FULL RESEARCH ARTICLE

Enhanced compatibility between coconut fibers/PP via chemical modification for 3D printing

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Abstract

Aiming to produce high-quality bio-based 3D printed products, in this work, coconut fibers were chemical modified using caprolactone. Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic reasonance (NMR) confirmed the grafting of the hydroxyl groups present on the surface of the fibers with caprolactone units. Furthermore, from contact angle (CA) analyses, the higher hydrophobicity of fibers after chemical treatment was confirmed, which improved its affinity with PP. The enhanced filler/matrix compatibility was reflected on the mechanical performance and processability of the ensuing composites. The modified fibers derived composites showed higher stiffness and higher melting flow index (MFI), when compared to the untreated counterparts. The composites were used to produce 3D printed specimens. Smother filaments were obtained using modified fibers, which confirms the better compatibility of fibers/PP. The surface of the 3D printed composite specimen produced using treated fibers, presented smooth surface, similar to the PP. This observation highlights the enhancement of the 3D printing quality due to the chemical modification of fibers.

Keywords Additive manufacturing · Fused filament fabrication · 3D printing · Chemical modification · Coconut fibers composites

1 Introduction

Polypropylene (PP) was first produced by G. Natta, by the polymerization of the propylene monomer in 1954 [1]. Nowadays, PP is used to replace engineering plastics, such as poly(ethylene terephthalate) (PET), polyamide (PA), polycarbonate (PC) or acrylonitrile butadiene styrene (ABS), in automotive industry, packaging or domestic appliances [1, 2]. Even though injection molding and extrusion are the two most used techniques for producing PP products, new processing methods are emerging, such as additive manufacturing [i.e., three-dimensional (3D) printing], which can be used to produce biomedical, aerospace, automotive, electronic, architectural, fashion, or domestic products [3]. This processing technique consists in constructing objects, by printing layer-by-layer enabling the preparation of products with new forms, shapes, and dimensions, which are impossible to obtain using conventional methods [4]. Furthermore, this technology offers the possibility of manufacturing complex components, in a reduced time, without the need of prototypes, molds or other expensive tools [5, 6].

Good chemical resistance, good processability, good impact resistance or good stiffness are some of the several advantages that made PP a very popular and high-demanded commodity plastic. In fact, PP is the third most consumed plastic material after polyethylene (PE) and poly(vinyl chloride) (PVC) [1, 2]. Yet, PP compared with other thermoplastics has significantly higher mold shrinkage, higher thermal expansion, poor UV resistance or poor oxidative resistance in the presence of certain metals [1]. Nonetheless, many fillers, such as fibrous materials can be used to enhance the properties of PP, such as its mechanical or thermal properties [7]. In particular, fillers such as wood flour, rice or coconut husks, hemp, flax or pine fibers have been used to produce lignocellulosic–PP-based composites. In addition, the use of these fibers have the advantage of contributing to

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Scheme 1 Schematic representation of the chemical modification reaction of coconut fibers
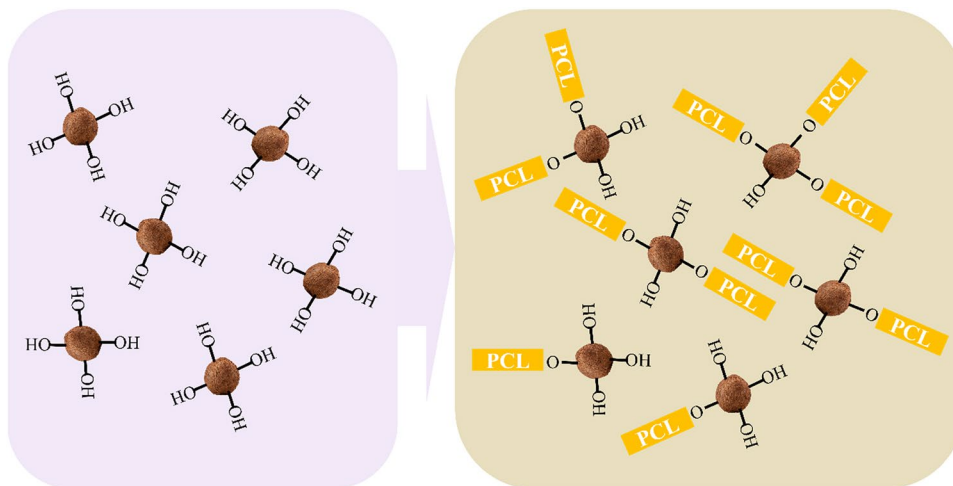
the enhancement of the eco-efficiency of the ensuing composites [8–10].

Coir fibers are derived from the husk of the coconut (*Cocos nucifera*) which is cultivated extensively in tropical countries for its fruits, whereas the husks and shells are mostly disposed as waste [11, 12]. Coir fibers have high content of lignin, which makes them stronger and subsequently interesting to be used as reinforcement filler [13]. Yet, most of these natural fibers are hydrophilic, while most commodity polymers are hydrophobic. This difference in the hydrophilic character may result in poor adhesion between the filler and matrix, aggregates of filler particles or poor dispersion which results in insufficient reinforcement. Hence, it may compromise or even jeopardize the mechanical properties of the ensuing composites [7]. Nonetheless, different routes can be used to overcome these problems, such as surface modification of fibers to make them more hydrophobic [7]. Abdullah et al. [14] studied the effect of alkali treatment on the mechanical and water-sorption properties of coconut fibers/polyester (PS) composites. It was reported that surface treatment of coconut fibers caused a significant increase on the tensile properties and that the treated fiber composites showed lower water absorption in comparison to those produced using untreated fibers [14].

