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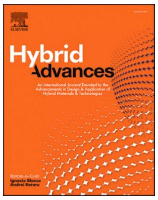

Nanocomposites of recycled and of virgin polyamide 6.6 with cellulose nanofibers

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ABSTRACT

The inherent properties of cellulose nanofibers (CNFs) make them an interesting and sustainable choice for reinforcing polymeric matrices intended for the automotive, electronic, construction, and packaging sectors. Effective recycling and reuse of polyamide 6.6 significantly reduce the environmental impact of automotive components throughout its entire life cycle. Nanocomposites of recycled polyamide 6.6 and CNF and of virgin polyamide 6.6 and CNF were processed through dissolution in a formic acid/water mixture followed by melt extrusion and injection molding. The results show that pure recycled polyamide exhibited a thermal degradation onset temperature 10 °C lower and a 9 % lower crystallinity compared to pure virgin polyamide. The method used for processing the nanocomposites resulted in homogeneous dispersion and good anchoring of CNF in both polymer matrices. The processing method and the presence of CNF reduce the thermal stability by up to 15 °C for recycled polyamide nanocomposites and up to 26 °C for virgin polyamide nanocomposites. The processing method did not significantly impair the elastic modulus and tensile strength of both recycled and virgin polyamides, showing a 3 % and 1 % reduction in tensile strength for recycled and virgin polyamides, respectively. The incorporation of 1 wt% and 2 wt% of CNF in virgin polyamide showed an increase in the elastic modulus of 16 % and 5 %, respectively, and a reduction in ductility. In summary, this work offers an alternative processing pathway for nanocomposites of recycled or virgin polyamide 6.6 with CNF; however, some improvements are still necessary to achieve the reinforcing effect of CNF on the mechanical strength of the matrices.

1. Introduction

During the last few years, research on polymer composites has been primarily focused on nanometric fillers. The advantages of nanocomposites compared to conventional composites include excellent thermal and mechanical properties, enhanced recyclability, transparency, and reduced weight [1,2]. In the case of vehicle components, lighter vehicles result in lower CO_2 emissions, thus enhancing sustainability. Additionally, the end-of-life of these components is extended, leading to longer warranty periods provided by the automotive industry. Furthermore, replacing metal components eliminates certain manufacturing steps, thereby improving productivity [3].

Synthetic fibers, such as aramid, glass, carbon, and others, are commonly employed as reinforcements for plastics. Nonetheless, these materials are costly and derived from non-renewable resources. In response, researchers have explored the utilization of natural fiber composites, particularly in the automotive industry, due to their full biodegradability and sustainability [4]. Most natural fibers consist of cellulose, hemicellulose, and lignin [5].

The processing temperature of lignocellulosic composites is constrained to ranges around 200 °C, as the initial degradation temperature of hemicellulose within wood fibers is around 230 °C. Consequently, the melt temperature of selected plastic materials must be below 200 °C, limiting the use of engineering thermoplastics such as polyamide in conventional melt extrusion and injection molding processes. Thermogravimetric analysis studies of the polymer components of wood indicate that the purified cellulose component exhibits greater thermal stability compared to other constituents. Consequently, these purified celluloses can be effectively utilized in conjunction with engineering thermoplastics [4,6].

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Cellulose nanofiber (CNF) is the most abundant purified nanomaterial derived from nature, with vast applications, sustainability, biocompatibility, low cost, availability, and outstanding mechanical properties [7–9]. The primary challenge in processing cellulose nanocomposites lies in effectively feeding the cellulose nanofibers into the extruder and achieving proper dispersion, given their high surface area and tendency to agglomerate due to hydrogen bonds within the cellulose fibrils. This issue can be addressed by first mixing the CNF in a suitable medium or liquid, which is then introduced into the extruder, or by initially drying the CNF before extrusion. Additionally, numerous studies have documented the use of hydrophilic polymers to enhance dispersion [4,10–15].

Jonoobi et al. [11] prepared CNF-reinforced polylactic acid (PLA) nanocomposites using a two-step process: first, a compound with a high concentration of CNF dissolved in a solvent mixture was prepared, followed by extrusion and injection molding. The results demonstrated good dispersion for CNF loading levels ranging from 1 to 3 wt%, with an observed increase in tensile strength and modulus of elasticity with higher nanofiber content. Souza et al. [14] analyzed samples containing 4 and 5 wt% CNF derived from curauá fibers in a polyvinyl alcohol matrix. The authors observed a significant increase in maximum stress of 36 % and 44 %, respectively, indicating good interfacial adhesion. These results suggest compatibility between the reinforcement and the hydrophilic matrix, as well as reinforcement achieved by using low CNF content.

Effective interaction at the reinforcement/matrix interface is crucial for enhancing the mechanical properties of a composite and preventing cellulosic reinforcement from absorbing moisture, swelling, and altering the final dimensions and properties of the composite. Strong interaction at the interface is facilitated when both the matrix and reinforcement exhibit a polar nature [6]. In this context, polyamide emerges as a favorable choice for a matrix compatible with cellulose nanofiber.

