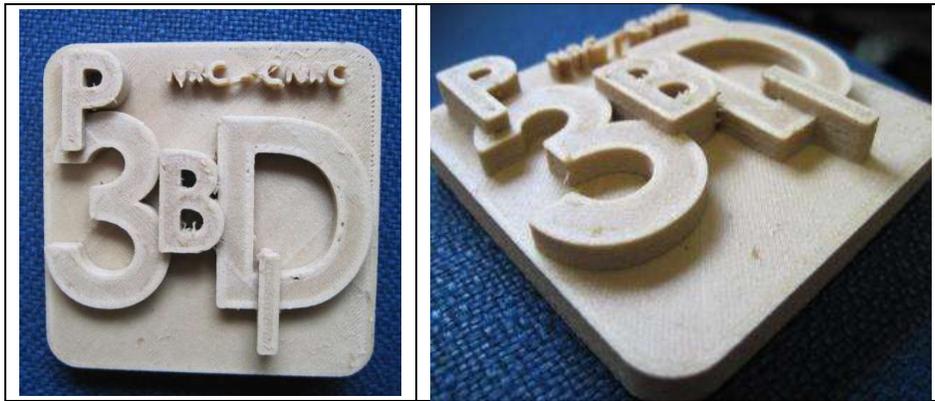


Figure 12: 3D printed parts obtained from PP - NBSK:NFC 80:20 biocomposite filaments

Summary

In this work, the effect of NBSK:NFC cellulosic mixtures was studied on the performance of PP, PA6, and PLA biocomposites. For the first time, with the purpose to fully take advantage from the effect of NFC fibrils themselves and to avoid the presence of agglomerates in the final materials, the NFC fibrils were used in mixtures with NBSK fibers, which played a role of transport carrier. These mixtures were studied first in terms of variation NFC's content in NBSK:NFC mixtures melt-blended in PP and PA6 matrices. The proportions of fibers/fibrils in NBSK:NFC mixtures were 100:0, 90:10, 80:20, and 70:30, in an un-pelletized fluffy form. When those mixtures were used at the same concentration, of 20 wt.%, in PP and PA6 and in the presence of appropriate coupling agents, the biocomposites shown microstructures having fine dispersions and distributions of fibers and, also, important increments in mechanical and thermal properties, from 20 up to 70 %. From SEM micrographs it was observed that the most efficient NBSK:NFC cellulosic mixture is 80:20, mixture which guarantees an excellent dispersion and highlights the role of the NFC fibrils. Further, this cellulosic fibers - fibrils mixture was considered to compound biocomposites based on PP, PA6, and PLA. The concentration of the mixture 80:20 was considered this time in a pelletized form at 10, 20, and 30 wt.% in each of three matrices. The biocomposites proved again excellent increments, up to 80 %, in tensile, flexural, impact, and thermal resistance when compared to uncompatibilized biocomposites and to pristine matrices. Moreover, when the biocomposites performance was compared to the one of composites commercially available, the biocomposites containing NBSK:NFC from this work proved to be at least equivalent in performance and even higher. Even in a pelletized shape, the NBSK:NFC 80:20 did not lose its reinforcement effect. Therefore, the pelletizing step was proved to not lead to an important attrition of the NBSK or NFC, while being recommended for easing fibers feeding and for the reduction of the transportation cost. PP and PLA biocomposites containing 20 wt.% NBSK:NFC 80:20 cellulosic mixtures demonstrated that can be recycled at least 5 times without losing their properties. And, not the least, PP and PA6 biocomposites containing 10 wt.% NBSK:NFC 80:20 mixtures proved their feasibility of being easy to use in filaments extrusion and

in the 3D printing, to fabricate complex geometries with low material and labor cost, less process complexity, and less overall cost compared to the conventional technologies. As final conclusion, NFC fibrils proved their feasibility to be used in NBSK:NFC mixtures to further reinforce thermoplastic polymers and the obtained biocomposites proved to be recyclable and adequate for uses in injection molding and 3D printing processes.

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