Similar to composites, polymer blending is also used to produce materials with properties beyond the range of the neat polymers [15]. Arcana et al. [16] study the mechanical and biodegradability properties of PP/polycaprolactone (PCL) polymer blends. It was reported that the mechanical properties of polymer blends decreased with increasing content of PCL, yet PCL effectively improved the degradability of the polymer blends.

Aiming at enhancing the properties of PP and to explore the possibility of its use in 3D printing, in this study, coconut fibers were chemical modified using caprolactone, as described in Scheme 1.

The hydroxyl groups present in the surface of the fibers were reacted with caprolactone moieties. This chemical modification increases the hydrophobic nature of fibers enhancing their compatibility with the polymer matrix. To evaluate the advantage of the chemical treatment, untreated and treated coconut fibers were used to produce PP composites which were extensively characterized. Furthermore, selected composites were used in additive manufacturing, to assess the 3D printing quality enhancement achieved using the chemically treated fibers.

2 Experimental

2.1 Materials

Coconut fibers were purchased in a local store and milled to a powder with a density of 1550 kg.m^{-3}. Caprolactone 99%, with a density of 1078 kg.m^{-3} and a flash point of 109 °C was supplied by Alfa Aesar. PP pellets with a density of 900 kg.m^{-3}, a Mw ~ 340,000 and average Mn ~ 97,000 was supplied by Sigma Aldrich. *p*-toluenesulfonic (PTS) acid used as catalyst was supplied by Sigma Aldrich.

2.2 Chemical modification of biomass

Coconut fibers were milled in 0.5 mm mesh using a Retsch cross beater mill SK1 (Haan, Germany). Next, they were modified in a 5 L reactor, using caprolactone (20% wt$_{\varepsilon\text{-caprolactone}}$/wt$_{coconut\ fibers}$) and PTS (10% wt$_{PTS}$/wt$_{coconut\ fibers}$). The reaction was carried out at 140 °C, during 2 h, under mechanical stirring. After reaction, the modified biomass was filtered under vacuum and washed with deionized water and acetone to remove unreacted monomer, catalyst and eventually oligomers and then dried at 105 °C in a ventilated oven.

Table 1 List the formulation used

Sample[a]	% coconut fibers	% modified coconut fibers
PP	0	0
PP-10unmod	10	0
PP-20unmod	20	0
PP-30unmod	30	0
PP-40unmod	40	0
PP-50unmod	50	0
PP-10mod	0	10
PP-20omd	0	20
PP-30mod	0	30
PP-40mod	0	40
PP-50mod	0	50

[a]Sample code: PP-*xy*, where *x* is the % (wt_{filler}/wt_{total}) of filler and *y* is the type of filler (unmod—unmodified and mod—modified)

Table 2 3D printing parameters

Parameter	Value
Layer height	0.5 mm
Wall thickness	1.2 mm
Infill density	100%
Printing temperature	190 °C
Build plate temperature	60 °C
Printing speed	40 mm.s^{-1}

2.3 Production of composites

PP pellets were blended with coconut fibers (0–50% wt/wt) in a Brabender W 30 EHT–Plastograph EC mixer, using 40 rpm at 180 °C for 5 min. The mixtures were processed in a Haake Minijet II Injector–Thermo Scientific injection molding machine at 180 °C, using 700 bar of pressure, a mold temperature of 125 °C, as listed in Table 1.

Next, selected mixtures (PP, PP-10unmod and PP-10mod) were extruded in a Felfil Evo Colours extruder using 9 rpm at 180 °C to produce the 3D printable filaments. The resulting filaments were used to 3D print specimens in an Anycubic Chiron 3D printer. TopSolid Missler Software was used to design the sketches and Ultimaker Cura was used to prepare the 3D printing model. In Table 2, the 3D print parameters are listed.

2.4 Characterization

The FTIR spectra were collected on a Perkin Elmer FTIR System Spectrum BX Spectrometer equipped with a single horizontal Golden Gate ATR cell. All data were recorded at room temperature, in the 4000 to 600 cm^{-1} range by accumulating 32 scans with a resolution of 4 cm^{-1}.

^{13}C solid-state Cross Polarization-Magic Angle Spinning Nuclear Magnetic Resonance (^{13}C CPMAS NMR) spectra were recorded on a Bruker Avance 400 spectrometer. Acquisition parameters were as follows: ca 7000 scans with a 90 proton pulse, a crosspolarization contact time of 1 ms, and a recovery delay of 2.5 s.

Static contact angles (CA) measurements were carried out using a Contact Angle System OCA20 goniometer (DataPhysics) equipped with SCA20 software using the sessile drop method.

SEM analyses were performed in an SU-70 (Hitachi) scanning electron microscope after vacuum-coating the samples with carbon to avoid electrostatic charging during examination and at accelerating voltage of 15.0 kV.

The density of the biomass samples was determined in accordance with the ASTM D4892-14 standard [17] using a helium pycnometer instrumentation. This device uses a calibrated test chamber and known volumes of helium to calculate the permeable volume of the test specimen. In other words, the volume of sample measured corresponds to the amount of three-dimensional space which is inaccessible to the gas used, i.e., is the volume of sample. The densities were determined by the ratio of the sample masses previously weighted to the determined volume. Densities of composites were determined using the immersion method. First, the dried samples were weighed, next immersed in deionized water and weighed again. The densities of composites (ρ, g.cm^{-3}) were calculated according to the following equation:

$$\rho = A/(A - B)\rho_0 \tag{1}$$

where A and B are masses (g) of the dried and immersed sample and ρ (kg.m^{-3}) is the density of deionized water. The values presented correspond to the average density determined for 5 specimens of each sample.