Polyamides have a wide range of applications, particularly in specialty plastic materials, where the combination of hardness, rigidity, abrasion resistance, and reasonable heat resistance is demanded in high-technology sectors. Therefore, their broad range of uses spans the textile industry, the construction market, electronics, and the automotive sector [4,16]. Consequently, effective recycling and reuse methods have become interesting subjects for the polyamide manufacturing industries. Government agencies, environmentalists, and technicians all agree that recycling is the most viable option for environmentally sound disposal of plastic waste [17,18].

Several reports on the recycling of polyamide 6 [19–25], polyamide 6.6 [26], polyamide 12 [27], polypropylene [20,28–31], polyurethane [32,33], acrylonitrile-butadiene-styrene [34], and various other polymers recycled through different methods have been carried out in the literature. These data provide a glimpse into the possibilities and magnitude of polymer recycling, which promotes a sustainable circular economy and offers significant benefits to society and the environment, such as energy conservation, resource conservation, and reduced environmental impacts. The development of new and sustainable material from recycled polyamide for application in the automotive sector is focus of the present study.

In this study, Technyl® recycled polyamide 6.6 from Rhodia Polyamide and Specialties Ltda was evaluated as polymer matrix. Technyl® polyamide 6.6 undergoes recycling through depolymerization followed by polymerization (chemical recycling). This method of recycling helps better preserve the material's properties. Titanium oxide is added to recycled resin to act as a whitener agent [35].

In general, the price of recycled plastic is 40 % lower than that of virgin resin, making the substitution of virgin resin with recycled resin beneficial for cost reduction and increased competitiveness, as well as aiding in environmental preservation. In the automotive components manufacturing industry, it is common practice to use up to 20 % recycled material mixed with virgin material. This limit of recycled content is permitted in mixture of virgin and recycled polyamide 6.6 under the claim that recycled does not interfere with the mechanical properties required by specific technical standards adopted by companies [35]. In addition, the Life Cycle Analysis (LCA) conducted by Rhodia Polyamide and Specialties Ltda, Valeo, and PSA Peugeot Citroën confirmed the environmental benefits obtained from using recycled polyamide in automotive applications. The three companies performed multi-criteria analyses of the entire life cycle of the radiator fan and reflector assembly, which are important components of automotive engine cooling. Valeo manufactures these automotive parts using Technyl® recycled polyamide 6.6 from Rhodia. The analysis was reviewed by an independent consultancy (BIO Intelligence Service), which compared the environmental impact of using Technyl® recycled polyamide to that of Technyl® virgin resin polyamide. The results showed that using Technyl® recycled polyamide significantly reduces environmental impact of the component throughout its entire life cycle [36].

Despite the significant technological interest in polyamides, there has been relatively little published research on polyamide 6.6/cellulose composites, and even fewer studies specifically on polyamide 6.6/CNF composites [4,37–40] and on recycled polyamide 6.6/CNF composites. The main challenge in the development of engineering polymer composites is related to the low thermal stability of cellulose materials and the relatively high temperature required in conventional processing of polyamides. Kaziltas et al. [4] extensively studied the application of microcrystalline cellulose as a reinforcing agent in molten polyamide 6 and 6.6, due to the fact that microcrystalline cellulose exhibits higher thermal stability when compared to other nanocellulosic structures. The authors [39] also evaluated the effect of microcrystalline cellulose composition on melt rheology and crystallization behavior of polyamide 6. Qua and Hornsby [37] obtained polyamide 6 composite films reinforced with cellulose nanocrystals via solution casting. The results demonstrate a significant improvement in the mechanical properties of the polymer matrix with the addition of a low content of cellulose nanofibers. In the study by Corrêa et al. [38], cellulose nanowhiskers were coated with polyamide 6, resulting in a material with higher thermal stability. This material was used in the production of nanocomposites, with only 1 wt% of nanowhiskers and polyamide 6, which were processed in the molten state at high temperatures. Sridhara et al. [40] prepared nanocomposite films of polyamide 6 and with up to 50 wt % CNF through solvent casting in formic acid and water mixtures. The mechanical property results of the films demonstrated an average 2.7-fold increase in both elastic modulus and tensile strength.

In this study, recycled polyamide 6.6 was utilized and compared to virgin polyamide 6.6. Thermal, mechanical, and morphological properties of both recycled and virgin polyamide 6.6, and of their nanocomposites with the addition of cellulose nanofiber were analyzed. In addition, an approach labeled pre-processing was employed to facilitate high-temperature processing and the production of nanocomposites with well-dispersed cellulose nanofibers within the matrices. The pre-processing method consists basically of dissolving polyamide in formic acid followed by its precipitation in water. The nanocomposites of recycled and virgin polyamide 6.6 and CNF were processed through pre-processing method followed melt extrusion and injection molding. The mechanical, thermal, and morphological properties of the materials were characterized by tensile test, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM), respectively. The findings showed that pure virgin polyamide exhibited higher thermal degradation compared to pure recycled polyamide. The processing method resulted in well-dispersed nanocomposites; however, it reduces the thermal stability and did not improve the mechanical properties of both nanocomposites obtained from recycled polyamide and virgin polyamide. The incorporation of 1 and 2 wt% CNF increased the elastic modulus and reduced the ductility of virgin polyamide. Based on the findings, we concluded that improvements are needed in the pre-processing stage to achieve the appropriate CNF content during melt processing for producing nanocomposites with improved mechanical response.

