

Melt extruded nanocomposites of polybutylene adipate-co-terephthalate (PBAT) with phenylbutyl isocyanate modified cellulose nanocrystals

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ABSTRACT: Traditional commodity polymers are widely used in several disposable or short-life items and take hundreds of years to decompose in nature. These polymers could be replaced in several uses by biodegradable polymers, like polybutylene adipate-co-terephthalate (PBAT) studied in this work. For this, nonetheless, it is necessary to improve some of the PBAT properties, like mechanical resistance and barrier properties. In this work, cellulose nanocrystals (CNC) were incorporated in PBAT with this intention, through melt extrusion. Aiming to avoid CNC aggregation during the drying and extrusion process, a CNC chemical modification with phenylbutyl isocyanate was done. It was possible to obtain PBAT-CNC melt extruded composites with an elastic modulus 55% higher and water vapor permeability 63% lower than the values of the pure polymer, without compromising PBAT biodegradation. Therefore, the composites prepared with these enhanced properties have great potential as substitutes for traditional commodity polymers.

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INTRODUCTION

The change in consumption habits in the last 50 years increased the volume of commodity polymers used in disposable or short-life items, as packaging.^{1,2} The plastic film market, for example, is dominated by these polymers, that have versatile properties, but are not biodegradable, taking hundreds of years to decompose in nature after disposal.³ Thus, it is imperative to think about the replacement of such polymers by biodegradable ones in many applications.

Polybutylene adipate-co-terephthalate (PBAT) is a flexible biodegradable polymer, with the certification seal of biodegradable and compostable material, given by the European Bioplastics (EN13432 standard criteria) and by the Biodegradable Polymers Institute (ASTM D6400 standard specification). Nonetheless, to increase its range of use, it is important to improve some of its properties, like mechanical resistance and barrier properties. This improvement can be achieved through the incorporation of reinforcement fillers, for instance.

Because of its small overall dimensions (nanometric thickness and length), high modulus, and biodegradability,^{4,5} cellulose nanocrystals (CNC) are potential materials for the reinforcement

of those polymers; some studies have already shown that CNC incorporation in polymers increases their mechanical and barrier properties.^{6–9} However, the majority of these studies have been done in samples obtained by solvent casting. Few studies have used melt extrusion, using different procedures and producing results very different between them. For example, Oksman *et al.*¹⁰ and Bondeson *et al.*¹¹ incorporated CNC into a poly(lactic acid) (PLA) matrix, using suspensions in the extruder, but only small improvements were observed in comparison with the pure PLA matrix. Goffin and coworkers,¹² on the other hand, observed the increase in the storage and loss modulus of PLA with the incorporation through melt extrusion of CNC grafted with PLA molecules. The study of Fortunati *et al.*¹³ showed an increase of 20% of the PLA elastic modulus after the addition of 5 wt % of CNC. Nevertheless, this increase could be related to the increase up to 100% of the PLA crystallinity with the addition of CNC treated with a surfactant. Until now, however, no study about the incorporation of CNC into a PBAT matrix through melt extrusion has been found.

In our previous work,¹⁴ CNC was modified with an aliphatic (octadecyl) and an aromatic (phenylbutyl) isocyanate and incorporated into a PBAT matrix through a solvent casting process.

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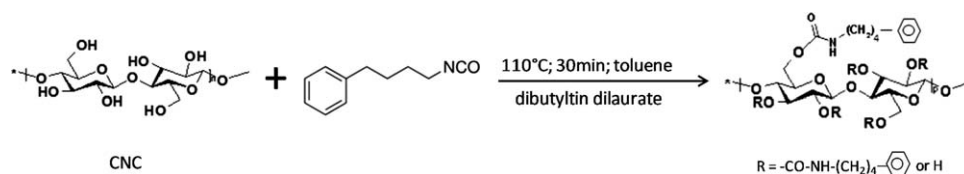


Figure 1. Scheme of the reaction of cellulose nanocrystals with phenylbutyl isocyanate.

The results showed an enhancement in the properties of the composites with the phenylbutyl isocyanate-modified CNC. The solvent casting was found to be a good procedure for laboratory screening tests; however, it was hard to scale-up to industrial applications, in which melt extrusion is more used. Melt extrusion, however, can present some drawbacks when processing biodegradable nanocomposites. For example, depending on the polymeric matrix, temperatures similar or even higher than the degradation temperature of many natural reinforcements, like the CNC itself, chitosan, and starch nanocrystals among others, must be used. Moreover, the use of dried CNC in conventional melt extrusion tends to induce its aggregation through the formation of strong hydrogen bonds. For that reason, the results found in CNC-polymer systems obtained by solvent casting cannot be directly compared to the same systems processed by melt extrusion, as already verified by Jiang *et al.*¹⁵ for composites of poly (3-hydroxy butyrate-co-3-hydroxyvalerate) (PHBV) with CNC.

Thus, in the present work, CNC were modified with phenylbutyl isocyanate and incorporated into a PBAT matrix through melt extrusion and barrier, thermal and bio-fragmentation properties of the composites were evaluated for the first time.

EXPERIMENTAL

Materials

The PBAT was supplied by NaturePlast, from France. The microcrystalline cellulose Avicel PH-101 (average particle size of 50 μm) and the sulfuric acid (96%) used for the production of the CNC were acquired from Sigma-Aldrich (Lyon, France). Anhydrous toluene (99.8%), dichloromethane ($\geq 99.5\%$), 4-phenylbutyl isocyanate (97%), and dibutyltin dilaurate (95%), used in the CNC chemical modification, were also purchased from Sigma-Aldrich. Chloroform ($\geq 99\%$), ethanol (96%), and acetone (99%) were from Chemie-Plus.