Thermogravimetric analyses (TGA) were performed using a SETSYS Evolution 1750 thermogravimetric analyzer (Setaram) from room temperature up to 800 °C, at a heating rate of 10 °C.min^{-1} and under oxygen flux (200 mL.min^{-1}).

Mechanical analyses were performed with a SHIMADZU AGS-X using a load cell of 1 kN and a deformation rate of 5.0 mm min^{-1}. Five specimens of each sample were tested.

Dynamic mechanical analyses (DMA) were carried out using a Tritec 2000 equipment (Triton Technologies) in 3 points bending mode using a strain factor of 32.4. Samples with dimensions of $10 \times 9 \times 6$ mm^3 were analyzed from -100 °C up to -50 °C at a constant heating rate of 2 °C.min^{-1} and at a frequency of 1 Hz.

Melt flow indexes (MFI) were determined according to the ISO 1133–1:2011 standard [18] using a Model 6 Advanced melt flow system of Ray-Ran. The material was

packed inside the barrel and heated up to 220 °C. After that a piston (of 5 kg) was introduced in the barrel which causes the extrusion of the molten polymer. The samples of the melted polymer were weighed and MFI is expressed in grams of polymer per 10 min of duration of the test.

3 Results and discussion

3.1 Modification of biomass

Coconut fibers were chemical modified, where the hydroxyl groups present on the surface of fibers were grafted with caprolactone moieties. The modification of fibers was confirmed by FTIR and CP-MAS ^{13}C NMR analysis, being the results presented in Fig. 1.

As it can be observed from Fig. 1a, the chemical treatment extensively modified the chemical structure of the fibers. The untreated coconut fibers present the typical absorption peaks of a lignocellulosic fiber: the band at 3330 cm^{-1} is attributed to the stretching vibration of O–H groups; the

(a)

(b)

Fig. 1 Spectra of modified and neat biomass: FTIR (**a**) and CP-MAS ^{13}C NMR (**b**)

peaks at 2800–3000 cm^{-1} are attributed to the stretching vibration of aliphatic C–H groups; the peak at 1730 cm^{-1} is attributed to the stretching vibration of C=O groups; the peak at 1610 cm^{-1} is attributed to the stretching vibration of aromatic C–H groups; the peaks at 1230 cm^{-1} and 1030 cm^{-1} are attributed to the stretching vibration of C–O groups [19, 20]. After the chemical modification, the intensity of the stretching O–H band is reduced, indicating that these groups reacted with caprolactone, to form ester groups. In addition, the doublet between 2800 and 3000 cm^{-1} associated with the symmetric and asymmetric stretching vibrations of the C–H bonds of the methylene groups is more clear and intense as while the intense peak at 1720 cm^{-1} of the carbonyl group, typical of caprolactone, is detected. Likewise, smaller peaks at 1290, 1240 and 1165 cm^{-1}, attributed to ether C–O vibrations, confirmed the grafting of caprolactone moieties on the fibers surface [16, 21].

From CP-MAS ^{13}C NMR analysis, similar results were observed. In the untreated fibers spectra, the typical carbons of cellulose are detected [22]: the peak at 65 ppm is attributed to the C-6; the peaks at 72–75 ppm are attributed to the C-2, C-3 and C-5; the peaks at 82–88 ppm are attributed to the C-4; and the peak at 105 ppm is attributed to the C-1. In addition, the typical peaks of hemicelluloses and lignin are revealed [23]: the peaks at 20 and 173 ppm are attributed to the acetyl methyl and carbonyl groups of hemicelluloses, respectively. Likewise, the peak at 55 ppm is attributed to the methoxy groups; the peaks in the region of 135 ppm are attributed to syringyl C-1, syringyl C-5 and quaiacyl C-2; and the peak at 153 ppm is attributed to syringyl C-3 and syringyl C-5 of lignin. After the chemical modification, the degree of substitution confirms the grafting reaction.

The chemical modification of the coconut fibers, was also confirmed by the contact angle (CA) formed by water with their surface. From the results presented in Table 3, it can be observed that the untreated fibers form a CA with water of 54.2°, while the treated counterparts present a CA of 68.2°. The increase of the CA is attributed the presence of caprolactone grafted on the surface of fibers, since it is more hydrophobic [24]. Furthermore, the modification approximates the hydrophobic character of fibers to the matrix polymer, which can improve the compatibility between them, as it will be discussed [25]. Similar results are reported in literature [26, 27].
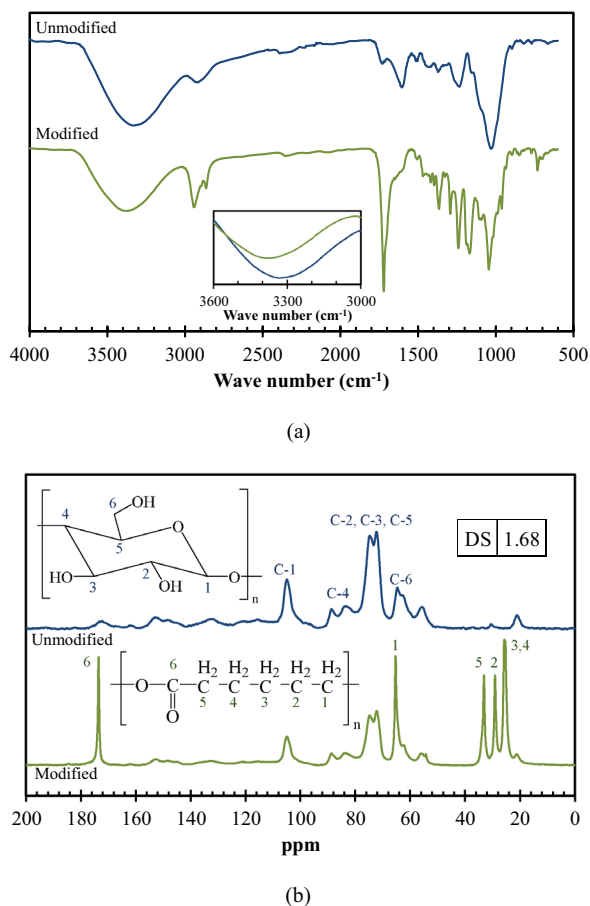
Table 3 Properties of raw materials

Sample	Contact angle with water (°)	Density (kg.m^{-3})
Unmodified fibers	54.2	1549.5
Modified fibers	68.2	1326.5
PP	87.0	966.1

The effect of the treatment of fibers was also studied by analyzing their morphology.