2. Material and methods

2.1. Materials

The recycled polyamide 6.6 and the virgin polyamide 6.6, designated as RecPA66 and PA66 respectively, used as thermoplastic matrices, were supplied by Rhodia Polyamide and Specialties Ltda, Brazil. PA66 (Technyl®) has a density of 1.14 g/cm^3, molar mass of 20,000 g/mol, and a melting point of 255–265 °C. Cellulose nanofiber (CNF) was employed as the reinforcement filler, comprising a blend of defibrillated bleached softwood pulps. The CNF has composition of 84.6 ± 4.4 wt% α-cellulose, 6.0 ± 1.1 wt% hemicellulose, and 9.4 ± 0.8 wt% lignin, has crystallinity degree of 75 %, and average diameter of 10–25 nm and length of 100–1100 nm, which corresponds to an aspect ratio of 110–30 [7–9]. The CNF was supplied by University of Toronto - Centre for Biocomposites and Biomaterials Processing, Canada. Formic acid (85 % purity) was utilized as a solvent to dissolve both recycled polyamide 6.6 and virgin polyamide 6.6 and was purchased from Synth.

2.2. Materials processing

Four samples were produced using RecPA66 and another four using PA66. Among these, one sample of each polyamide was directly processed by extrusion and injection molding (labeled as RecPA66 and PA66 samples), while the other three underwent pre-processing (P) method prior to extrusion and injection molding (labeled as P-RecPA66 and P-PA66 samples). The P-PA66 and P-RecPA66 samples were obtained by dissolving 10 g of polymer in 35 ml of formic acid. A suspension with 12 wt% of CNF dispersed in formic acid was added to the polymer solution with constant stirring and heating at 45 °C to prepare the CNF nanocomposites. The polymer solutions and CNF suspension concentrations were defined after several tests aimed at obtaining homogeneous final solutions that are well dispersed and have good viscosity for dripping. The final solutions containing the polymer and CNF were then added dropwise to 1 L deionized water, resulting in precipitated materials. The precipitated materials were subsequently dried in a vacuum oven at 100 °C for 48 h. The samples were produced by extrusion and injection molding to obtain the test specimens. Before the extrusion, the samples were dried in an oven at 100 °C for 12 h. The materials were melt-mixed using a twin-screw extruder (DSM Xplore) of 150/18 (L/D) length/diameter screw ratio. The melt temperature profile was set at 270 and 280 °C from the feeding zone to the die at 100 rpm rotor speed. Each extruded material was quenched in water bath at room temperature and then granulated. The granules were dried at 40 °C for 24 h prior to the injection molding process which was conducted in an Haake MiniJet II machine (Thermo Fisher Scientific), using a barrel temperature of 280 °C, mold temperature of 40 °C, and injection pressure of 4 bar. Specimens' dimension followed Type V geometry, dumbbell-shaped specimen was 38 mm long, 15 mm wide, and 3 mm thick, according to ASMT D1708. The final compositions of the samples and processing methods used are presented in Table 1. This study aimed to evaluate the influence of a low content of up to 2 wt% CNF on the properties of polyamide 6.6. The choice to prepare the nanocomposites with low CNF addition (1 and 2 wt%) was based on good results published in the literature [11,38]. All injection-molded samples were dried at 40 °C under vacuum for 24 h prior to characterization tests.

Table 1
Composition and processing of the samples.

Sample	Polymer	CNF (wt. %)	Pre-processing (P)	Extrusion/ Injection
RecPA66	RecPA66	0		X
P-RecPA66	RecPA66	0	X	X
P-RecPA66-1F	RecPA66	1	X	X
P-RecPA66-2F	RecPA66	2	X	X
PA66	PA66	0		X
P-PA66	PA66	0	X	X
P-PA66-1F	PA66	1	X	X
P-PA66-2F	PA66	2	X	X

2.3. Materials characterization

Thermogravimetric analysis (TGA) was conducting using a PerkinElmer instrument type Pyris 1. The samples were analyzed over a temperature range of 25 °C to 750 °C, with a heating rate of 10 °C/min, under a nitrogen atmosphere with a flow rate of 20 ml/min. Two specimens of each sample were analyzed.

Differential Scanning Calorimetry (DSC) analyses were performed using a PerkinElmer instrument type 8000. The sample were analyzed over a temperature range of 25 °C to 350 °C, with heating and cooling rates of 10 °C/min, under a nitrogen atmosphere with a flow rate of 20 ml/min. Two specimens of each sample were analyzed.