Cellulose Nanocrystals Production

About 100 g of microcrystalline cellulose Avicel were submitted to acid hydrolysis with 1 L of sulfuric acid aqueous solution (62.4 wt %) at 44 $^{\circ}\text{C}$ for 130 min, following the procedure adapted from Bondeson *et al.*¹⁶ At the end of the reaction, the suspension was submitted to successive cycles of centrifugation, washing with water, and re-dispersion, in order to remove the acid. These operations were repeated until the supernatant became turbid because of the presence of the non-precipitated CNC. The centrifugation was performed in a Sigma EK15 centrifuge for 20 min at 10,000 rpm and 4 $^{\circ}\text{C}$. The dispersion was done using a high-speed homogenizer Ultra Turrax from IKA at 12,000 rpm. The CNC suspension was then submitted to dialysis until neutral pH, sonified for CNC dispersion (in a Branson

250 sonifier), and filtered for the impurities removal (with Nylon filter of 31 μm of porosity).

CNC Chemical Modification

CNC chemical modification with 4-phenylbutyl isocyanate was done as described in our previous work¹⁴ and it is schematized in Figure 1.

Solvent exchange was done from the CNC water suspension to toluene, using acetone and dichloromethane as intermediate solvents, with repeated cycles of centrifugation and dispersion. Then, 3 g of CNC, 200 mL of anhydrous toluene and 2 mL of the catalyst dibutyltin dilaurate were added to a three-necked flask under nitrogen atmosphere and constant stirring. After heating at 90 $^{\circ}\text{C}$ in oil bath, 16.41 g (0.055 mol) of 4-phenylbutyl isocyanate were introduced into the reaction medium. The temperature was raised to 110 $^{\circ}\text{C}$ and the reaction was maintained for 30 min. At the end, the modified CNC (in which some of the hydroxyls groups were substituted for urethane groups) was submitted to a solvent exchange procedure (centrifugation and dispersion cycles) from toluene to chloroform, using dichloromethane and ethanol as intermediate solvents. The CNC suspension in chloroform was sonified, transferred to PTFE plates, and let under hood several days until complete evaporation of the solvent, in order to recover the modified CNC. The non-modified and modified CNC are referenced in the text as CNC and CNCpb, respectively.

Nanocomposites Preparation

The nanocomposites were prepared through melt extrusion in a co-rotational conical twin-screw DSM Xplore micro-extruder of 15 cm^3 . The extrusion temperature was set at 150 $^{\circ}\text{C}$, with a screw velocity of 100 rpm and a residence time of 5 min. The measured melt temperature was 160 $^{\circ}\text{C}$. Before extrusion, the PBAT pellets were oven dried for 2 h at 75 $^{\circ}\text{C}$. The powders of modified and non-modified CNC were also oven dried for 2 h at 60 $^{\circ}\text{C}$ just before the extrusion. The CNC was added to the PBAT matrix in order to obtain the following CNC contents: 2.5, 5.0, and 10.0 wt %.

The extruded composites were dried at 75 $^{\circ}\text{C}$ for 2 h and thermo-pressed for film preparation at 170 $^{\circ}\text{C}$ with 10 ton of pressure during 4 min. The cooling was done at room temperature. The composites with non-modified CNC are referenced in the text, depending on the CNC content added, as 2.5CNC, 5CNC, and 10CNC and the composites with modified CNC are named 2.5CNCpb, 5CNCpb, and 10CNCpb.

Characterizations of the Materials

To calculate CNC dimensions, atomic force microscopy (AFM) was used: a drop of a very diluted CNC suspension (10^{-3} wt

%) was deposited on the mica sample holder of a Veeco Bruker dimension icon equipment and analyzed after complete drying.

To analyze the presence of urethane groups on the surface of the CNC, attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was done in the dried powders of the modified and non-modified CNC using a Perkin Elmer 65 Spectrometer. The analyses were done between 700 cm^{-1} and 4000 cm^{-1} , with 32 scans, and resolution of 4 cm^{-1} .

The thermal properties of the nanocomposites were studied by differential scanning calorimetry (DSC) using a Q2000 equipment from TA Instruments. Cycles of heating and cooling, from -70 to $200\text{ }^{\circ}\text{C}$ were done, at rates of $10\text{ }^{\circ}\text{C min}^{-1}$. During the heating cycle, the glass transition (T_g) and melting temperatures (T_m) of the thermopressed samples were measured. On the cooling cycle, after thermal history was erased, the onset of crystallization and maximum crystallization temperatures (T_{c_onset} and T_{c_max} , respectively) of the samples were analyzed. The crystallinity degree (X_c) of pure PBAT and the nanocomposites was obtained according to eq. (1):

$$X_c = \frac{\Delta H_m}{\Delta H_{100\%}} \times 100 \quad (1)$$

where ΔH_m is the enthalpy of the melting peak and $\Delta H_{100\%}$ is the theoretical enthalpy of the melting of 100% crystalline PBAT, or 114 J g^{-1} .^{17,18} The values of all composites were normalized considering the real polymer content in each one (subtracting the CNC content). At least two samples of each composition were analyzed

To analyze the thermal stability of the materials, thermogravimetric analyses (TGA) were done in a Q50 equipment from TA Instruments under nitrogen atmosphere, within a temperature range of 25 to $800\text{ }^{\circ}\text{C}$ and a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

The tensile tests were performed using samples cut from the thermo-pressed films with dimensions of $20 \times 5 \times 0.2\text{ mm}$. A RSA3 machine from TA Instruments was used, with a velocity of 4 mm min^{-1} and space between grips of 10 mm . At least four samples were analyzed for each composition.