As it can be observed in Fig. 2, the treatment did not induce significant changes on the morphology of fibers. Yet, the fibers seem to present smoother surface after the chemical modification. Manjula et al. [28] studied the influence of chemical treatment on the coir fibers, reporting that a rougher surface with irregular strips was observed in the untreated fibers. In turn, the treated fibers presented a smoother morphology, which was attributed to the removal of fatty acids, lignin and impurities present on the fiber surface. Similar results were also reported by Mir et al. [29], who reported that the adhesion between fibers and polymer was increased after being chemically treated. Therefore, the removal of fatty acids, lignin and impurities present on the fiber surface, together with better adhesion between fibers and polymer are expected to be noticed on the mechanical properties of composites, as it will be discussed later.
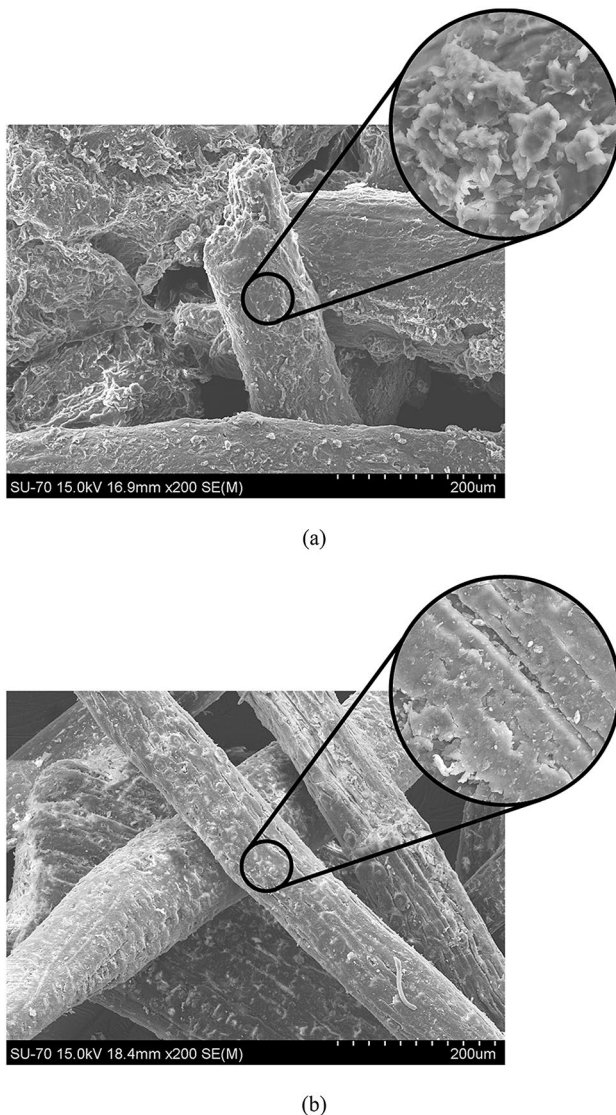
As it can be seen from Table 2, the chemical treatment reduced the density of fibers. Normally, the reduction of density of fibers after modification is attributed to the defibration [30], yet this was not observed in SEM images. However, as already discussed, the removal of impurities may contribute to the lower density of treated biomass. Furthermore, the caprolactone moieties grafted on the fibers surface can reduce their density, since it is lighter than coconut fibers [31, 32].

Finally, the impact of chemical treatment was evaluated on the thermal degradation of fibers, being the results presented in Fig. 3.

As it can be observed from Fig. 3, the thermal degradation of the unmodified biomass is characterized by a single step at 260 °C, which is attributed to the degradation of cellulose and anhydroglucose units [33]. After modification, the thermal degradation step of fibers was shifted to 350 °C. Normally, caprolactone oligomers decomposes at 430 °C [34]; therefore, the results presented in Fig. 3, suggest that caprolactone moieties were grafted on the fibers surface, enhancing their thermal stability.

3.2 Production of composites

To access the effect of the chemical modification on the mechanical performance of the ensuing composites, both untreated and treated fibers were blended with PP (up to 50% (wt/wt)) and the results are presented in Table 4.

As it can be seen from the results presented in Table 4, the addition of fibers increased the density of composites. The addition of natural fibers to polymeric materials can have different effects on the density of the composites produced, because different types of fibers have distinct densities [9].