Modulus of elasticity (E), tensile strength (σ_{max}), and elongation at break (ε) were measured via tensile test. Injection molded specimens were previously conditioned in an environment with a relative humidity of 45 ± 2 % for 48 h. Testing was conducted in according ASTM D638 using a universal Emic DL3000 testing machine, with a test speed of 5 mm/min and load cell of 500 kgf. Ten specimens of each sample were tested.

Scanning electron microscope (SEM) was employed to analyze the fracture surfaces of the samples, aiming to verify the dispersion of the CNF within the polymer matrices. The samples were cryogenic fractured with liquid nitrogen and coated with a thin layer of platinum by Scancoat Six Sputter Coater® equipment, and analyzed under a Magellan 400L SEM. Micrographs were collected from a secondary electron detector at acceleration voltage of 2 kV. Three specimens of each sample were analyzed.

3. Results and discussions

3.1. Thermogravimetric analyses (TGA)

The thermal stability of the produced material was evaluated by TGA. Fig. 1(a)–(b) show the representative TG curves of the pure CNF and the samples processed using recycled polyamide and virgin polyamide, respectively. Table 2 summarizes the temperature of mass loss onset (T_{onset}), the maximum mass loss rate temperature (T_{max}), and the residual mass at 750 °C of the studied materials.

The pure CNF exhibits a first mass loss around 100 °C, corresponding to the sample's water loss, Fig. 1(a) and (b). The TG curve remained relatively constant until approximately 295 °C, and the mass loss from room temperature to this point was around 10 %. Thermal decomposition of the CNF begins around 295 °C (T_{onset}), corresponding to the decomposition of cellulose, and continues until reaching nearly constant mass around 430 °C. The maximum rate of mass loss (T_{max}) for the CNF occurs at 390 °C. The residue content at 750 °C was approximately 6.5 %. This improved thermal stability compared to other natural fibers is attributed to the CNF's production process, which removes a significant amount of lignin and hemicellulose. Because of greater thermal stability compared to wood fibers, CNF could be used with engineering thermoplastics. These results are consistent with those reported in the literature [7–9].

In comparing the TGA results of RecPA66 and PA66 samples it can be concluded that the chemical recycling reduced the thermal stability of polyamide, as evidenced by a decrease of 10 °C in the T_{onset}. Similar behavior was observed by Fernandes et al. [35]. The formic acid pre-processing method did not influence the T_{onset} of both recycled and virgin polyamides. However, it reduced the T_{max} of the recycled polyamide by 35 °C, Table 2.

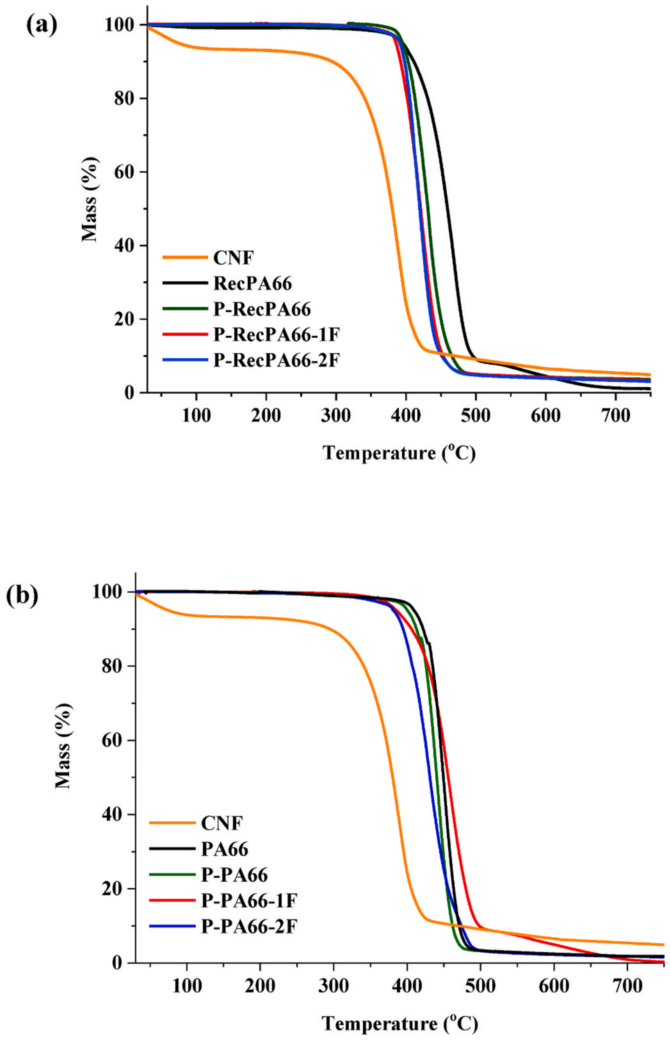

Fig. 1. TG curves of pure CNF and (a) the samples processed using recycled polyamide and (b) samples processed using virgin polyamide.

Table 2
Temperature of mass loss onset (T_{onset}), temperature of maximum mass loss rate (T_{max}), and the residual mass percentage of CNF, pure polymers, and nanocomposites.