The water vapor permeability of the nanocomposites and pure PBAT was determined following the ASTM E96/E96M-05 standard procedure. Samples with square shape of 20 cm of side were cut from the films. These samples were glued in a double aluminum paper (above and below the films) which had a central circular opening of 14 mm of diameter; the assemblies were fixed as covers of glass pots with 2 mL of distilled water, using epoxy resin. After the determination of the initial weight, the samples were transferred to desiccators with silica gel, under controlled temperature ($20\text{ }^{\circ}\text{C}$) and humidity (22%). Periodic weighting of the samples was done during 25 days. The water vapor permeability coefficient (P_{WV}) of each sample was determined from eqs. (2) and (3):

$$P_{WV} = \frac{WVT \cdot e}{S(R_1 - R_2)} \quad (2)$$

$$WVT = \frac{G}{t \cdot A_p} \quad (3)$$

where WVT is the water vapor transmission rate ($\text{g m}^{-2}\text{ h}$), e is the thickness of the film (m), S is the water vapor saturation

pressure at the test temperature (Pa), $R_1 (=1)$, and $R_2 (=0.22)$ are the relative air humidity in each one of the sample surfaces, G is the mass change, t is the time (s), and A_p is the effective area for permeation (m^2). The water vapor saturation pressure S at the test temperature ($20\text{ }^{\circ}\text{C}$) was 2.3 kPa .¹⁹ This test was done in three samples of each composition.

The test of disintegration under defined composting conditions, also called bio-fragmentation test, was based on EN 14045 standard procedure. The initial weights of the dried films (discs with 14 mm of diameter and 0.2 mm of thickness) were determined. The samples were then buried in an organic composting medium at controlled temperature and humidity (around 50%). Weighting of the samples was done every month, during six months. For these measurements, the samples were unearthed carefully, washed with water, and dried before weighting. Two samples per composition were analyzed. Two sheets of microcrystalline cellulose (discs with 14 mm of diameter and 1.3 mm of thickness) were also buried in the same system as control samples. The organic compound used was supplied by Provaso Industry and Commerce of Organic Fertilizers, from Brazil, and was composed by natural phosphate, sugarcane bagasse, charcoal, limestone, and poultry manure. The compound has a carbon: nitrogen ratio of 18:1, 1% of nitrogen, and pH between 6 and 7.

RESULTS AND DISCUSSION

Cellulose Nanocrystals

An AFM micrograph of the cellulose nanocrystals obtained from microcrystalline cellulose is shown in Figure 2. The CNC average width, measured from this micrograph, was $12.0 \pm 0.3\text{ nm}$. However, because the AFM tip tends to cause a broadening effect in the CNC size,²⁰ more accurate measurements of their length and width were obtained through transmission electron microscopy (TEM) micrographs,¹⁴ resulting in average values of $143 \pm 71\text{ nm}$ and $11 \pm 4\text{ nm}$, respectively.

The grafting of CNC with phenylbutyl isocyanate was confirmed by ATR-FTIR, as observed by the surging of the urethane band at 1704 cm^{-1} (Figure 3). The degree of substitution (DS) resulting from the reaction of CNC hydroxyls with phenylbutyl isocyanate, calculated in our previous work¹⁴ was 0.25.

Nanocomposites

Photographs of pure PBAT film and the composites are shown in Figure 4. After the addition of non-modified CNC it is possible to see at naked eye the surging of brown aggregates throughout all the samples. On the other hand, the pure PBAT and the composites with chemically modified CNC did not have these brown aggregates. Therefore, even if micrographs of transmission electron microscopy were not done (due to the difficulty on cutting the samples by cryo-ultramicrotomy), at a macroscale, the presence of brown aggregates indicated that a bad dispersion of non-modified CNC in the PBAT matrix occurred. CNC and PBAT were added together in the extruder, after drying. The complete drying of non-modified CNC favors its aggregation through the formation of hydrogen bonds, hardly disrupted during the mixture with the high viscosity polymer melt in the extrusion process. The brown color of the



Figure 2. AFM micrograph of CNC obtained from microcrystalline cellulose. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

aggregates can also be due to CNC degradation, as afterwards discussed. The surging of brown aggregates of CNC in polymeric samples was also identified by Menezes, Dufresne, and coworkers²¹ as being a signal and a consequence of the bad CNC dispersion within the matrix and bad interaction with the matrix.

In the case of modified CNC (CNCpb), these aggregates were not observed and samples were homogeneous, similar to the pure PBAT. This was the consequence of the chemical modification, with the reaction of part of the hydroxyls with the isocyanate, resulting in a better dispersion and distribution through the polymeric matrix (see also Figure 4).

Thermal Properties. Table I presents the results of T_g , T_m , T_{c_onset} and T_{c_max} and X_c of the composites and the pure polymer obtained by differential scanning calorimetry (DSC). Regarding the T_g , it can be observed that the incorporation of non-modified and modified CNC did not alter this parameter, which means that the flexibility of the PBAT matrix at low temperatures was kept. T_m , on the other hand, had a slight decrease with the addition of 5 and 10 wt % of non-modified CNC, indicating that the incorporation of these contents of non-modified CNC promoted the crystallization of slightly less perfect PBAT crystals; however, when modified CNC was added, crystals of the same perfection as in the pure PBAT were produced.