(a)

(b)

Fig. 2 SEM images of modification of biomass: before (**a**) and after (**b**) the chemical modification
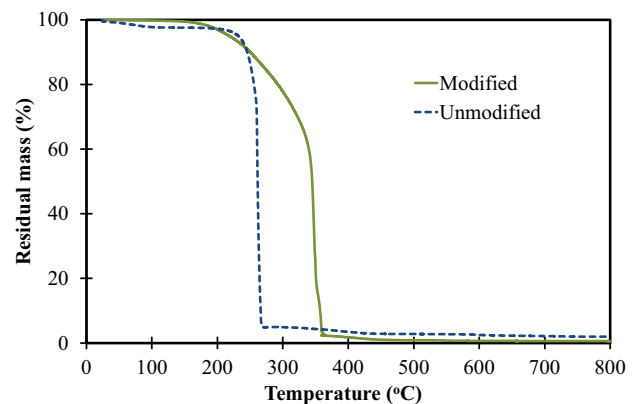
Fig. 3 Thermal degradation of biomass before and after the chemical modification

Table 4 Properties of composites

Sample	Density (kg.m^{-3})	Young modulus (MPa)	Elongation at break (%)
PP	966.1 ± 33.1	511.3 ± 8.1	12.8 ± 2.0
PP-10unmod	977.0 ± 12.7	561.8 ± 18.8	10.1 ± 0.2
PP-20unmod	983.0 ± 21.4	586.4 ± 17.5	7.1 ± 0.0
PP-30unmod	1044.1 ± 23.9	591.4 ± 13.4	6.4 ± 0.6
PP-40unmod	1090.7 ± 15.9	597.5 ± 12.6	5.5 ± 0.8
PP-50unmod	1119.0 ± 37.4	626.8 ± 10.6	4.4 ± 0.2
PP-10mod	1015.7 ± 45.7	655.7 ± 19.5	10.6 ± 0.5
PP-20mod	1052.9 ± 37.9	674.4 ± 18.4	8.5 ± 0.7
PP-30mod	1073.0 ± 44.7	683.2 ± 20.4	7.2 ± 0.3
PP-40mod	1119.3 ± 33.2	696.4 ± 12.2	6.7 ± 0.5
PP-50mod	1212.3 ± 30.8	727.8 ± 11.3	6.8 ± 0.0

Since coconut fibers are denser than PP, the density of coconut fiber/PP composites was expected to be higher than the neat PP. In fact, Das and Biswas [35] studied the effect of coir fiber on the physical behavior of coir fiber–epoxy composites and reported that the density of composites increases with the increase in fiber content. Furthermore, the higher density of the modified fibers-based composites can be attributed to the higher density of the modified fibers used.

In a similar manner, the addition of fibers increased the stiffness of composites. As it can be seen from the results presented in Table 4, the presence of fibers increased the Young modulus of the materials and reduced their elongation at break, which is in agreement with a filler reinforcing effect. Indeed, the increase of stiffness of materials by adding natural fibers is widely reported in literature [10]. In addition, the enhanced mechanical properties of the modified fiber-based composites, can be attributed to the removal of fatty acids and impurities present on the fiber surface, together with the caprolactone moieties grafted on the fibers surface, as previously discussed. Even small substitution of hydroxyl groups in lignocellulosic material by moieties compatible with the matrix is sufficient to improve the interaction of the hydrophilic reinforcement material with the hydrophobic polymeric matrix, thus increasing the adhesion between them [20].
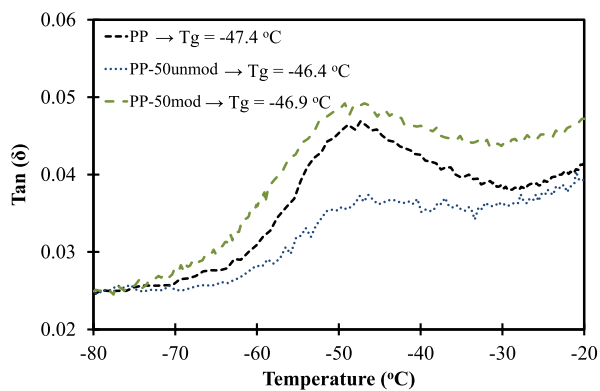
The CA formed with water (see Fig. 4) of neat PP (87.0°) decreases with the addition of untreated fibers (56.5°), since the natural fibers are known to be hydrophilic. In fact, the hydrophilic character of the natural fibers is associated with the hydroxyl groups present in their surface, making them poorly compatible with a polymeric matrix [36]. In turn, the addition of modified fibers grafted yields materials with higher CA (72.0°) [24, 37]. This meant that the chemical treatment increased the hydrophobicity of the fibers, which contributes to a better compatibility between them with the
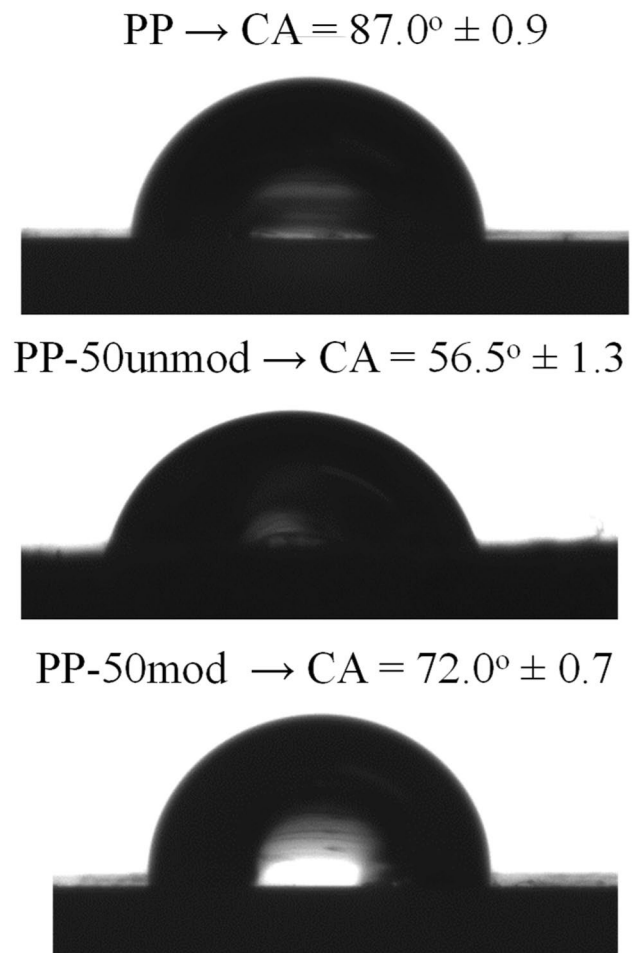
Fig. 4 Contact angle of neat PP and composites containing 50%w/w of modified and unmodified fibers
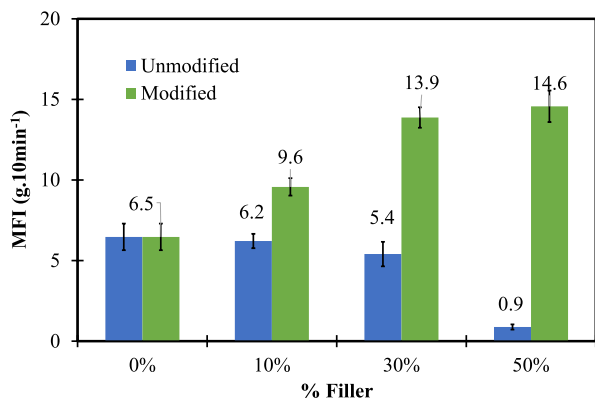
matrix and enhancing the mechanical properties of the ensuing composites.