Sample	Tonset (°C)	Tmax (°C)	Residue (%) at 750 °C
CNF	295 ± 1	390 ± 1	6.5 ± 0.0
RecPA66	360 ± 0	465 ± 1	1.1 ± 0.1
P-RecPA66	360 ± 1	430 ± 2	4.0 ± 0.1
P-RecPA66-1F	345 ± 1	420 ± 1	3.9 ± 0.2
P-RecPA66-2F	350 ± 1	417 ± 1	3.6 ± 0.1
PA66	370 ± 1	440 ± 1	1.0 ± 0.0
P-PA66	370 ± 1	450 ± 0	1.0 ± 0.1
P-PA66-1F	348 ± 2	460 ± 1	0.5 ± 0.2
P-PA66-2F	344 ± 0	430 ± 1	1.0 ± 0.2

Regarding the samples processed using recycled polyamide, Fig. 1 (a), all samples exhibit a single maximum stage mass loss between 295 and 500 °C, referring to the PA66 thermal degradation. The RecPA66 showed the highest thermal stability between the samples. The mass loss onset temperature (T_{onset}) and the maximum mass loss rate temperature (T_{max}) decreased up to 15 °C and 13 °C, respectively, for the P-RecPA66-1F and P-RecPA66-2F nanocomposites, comparing to the P-RecPA66 sample, indicating the influence of CNF on the reduction of thermal stability of the nanocomposites. As discussed above, CNF decomposes at lower temperature ($T_i = 295$ °C) in comparison to the PA66 matrix ($T_i = 360$ °C), consequently reducing the thermal stability of the nanocomposites.

Regarding the samples processed using virgin polyamide, Fig. 1 (b), similar trend in thermal stability was observed for those samples. PA66 sample showed the higher stability, followed by P-PA66, P-PA66-1F, and P-PA66-2F samples. The results of these samples once again evidenced that the pre-processing method and the presence of CNF decreases the thermal stability of the material. Additionally, both virgin polyamides, whether pre-processed or not, showed a 10 °C higher T_{onset} in comparison to recycled polyamides, whether pre-processed or not, as can be seen in Table 2. Overall, the presence of CNF content in the nanocomposites reduces their thermal stability, due to the clustering of CNFs acting as nucleation sites for degradation. A similar behavior was observed in CNF/PA6 nanocomposites films [40] and microcrystalline cellulose filled polyamide 6 composites [4].

3.2. *Differential scanning calorimetry (DSC)*

The thermal properties of the produced material were evaluated by DSC. Towards to facility the data comparison, average crystallization temperature (T_c), crystallization enthalpy (ΔH_c), melting temperature (T_m), melting enthalpy (ΔH_m), and crystallization degree (X_c) of the samples were summarized in Table 3.

The DSC results showed that, overall, pre-processing method did not significantly influence the crystallization and melting thermal properties of samples with either recycled polyamide or virgin polyamide, and it did not substantially alter the degree of crystallinity of the samples. Recycled polyamide showed lower T_c in comparison to virgin polyamide. This result shows the influence of chemical recycling on the crystallization temperature of PA66. Cooling curves exhibited a well-defined exothermic peak between 220 °C and 225 °C for all samples with recycled polyamide and between 218 °C and 230 °C for samples with virgin polyamide. The greatest influence of pre-processing method was observed in a 5 °C increase in the crystallization temperature of the P-RecPA66 sample compared to the RecPA66 sample. The incorporation of 1 and 2 wt% of CNF resulted in a reduction up to 12 °C in the crystallization temperatures of the pre-processed virgin polyamide, sample P-PA66, as can be seen in Table 3.

The DSC heating curves exhibit two endothermic peaks, one around 244 °C (T_{m1}) and other around 252 °C (T_{m2}) for the samples with recycled polyamide, and one around 247 °C (T_{m1}) and other around

Table 3
Crystallization temperature (T_c), crystallization enthalpy (ΔH_c), melting temperature (T_m), melting enthalpy (ΔH_m), and crystallinity degree (X_c) of pure polymers and nanocomposites.

Sample	Tc (°C)	ΔHc (J/g)	Tm1 (°C)	Tm2 (°C)	ΔHm (J/g)	Xc (%)
RecPA66	220 ± 1	−43 ± 2	245 ± 2	251 ± 2	48 ± 2	25 ± 2
P-RecPA66	225 ± 1	−45 ± 2	244 ± 2	253 ± 2	46 ± 2	24 ± 2
P-RecPA66-1F	224 ± 2	−48 ± 3	245 ± 3	254 ± 3	51 ± 4	26 ± 3
P-RecPA66-2F	221 ± 2	−45 ± 4	242 ± 3	250 ± 3	38 ± 3	19 ± 3
PA66	229 ± 1	−37 ± 2	250 ± 1	258 ± 2	32 ± 1	16 ± 3
P-PA66	230 ± 2	−37 ± 2	249 ± 2	259 ± 2	30 ± 2	15 ± 3
P-PA66-1F	219 ± 3	−41 ± 2	244 ± 3	249 ± 4	46 ± 3	24 ± 3
P-PA66-2F	218 ± 3	−38 ± 3	243 ± 4	250 ± 2	42 ± 3	22 ± 3