The CNC nucleation effect was verified from the analysis of the values of the T_{c_onset} ; this temperature increased with the increasing addition of modified and non-modified CNC, the increase, however, being higher when modified CNC were present (Figure 5). Thus, independent of the CNC surface

treatment, their surface acted as nucleation sites for the PBAT macromolecules, accelerating its crystallization. It is worthwhile to recall that a nucleating agent provides an additional surface for the developing of a crystal nucleus. Therefore, the nucleation step of the overall crystallization process is accelerated, and on cooling, the overall crystallization temperatures will be higher. Usually each particle of nucleating agent will generate a crystal nucleus, and if the amount of nucleating agent is high, high amount of small crystallites will be produced at a given temperature. Because both crystallization steps (nucleation and growth) are diffusion dependent, any constraint to polymer diffusion will decrease both steps. Thus, probably, the modified CNC was more effective as nucleating agent (bringing forward T_{c_onset}) because the PBAT macromolecules were already physically “attached” to the CNC surface.

On the other hand, the volumetric amount of crystals (% of crystallinity, regardless of the sizes of the crystals) increased with the increase in the amount of CNC, modified and non-modified; that is, as the amount of nucleating agent (CNC) increased, the amount of crystals increased, as expected. It is also observed that the % of crystallinity in the nanocomposites with modified CNC was slightly lower than of the nanocomposites with non-modified CNC. It is again worthwhile to recall that during the growth of a polymeric crystal, impurities (or in this case, CNC) will be driven off to the boundaries of the crystal; however, if the impurities are physically “attached” to the macromolecules, its expelling probably will be difficult. Thus, the lower % of crystallinity in the modified CNC nanocomposites was probably due to the existence of fewer nucleus and to the constraint to grow promoted by the “attachment” of the PBAT macromolecules to the CNC surfaces. In other words, the modified CNC accelerated the nucleation step, acting as an efficient nucleating agent, but because the amount of nuclei was small and the diffusion to grow was hindered by the “attachment” of the macromolecules to the CNC surface, fewer amount of crystallites grew. The increase in crystallinity with

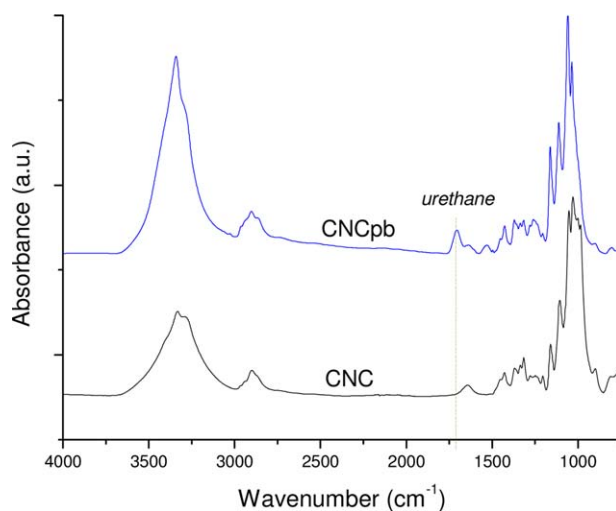


Figure 3. ATR-FTIR spectra of non-modified (CNC) and modified CNC (CNCpb). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

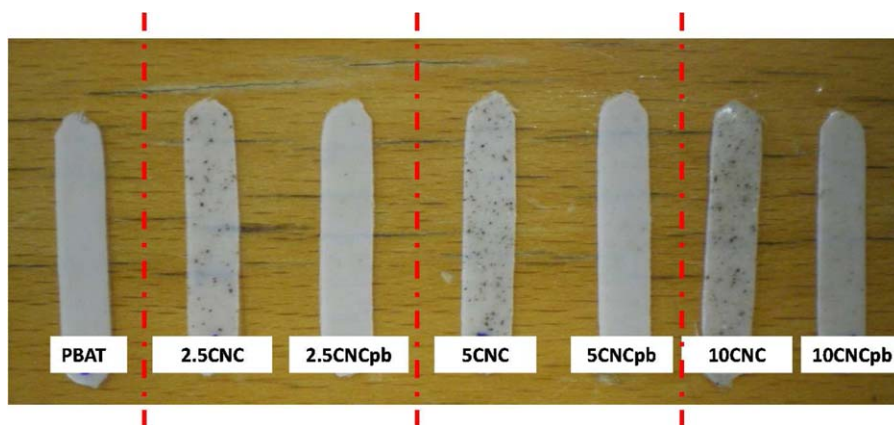


Figure 4. Extruded and thermo-pressed samples: pure PBAT matrix (PBAT) and PBAT composites with 2.5, 5.0, and 10.0 wt % of non-modified (samples 2.5CNC, 5CNC, and 10CNC) and modified CNC (samples 2.5CNCpb, 5CNCpb, and 10CNCpb). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CNC addition was also verified by Siqueira *et al.*²² in composites of poly(caprolactone).