Despite of the enhancement of mechanical properties, the addition of fibers can jeopardize the processability of the materials. Hence, the processability of the composites was estimated by measuring the T_g and MFI of composites, being the results presented in Fig. 5.

Normally, the T_g of composites is expected to increase when fillers are added as the mobility of the molecular chains tends to be hindered. As it can be seen from Fig. 5a, the presence of fibers increased the T_g of PP from − 47.4 °C up to − 46.4 °C and − 46.9 °C, when filled with treated and untreated fibers, respectively. Even though no significant differences on the values of T_g were observed, the increase of T_g is associated with interfacial bonding as Geethamma et al. [38] reported. Furthermore, narrow peaks of the tan (δ) curves indicate better miscibility [39–41], as observed for the PP-50mod sample, suggesting the better compatibility of modified fibers with matrix, as previously discussed.

(a)

(b)

Fig. 5 Processability of PP composites with different contents of fibers modified and unmodified: T_g (**a**) and MFI (**b**)

Fig. 6 Thermal degradation of neat PP and composites containing 50%w/w of modified and unmodified fibers

et al. [45], reported that the better dispersion of fibers in the matrix can increase the MFI of the composites. In addition, a higher MFI, i.e., shorter residence time in the extruder, can result in lower thermal degradation.

Finally, the thermal degradation of composites was also analyzed, being the corresponding TGA results presented in Fig. 6. Analyzing the thermal decomposition profile of PP, it can be observed that it consisted in single degradation step at a maximum rate at 250 °C, that the addition of unmodified fibers does not improve the thermal stability of the composite, and finally that the presence of modified fibers results in more thermally stable materials. As reported by Ndiaye et al. [46], the composites higher thermal stability is due to the thermal protection effect induced by the fibers, which can: (i) immobilize the free radicals formed during the initiation of the degradation of the polymer and (ii) inhibit the diffusion of volatile degradation products because of the interaction with the fiber. Furthermore, the higher thermal stability of PP-50mod sample, can be associated to the better thermal stability of the fibers, as previously discussed.

Overall, the treatment of fibers contributed to the enhancement of the mechanical performance, as well as to the better processability of the ensuing composites.

3.3 3D printing

After evaluating the effect of the chemical modification of fibers on the properties of the composites, the fibers were used to produce filaments, to be used in 3D printing.

As it can be seen from the SEM images presented in Fig. 7, the presence of fibers leads to rougher filaments. It is known, that the presence of a filler, can originate rougher filaments, which can be associated to poor wetting of fillers by the matrix [47–49]. Yet, the surface of the modified fibers based-filament seems to be smother than that the unmodified fibers counterparts. Furthermore, voids on the cross section