254 °C (T_{m2}) for the samples with virgin polyamide, Table 3. This behavior of presenting two peaks, characteristic of PA66, is attributed to the phenomenon of recrystallization, in which small or defective crystals melt at a lower temperature (first endothermic peak), recrystallize, and finally melt at a higher temperature (second endothermic peak). Similar phenomena were also observed by other authors [41–45]. Recycled polyamide showed 9 % lower degree of crystallinity in comparison to virgin polyamide. This result indicates that the chemical recycling reduces the crystallinity of PA66. The same trend was reported in the study of Fernandes et al. [35].

The incorporation of 1 and 2 wt% of CNF resulted in a reduction of 6–10 °C in the melting temperatures and an increase of 8 % in the degree of crystallinity of the pre-processed virgin polyamide, sample P-PA66. These results are indicative of the effective incorporation of CNF into the polyamide, as the good interaction of cellulose nanofibers affects the mobility and rigidity of the polymer matrix chains, thereby increasing the degree of crystallinity and the melting temperature. A similar effect was reported by Lu et al. [12], Salehi-Mobarakeh et al. [43], and Zhang et al. [45]. In contrast, Shidhara et al. [40] observed a decrease in T_m with the increase in CNF content in CNF/PA6 nanocomposite films produced via casting. The authors described that there is a reduction in the crystalline order, suggesting that the evaporation of formic acid results in the formation of a metastable crystalline structure. In the case of recycled polyamide, the DSC results did not show any trend.

3.3. Tensile test

The mechanical properties of the produced material were evaluated by tensile test. Fig. 2(a)–(c) show the modulus of elasticity (E), tensile strength (σ_{max}), and elongation at break (ε), respectively, of the samples processed using recycled and virgin polyamides.

The virgin polyamide (PA66 sample) shows higher modulus of elasticity and tensile strength in comparison to the recycled polyamide (RecPA66 sample), however the virgin resin has much lower elongation at break than recycled resin. These results evidence the influence of chemical recycling on the mechanical properties of PA66.

The tensile test results show that the pre-processing method did not significantly impair the elastic modulus and tensile strength of both recycled and virgin polyamides. An increase in elastic modulus of 6 % was obtained for the recycled polyamide, Fig. 2 (a). The reduction in tensile strength was 3 % and 1 % for the recycled and virgin polyamides, respectively, Fig. 2 (b). Samples that underwent pre-processing method showed a significant reduction in plastic deformation compared to samples that did not undergo pre-processing. In the case of recycled polyamide, the reduction in elastic deformation was 89 %, and for virgin polyamide, the reduction was 10 %, Fig. 2 (c).

Regarding the CNF incorporation, the P-PA66-1F and P-PA66-2F nanocomposites, i.e. with the addition of 1 wt% and 2 wt% of CNF in virgin polyamide, showed an increase in the elastic modulus of 16 % and 5 %, respectively, Fig. 2 (a). It is common for cellulose-reinforced composites to exhibit an increase in elastic modulus, as cellulose is a highly crystalline material. When CNF is well-dispersed in the polymer matrix, it can act as a physical crosslinker, enhancing the strength and stiffness of the material [8,10–12,46]. The increase in strength and stiffness is a strong indicator that the nanocellulose is uniformly dispersed in the polymer matrix and that interfacial adhesion is ensured by the formation of hydrogen bonds between the hydroxyl groups of cellulose and the amine groups of the polymer matrix [37,38]. Corrêa et al. [38] reported a 45 % increase in the elastic modulus of the nanocomposite with 1 wt% of coated cellulose whiskers in comparison to pure polyamide 6. All nanocomposites exhibited a reduction in tensile strength and elongation at break compared to pure polymers, Fig. 2(b)–(c). The reduction in tensile strength was on average 5 % for the recycled polyamide and on average 10 % for the virgin polyamide. The reduction in elongation at break was on average 40 % and 81 % for the recycled and virgin polyamides, respectively. This ductility reduction by reinforced addition is usually observed in thermoplastic composites [37,43].