However, these results need more confirmation tests to be conclusive because, as already known, the crystallization kinetics of a polymer matrix in a nanocomposite is strongly dependent on the polymer-reinforcement interactions, reinforcement characteristics (shape, dimensions, rigidity) but also on the applied processing conditions (temperature, pressure, and cooling rate), as numerous studies have already shown.^{23–25} The correlation between a better dispersion and interactions of CNC with the polymeric chains and the lower crystallization was also pointed out by Roohani *et al.*²⁶

The thermal stability of the nanocomposites with modified and non-modified CNC was evaluated through thermogravimetric analysis and the results are presented in Table II, where T_{onset} and T_{max} are the temperatures when the mass loss begun and a higher mass loss rate occurred (this last one given by the peak of the mass loss derivative curve), respectively. PBAT began to lose mass at 388 °C and had a T_{max} around 411 °C, while the CNC began to lose mass at 198 °C and had a T_{max} of 297 °C. Thus, in the case of composites, the T_{onset} is related to the temperature of CNC degradation, while their T_{max} refers to the temperature of PBAT higher mass loss. It can be observed therefore that the grafting of the phenylbutyl isocyanate into the CNC allowed the increase of the T_{onset} of the composites having similar CNC contents by approximately 20 °C. This best CNC

thermal stability after the chemical treatment can be a consequence of: (1) the partial removal of sulfate groups from the CNC surface due to the acid hydrolysis reaction⁶ and (2) a better polymer-CNC interaction.²³ On the other hand, the temperature at which a higher mass loss rate occurred in the composites (around 400 °C) was not altered.

The temperatures of the extrusion process (machine set point at 150 °C and measured melt temperature at 160 °C) and of the thermo-pressing (170 °C) were smaller than the CNC onset degradation temperature. However, degradation of the non-modified CNC during extrusion and thermo-pressing could have occurred due to the long residence times of these processes (5 and 4 min, respectively). This degradation could have contributed to the brown color of the aggregates, seen earlier in Figure 4. In the case of the composites with modified CNC, the significant increase of 20 °C in the onset degradation temperature probably avoided their degradation. This result shows that the CNC chemical modification with phenylbutyl isocyanate increased the possibility of their processing with different polymeric matrixes or through different processes where higher temperatures might be needed, thus enlarging their range of applications.

Mechanical Properties. A standard stress-strain curve for one tensile sample of each of the nanocomposites is shown in Figure 6(a), while the results of all the tensile tests (elastic modulus E , yield stress σ_y , and yield strain ϵ_y) for all the samples are shown

Table I. T_g , T_m , $T_{c_{\text{onset}}}$, $T_{c_{\text{max}}}$, and X_c of the Nanocomposites Calculated from DSC

	T_g (°C)	T_m (°C)	$T_{c_{\text{onset}}}$ (°C)	$T_{c_{\text{max}}}$ (°C)	X_c (%)
PBAT	-35.0 ± 1.8	120.0 ± 1.3	90.5 ± 0.4	75.0 ± 1.4	19.0 ± 2.5
2.5CNC	-35.2 ± 2.7	120.2 ± 2.0	94.0 ± 2.8	77.2 ± 4.2	19.0 ± 3.7
2.5CNCpb	-34.4 ± 1.3	120.1 ± 1.5	95.2 ± 3.3	76.3 ± 4.9	20.6 ± 1.2
5CNC	-35.1 ± 1.0	117.3 ± 0.9	95.6 ± 1.4	76.4 ± 4.2	24.4 ± 1.4
5CNCpb	-36.0 ± 0.5	120.0 ± 1.0	97.9 ± 0.7	78.0 ± 2.1	20.0 ± 1.7
10CNC	-36.0 ± 1.3	117.4 ± 1.9	97.3 ± 0.0	77.0 ± 2.1	26.8 ± 2.1
10CNCpb	-35.0 ± 1.4	120.1 ± 0.9	98.4 ± 0.1	81.0 ± 1.4	22.5 ± 0.6

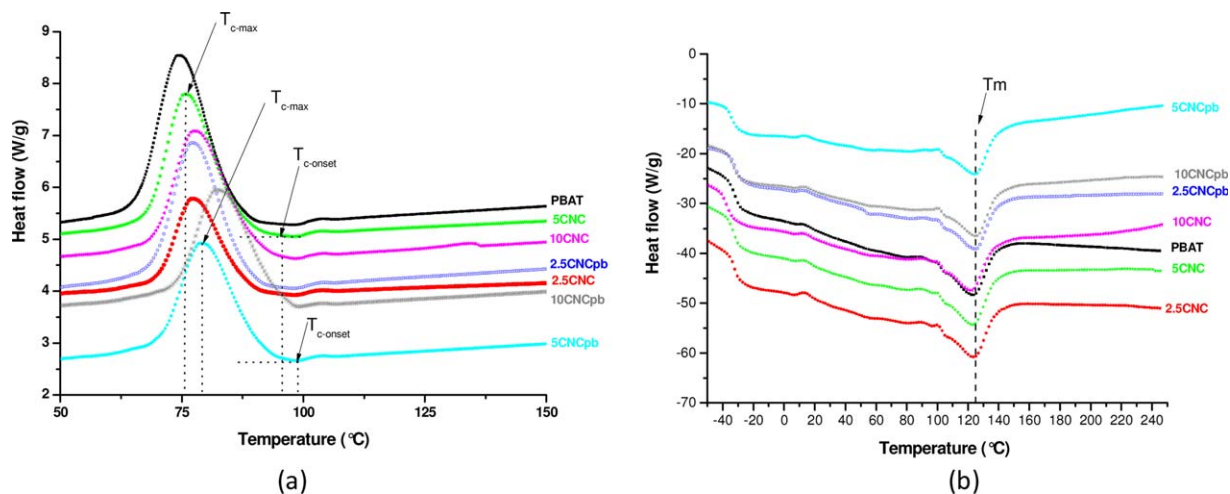
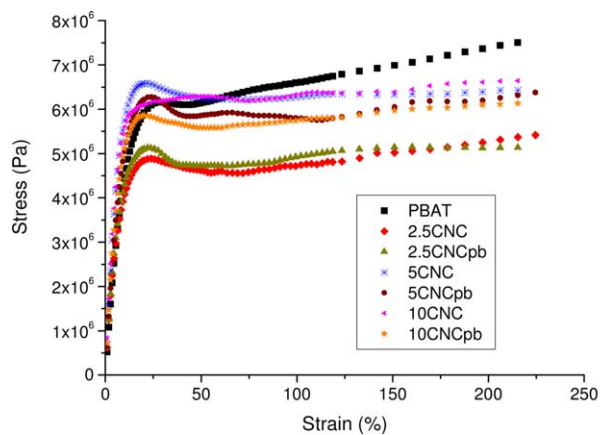