In addition, the processability of the materials produced, was evaluated by measuring the MFI of the materials. A higher MFI values is preferable, since it means that it is easier for the material to flow [42]. As it can be observed from the results presented in Fig. 5b, depending on the type of fibers used, distinct MFI values were obtained. While the untreated fibers reduce the MFI of composites, the treated counterparts induce a significant increase of MFI. Caraschi and Leão [43] used wood flour as reinforcement of PP, reporting that the MFI of composites decreased with the increase in fiber content, because the incorporation of rigid fillers to the polymeric matrix limits their free mobility, increasing the material apparent viscosity. This observation is in agreement with the MFI results obtained for the unmodified fibers-based composites. In turn, Soleimani et al. [44], who studied the effect of fiber pretreatment on the physical properties of flax fiber-PP composites, reported that the MFI of treated fibers based composites, was higher than those containing untreated fibers. This was attributed to the better dispersion of treated fiber in the matrix. Likewise, Naldony
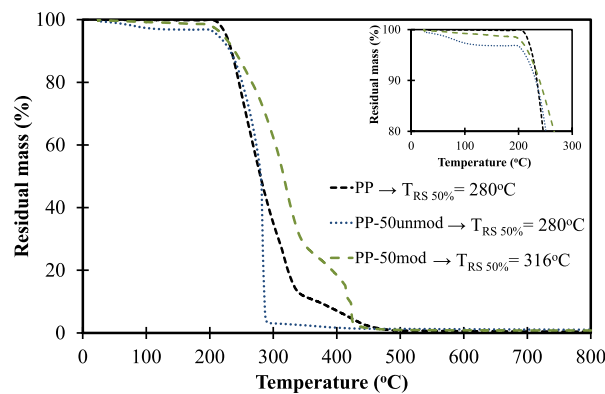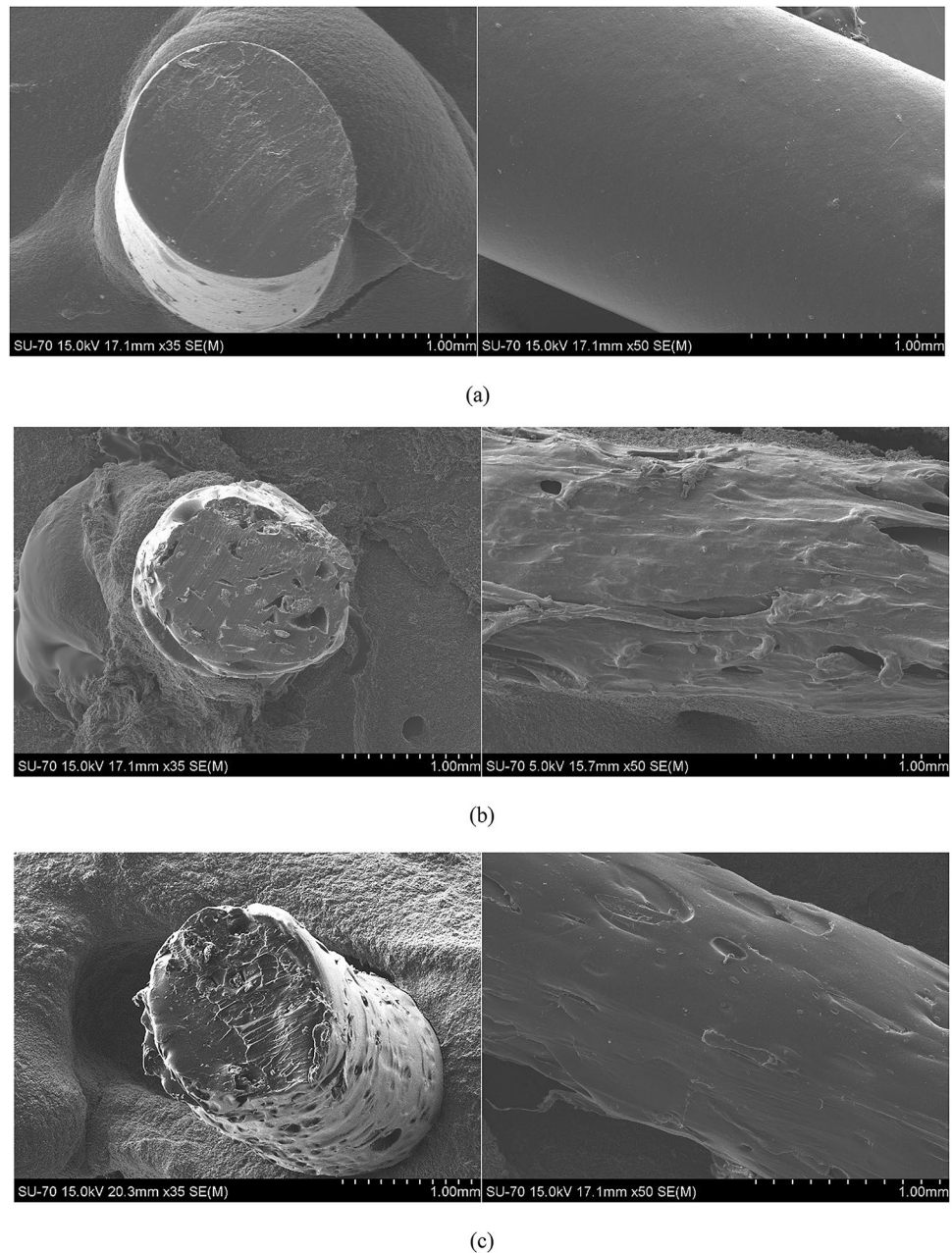
Fig. 7 SEM images of cross section a surface of filaments: PP (**a**), PP-10unmod (**b**) and PP-10mod (**c**)

(a)

(b)

(c)

of unmodified-based filament are detectable, suggesting poor wettability, which can compromise the performance of the 3D printing, and subsequently the performance of the 3D printed objects. This is not the case for the filaments containing modified fibers. The better quality of the modified-based filament can be due to the chemical modification, which contributed to a better distribution of the filler in the matrix, as previously discussed. In fact, Lacerda et al. [49] modified cork via atom transfer radical polymerization (ATRP) to produce 3D composites, and reported that the modification improved the compatibility between filler and matrix, resulting in a better distribution of cork in the filaments.

Afterwards, the filaments were used to produce 3D printed objects, being their images presented in Fig. 8.