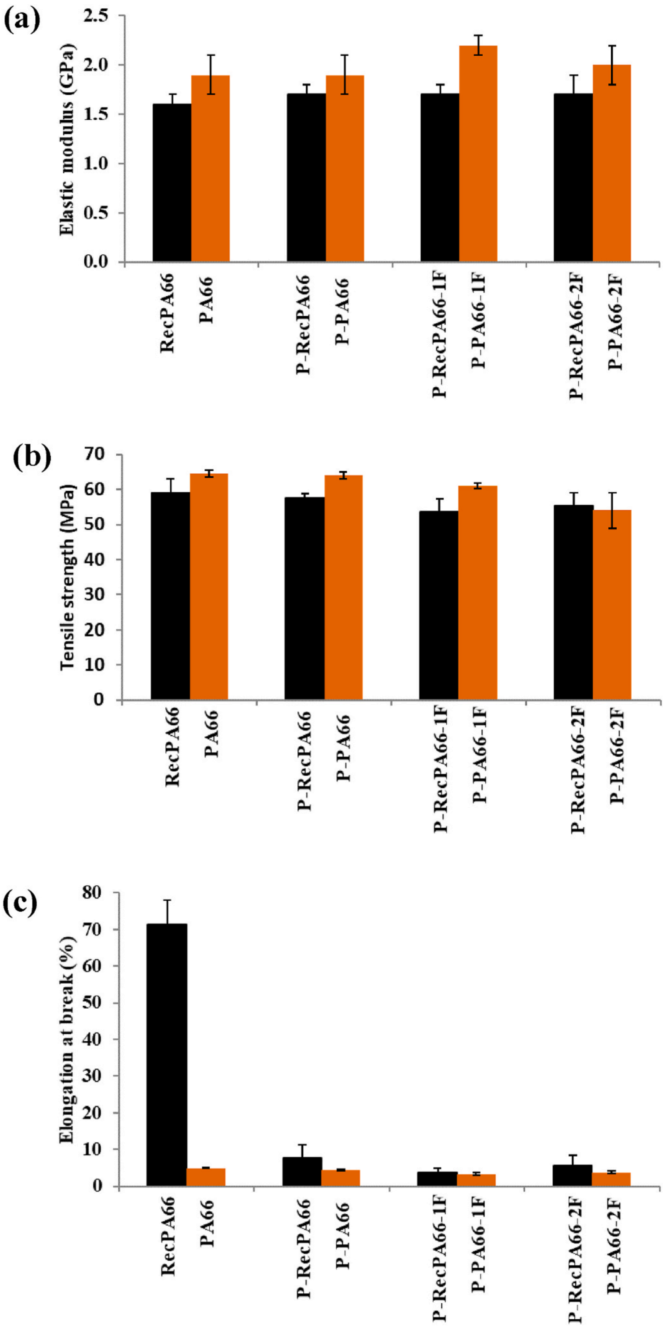

Fig. 2. (a) Modulus of elasticity (E), (b) tensile strength (σ_{max}), and (c) elongation at break (ε) of the samples processed using recycled and virgin polyamides.

3.4. Scanning electron microscope (SEM)

Fig. 3(a)–(f) show representative SEM images of the fracture surface of RecPA66, P-RecPA66, P-RecPA66-1F, P-PA66-1F, P-RecPA66-2F, and P-RecPA66-2F specimens, respectively, aiming to analyze the dispersion of the CNF within the polymer matrices. The fracture surface of the pure PA66 occurs in a completely brittle manner, as can be seen in Fig. 3(a)–(b). Similar morphology was observed for the PA66 and P-PA66 samples, therefore, the images are not presented.