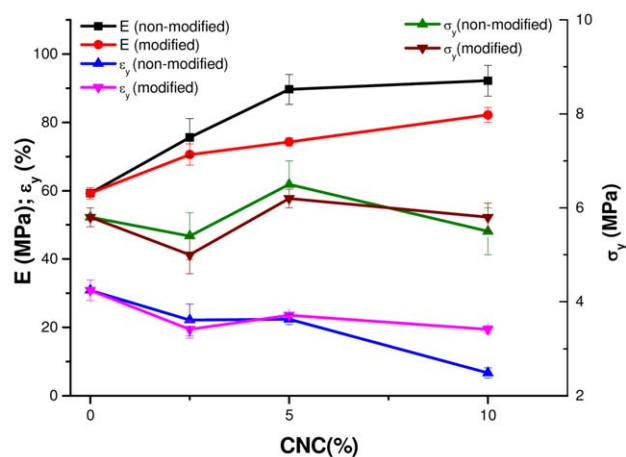
Figure 5. (a) Cooling DSC curves, with the indication of T_{c_onset} and T_{c_max} of the samples 5CNC and 5CNCpb, for comparison; and (b) second heating DSC curves, with the indication of T_m . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in Figure 6(b), with the standard deviation. PBAT is very ductile and after the incorporation of the CNC, its ductility was maintained: none of the nanocomposites broke during the tests (like PBAT) and their elongations were above 200% (when the machine extension limit was reached). Thus, due to limitations of the tensile testing machine (which did not allow the measuring of the breaking point), the stress and the strain at the yield point (σ_y and ϵ_y , respectively) were instead analyzed.

The addition of non-modified and modified-CNC increased the elastic modulus E of the PBAT. The highest elastic modulus was observed in the 10 wt % non-modified nanocomposite (increase of 55% in the elastic modulus). However, samples made of this composition (and the other compositions with non-modified CNC) had a high concentration of large CNC agglomerates and large interfacial voids between the CNC aggregates and the PBAT matrix, which could be seen at naked eye, as shown in Figure 4. These agglomerates and voids were large enough to compromise the yield strain of the samples. The average yield strain of the 10CNC composite was 65% smaller than the average yield strain of the 10CNCpb. In our previous work,¹⁴ in which composites of PBAT with 10 wt % of CNC were prepared by solvent casting, the increase in PBAT elastic modulus was even higher (77%), which we attributed to a better CNC dispersion in the PBAT matrix due to the mixing process (in



(a)



(b)

Table II. T_{onset} and T_{max} of the Nanocomposites from TGA Curves

	T_{onset} (°C)	T_{max} (°C)
PBAT	388	411
CNC	198	297
2.5CNC	238	411
2.5CNCpb	262	417
5CNC	222	413
5CNCpb	255	416
10CNC	223	407
10CNCpb	244	414

Figure 6. (a) Standard stress–strain curve of the nanocomposites; (b) Elastic modulus (E), yield stress (σ_y), and yield strain (ϵ_y) of the nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Water Vapor Permeability (Units in Conformity with ASTM E96) and Weight Losses of the Samples During the Bio-Fragmentation Tests (Standard Deviation is 0.40)

	P_{wv} (10^{-10} g $\text{Pa}^{-1} \text{s}^{-1} \text{m}^{-1}$)	Reduction (%)	Weight loss (%)			
			PBAT	5CNC	5CNCpb	
PBAT	2.52 ± 0.46		30 days	1.37	1.61	0.45
2.5CNC	2.13 ± 0.88	15	60 days	2.23	2.69	2.80
2.5CNCpb	0.92 ± 0.22	63	90 days	2.18	2.92	2.64
5CNC	1.54 ± 0.25	39	120 days	2.43	4.50	3.17
5CNCpb	1.17 ± 0.37	54	150 days	2.50	7.42	3.17
10CNC	12.70 ± 6.16	—	180 days	2.23	8.89	2.57
10CNCpb	0.92 ± 0.24	63				