In Fig. 8, the SEM images of the surface of the 3D printed objects are presented, where it can be seen that untreated fibers can jeopardize the surface of the 3D printed composite. This can be associated to the poor melt-diffusion and interfusion of the printed layers as the SEM images of the filament's as suggested by Naskar et al. [50]. In fact, this issue is one of the main challenges of the 3D printed fiber composites. Nonetheless, the surface of the 3D printed composite produced using treated fibers, presented smooth surface, similar to the PP. These results highlight the fact
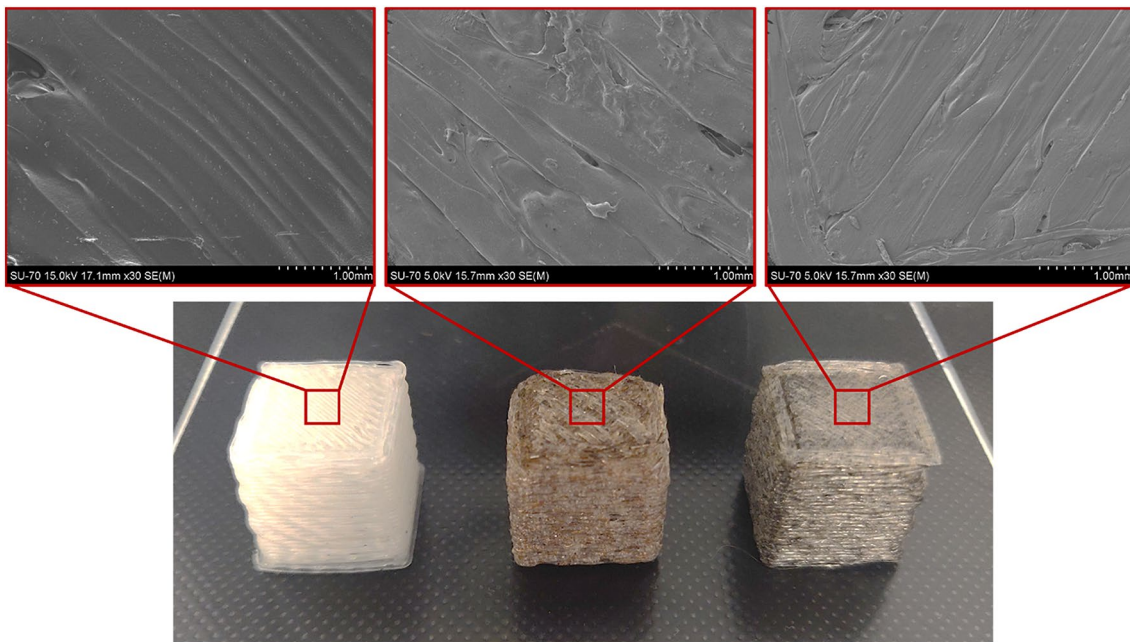
**Fig. 8** Images of 3D printed objects (left to right): PP, PP-10unmod and PP-10mod

that the chemical modification of fibers enhance the quality of 3D printed products.

To further evaluate the enhancement of the quality of 3D printed objects using modified biomass, the mechanical properties of the 3D printed materials were compared. In Fig. 9, the $50 \times 10 \times 2.5$ mm mechanical test specimens and corresponding Young modulus are presented.

Analyzing the results presented in Fig. 9, it can be observed that the mechanical properties values of 3D printed specimens, corroborate the mechanical properties results of filaments, since the addition of fibers increase the stiffness of materials. Moreover, as observed, the modified biomass further enhances the stiffness of the 3D printed specimens, due to the facts previously mentioned. Hence, the results reinforce the claim of high-quality 3D printed polymer using modified coconut fibers.

4 Conclusions

In this work, coconut fibers were chemically modified to be used as natural filler in 3D printing of polymer composites. The chemical modification consisted in the reaction between the hydroxyl groups of fibers with caprolactone, aiming at improving the compatibility between the fibers and matrix. Spectroscopy, SEM and TGA analysis confirmed the grafting of caprolactone units on the surface of the fibers. Afterwards, the fibers were mixed with PP and the results indicate the enhancement of the mechanical properties of composites. Moreover, analyzing the processability of the treated
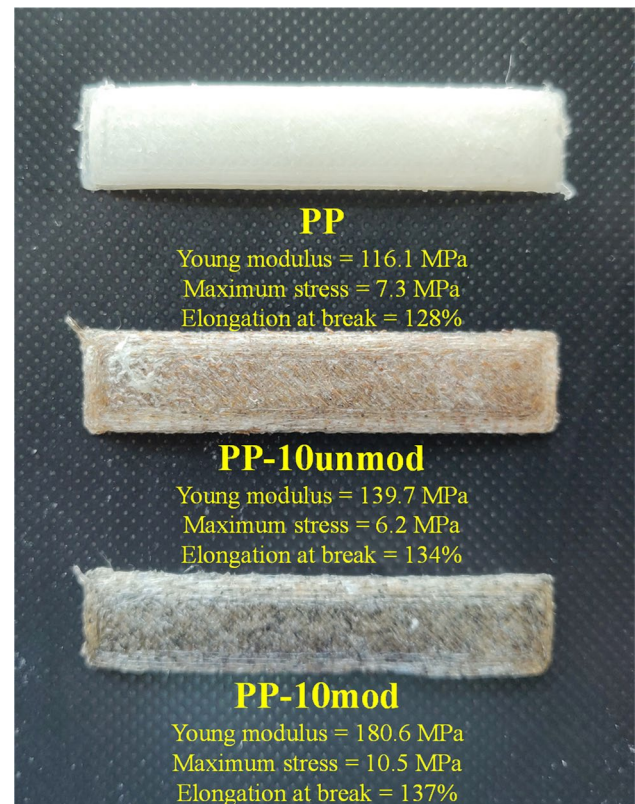
Fig. 9 Images of 3D printed mechanical test specimens and ensuing mechanical properties values (top to bottom): PP, PP-10unmod and PP-10mod

fibers-based composites by *Tg* and MFI values as well as TGA results, the advantage of the chemical treatment was confirmed. The enhancement of the mechanical properties and the processability of the materials was attributed to the better compatibility between the treated fibers and matrix. Finally, the high quality of the 3D printed objects was verified, highlighting the advantage of the chemical modification of fibers.

Data availability Not available.

Code availability Not applicable.

Declarations

Conflict of interest Nothing to declare.

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