The SEM micrographs of the nanocomposites with 1 wt% and 2 wt%

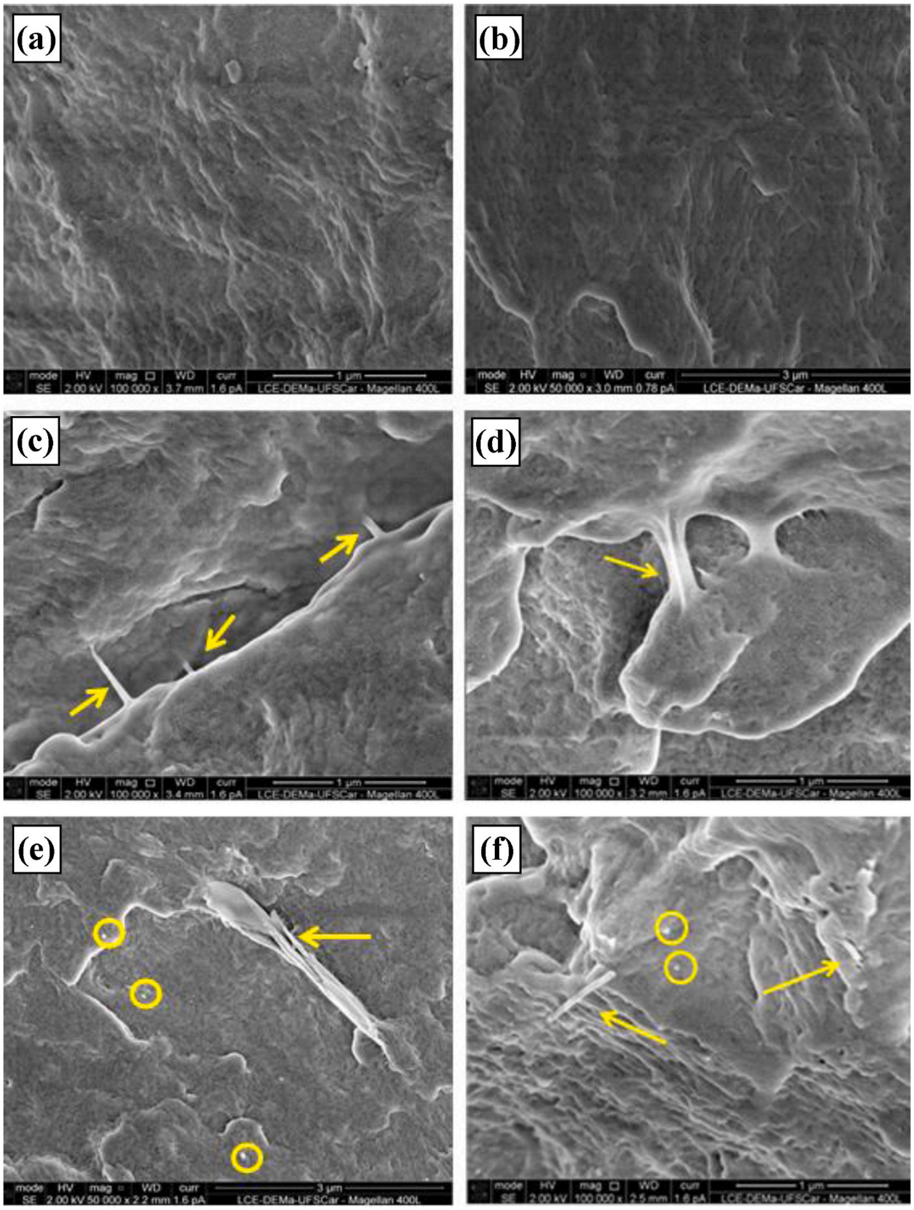

Fig. 3. SEM of the fracture surface of (a) RecPA66, (b) P-RecPA66, (c) P-RecPA66-1F, (d) P-PA66-1F, (e) P-RecPA66-2F, and (f) P-RecPA66-2F samples.

of CNF are shown in Fig. 3(c)–(f), respectively. It is evident that the morphology of the nanocomposites was quite similar, but relatively different than those of pure polyamide (RecPA66, P-RecPA66, PA66, and P-PA66) samples. The distribution of CNF appears to be homogeneous, with no agglomerations observed in all nanocomposite samples, regardless of the CNF content or the polymer matrices. The images evidenced domains of CNF in the horizontal (perpendicular to the flow – highlighted by yellow arrows) and vertical (parallel to the flow – highlighted by yellow circles) directions, showing well-dispersed cellulose nanofibers within the polyamide matrices. The polymer matrix domains are adjoined by CNF domains, demonstrating good adhesion between them. Strong interaction at the interface is observed, as both polymer matrices and CNF exhibit a polar nature. Shidhara et al. [40] also observed good dispersion and distribution of CNF for all formulations (10–50 wt% of CNF) of CNF/PA6 nanocomposite films produced via casting.

4. Conclusions

Recycled and virgin polyamide 6.6 resins and their cellulose nanofiber nanocomposites, were prepared using the formic acid pre-processing method and melt extrusion/injection molding. TGA results indicated that virgin polyamide exhibited higher thermal stability, a 10 °C higher onset temperature, compared to recycled polyamide. However, both recycled and virgin polyamides showed decreased thermal stability due to the pre-processing method and the presence of CNF. DSC results did not reveal any significant trends overall. The pre-processing method did not notably influence the crystallization and melting behavior of the samples. The incorporation of CNF led to reductions in both the T_c and T_m of virgin polyamide. Additionally, recycled polyamide 6.6 exhibited a lower degree of crystallinity compared to virgin polyamide 6.6. The pre-processing method did not significantly impair the elastic modulus and tensile strength of both recycled and virgin polyamides. The samples with CNF showed an increase in the modulus of elasticity of virgin polyamide and a decrease in the tensile strength and elongation at break of both recycled and virgin polyamides. Good dispersion of CNF in the polymers matrices was seen in the SEM micrographs of the nanocomposites. Overall, it can be concluded that the pre-processing method and extrusion used to disperse and incorporate CNF do not affect significantly the elastic modulus and the maximum tensile strength of the nanocomposites, indicating an alternative for the use of recycled polyamide 6.6, depending on the application. However, the incorporation of higher CNF contents in polyamide 6.6 using the same preparation methodology is recommended to achieve nanocomposites with better mechanical properties. In theory, by the formic acid pre-processing, a good dispersion is assured between both components. Our research group intends to evaluate the preparation of master-batches containing CNF with both virgin and recycled polyamide 6.6 polymers. This will be done by pre-processing with formic acid/water mixture and then dilute it to the appropriate CNF content during the melt processing, aiming to produce nanocomposites with a higher CNF content and consequently better mechanical performance.

CRediT authorship contribution statement

Daiane Benaducci: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Vinicius de Oliveira:** Writing – original draft, Validation, Methodology, Data curation. **Wiliam Tai Yin Tze:** Writing – review & editing, Validation, Resources, Formal analysis. **Islam Hafez:** Writing – review & editing, Validation, Investigation, Conceptualization. **Marcia Cristina Branciforti:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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