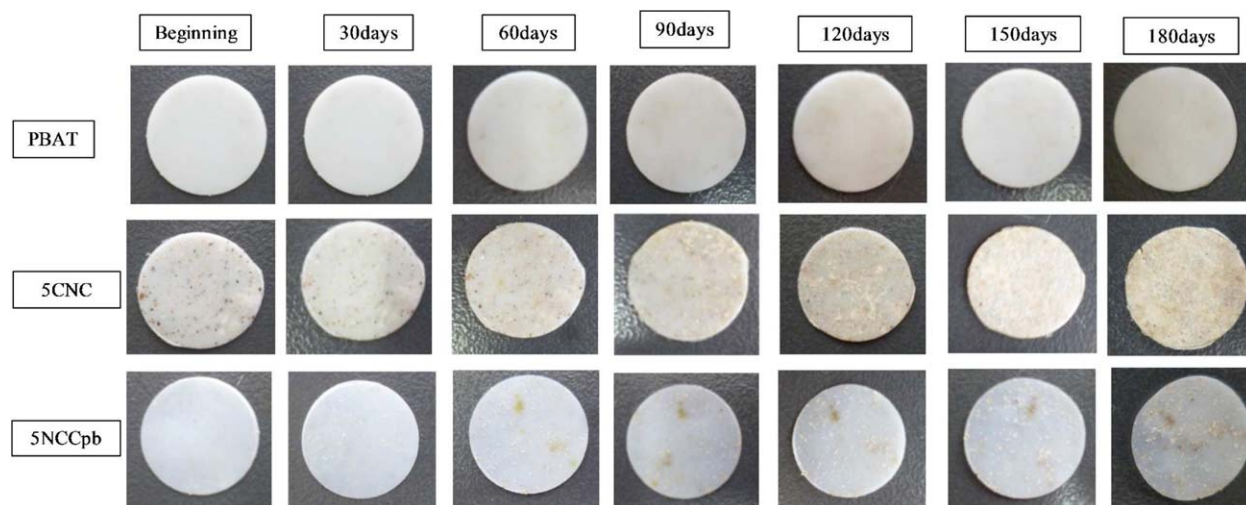
suspension, without drying the CNC). Nonetheless, solvent casting is a procedure hard to scale-up to industrial applications, in which melt extrusion is more used, and the increase in PBAT elastic modulus attained in this work by melt extrusion compounding can be considered significant. In the study of Fortunati *et al.*,¹³ the addition of 5 wt % of non-modified CNC by melt extrusion increased the PLA elastic modulus around 20%, but a decrease of approximately 30% and 60% of the tensile strength and the strain at break, respectively, was observed. No study about composites of PBAT with CNC was found.

The composites with CNCpb also had an elastic modulus considerably higher than the values of the pure PBAT, and higher CNC contents led to higher increases. With the addition of 10 wt % of modified CNC, the elastic modulus of PBAT increased 39% and, contrary to the similar composition with non-modified CNC, the samples were homogeneous and without large CNC aggregates and voids as shown in Figure 4. Nevertheless, the moduli of the composites with modified CNC were smaller than the moduli of the non-modified CNC with similar CNC contents. This result is probably the consequence of the higher crystallinities observed in the composites made of non-modified CNC and PBAT, as shown before. Higher

crystallinities increase the rigidity of the material and consequently the elastic modulus.

Thus, in terms of mechanical properties, the best compositions were the ones with non-modified CNC; however, samples made with non-modified CNC were heterogeneous, with large agglomerates of CNC and interfacial voids. On the other hand, samples with modified CNC had slightly lower mechanical properties, but were homogenous without formation of large CNC agglomerates. Thus, the CNC chemical modification allowed a better dispersion of the CNC throughout the PBAT matrix, allowing the production of more homogeneous samples, with better mechanical properties than the pure PBAT.

Water Vapor Permeability. The addition of CNC reduced the water vapor permeability (P_{wv}) of the PBAT films, as shown in Table III. A similar behavior was observed by Paralikar *et al.*,²⁷ that attributed this result to the physical barrier provided by the nanocrystals, which created a tortuous path for the permeating moisture as already observed in other nanocomposites.^{28,29} The reduction of water vapor permeability was higher for the chemically treated CNC, which led to a reduction of

**Figure 7.** Photographs of samples during the evolution of the bio-fragmentation test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

approximately 63%, probably due to a better CNC dispersion and distribution in the matrix and a better polymer-CNC interaction.

The only exception was the composite with 10 wt % of non-treated CNC (10CNC), which had poor permeability compared with the permeability of the pure PBAT. This result was probably due to the presence of voids in the CNC-PBAT interface of this particular composite, as commented before. These voids induced a drastic decrease in the barrier properties of the film.

Bio-Fragmentation Evaluation. The test of bio-fragmentation (or disintegration of samples under defined composting conditions) was monitored during six months with samples of pure PBAT and nanocomposites of PBAT with 5 wt % of modified and non-modified CNC (5CNCpb and 5CNC, respectively). The samples were unearthed from time to time and weighed. Photographs of the samples at the beginning, after 30, 60, 90, 120, 150, and 180 days of testing are shown in Figure 7, and the weights measured during this period are displayed in Table III.

The PBAT degradation was probably initiated by hydrolysis,³⁰ due to the humidity contained in the organic compound (around 50%) where the samples were buried. The hydrolysis reduces the size of the polymeric chains until they become digestible by microorganisms, thus initiating their biodegradation.

It is possible to observe from the results of Table III that there was no significant difference between the weight losses of all the samples during the first 90 days of the test, considering the standard deviation of 0.40. This was probably the time necessary for the degradation by hydrolysis of the superficial layer of PBAT to occur; this layer covers all the films, and therefore, no significant difference between the kinetics of degradation of all the samples was observed. After the fourth month of the test, however, the internal parts of the samples were more exposed to water penetration and to the attack of microorganisms; thus, a higher weight loss in the nanocomposite with non-modified CNC was observed, which begun to show a rough surface and a visually deteriorated aspect, besides a color change (Figure 7). A high crystallinity degree should decrease cellulose exposition to water penetration and to the attack of microorganisms; however, the higher crystallinity of the 5CNC composite (24.4%) in comparison with the pure PBAT (17.3%) was not enough to hinder cellulose exposition to water and/or microorganisms. It is worthwhile to recall that there are another aspects governing the biodegradation kinetics, besides crystallinity, as the biodegradability of the components (CNC is more biodegradable than PBAT), the existence of interfacial voids between CNC and PBAT in composites, the compatibility between them, and also the CNC dispersion, distribution, and content. After 90 days, the other factors mentioned were predominant to the higher weight loss of this sample.

The chemical grafting decreased the nanocrystals hydrophilic character, as showed in our previous work,¹⁴ and induced their compatibilization with the PBAT matrix, forming a better inter-

face. These factors resulted in a weight loss of the 5CNCpb composite substantially smaller than the one observed in the unmodified 5CNC composite after the fourth month of testing and slightly similar to the pure PBAT; that is, the incorporation of 5 wt % of modified CNC into the PBAT matrix did not affect its biodegradation rate.

Cellulose is naturally biodegradable, as confirmed by the complete disappearance after 30 days of the microcrystalline cellulose used as a control sample. This confirmed that the soil conditions used were suitable for biodegradation.

According to the EN13432 and ASTM D6400 standard procedures, a biodegradable material must lose at least 90% of its mass during three months of test under controlled composting conditions. Nonetheless, the biodegradability rate of a material is strongly dependent³¹ on the environment conditions (temperature, humidity, quantity of microorganisms, presence of oxygen, etc.) and on the material shape and size (surface area, roughness, etc.). Thus, the bio-fragmentation test had the objective of evaluating the impact of unmodified and modified CNC addition in the PBAT biodegradability and the results obtained must be analyzed in a qualitative and comparative way.

CONCLUSIONS

In the present work, cellulose nanocrystals (CNC) were successfully obtained from microcrystalline cellulose and were chemically modified with phenylbutyl isocyanate. Composites made of modified and non-modified CNC and PBAT matrix were prepared by melt extrusion. The addition of non-modified and modified CNC increased the elastic modulus of PBAT by approximately 55%. The chemical modification of CNC with phenylbutyl isocyanate increased their thermal stability by 20 °C, thus enlarging the possibilities of processing and applications. Moreover, the addition of CNC decreased considerably the water vapor permeability of PBAT and this decrease was higher in the modified CNC-based composites (up to 63%). In addition, the CNC incorporation did not compromise the PBAT biodegradation, even after their chemical modification.

In this work, it was possible, therefore, to prepare polymeric composites reinforced by CNC with enhanced properties using melt extrusion, a process widely used in the plastics industry. The improved elastic modulus, thermal stability, and water vapor permeability extend the possibilities of PBAT application.

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REFERENCES

1. PlasticsEurope—Association of Plastics Manufacturers; EPRO—European Association of Plastics Recycling & Recovery Organisations, Plastics—The facts: An analysis of European Plastics Productions, Demand and Waste Data; http://www.plasticseurope.org/documents/document/20150227150049-final_plastics_the_facts_2014_2015_260215.pdf (Accessed September 10, 2015).
2. American Plastics Council, Understanding Plastic Film: Its uses, Benefits and Waste Management Options; <https://plastics.americanchemistry.com/understanding-plastic-film> (Accessed September 10, 2015).
3. Sha, A. A.; Hasan, F.; Hameed, A.; Ahmed, S. *Biotechnol. Adv.* **2008**, *26*, 246.
4. Habibi, Y.; Lucia, L. A.; Rojas, O. J. *Chem. Rev.* **2010**, *110*, 3479.
5. Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J. *Chem. Soc. Rev.* **2011**, *40*, 3941.
6. Liu, D. Y.; Yuan, X. W.; Bhattacharyya, D.; Easteal, A. J. *XPress Polym. Lett.* **2010**, *4*, 26.
7. Habibi, Y.; Goffin, A. L.; Schiltz, N.; Duquesne, E.; Dubois, P.; Dufresne, A. *J. Mater. Chem.* **2008**, *18*, 5002.
8. Sanchez-Garcia, M. D.; Lagaron, J. M. *Cellulose* **2010**, *17*, 987.
9. Fortunati, E.; Peltzer, M.; Armentano, I.; Torre, L.; Jiménez, A.; Kenny, J. M. *Carbohydr. Polym.* **2012**, *90*, 948.
10. Oksman, K.; Mathew, A. P.; Sain, M. *Plast. Rubber Compos.* **2009**, *38*, 396.
11. Bondeson, D.; Oksman, K. *Compos. A* **2007**, *38*, 2486.
12. Goffin, A. N.; Raquez, J. M.; Duquesne, E.; Siqueira, G.; Habibi, Y.; Dufresne, A.; Dubois, P. *Biomacromolecules* **2011**, *12*, 2456.
13. Fortunati, E.; Armentano, I.; Zhou, Q.; Iannoni, A.; Saino, E.; Visai, L.; Berglund, L. A.; Kenny, J. M. *Carbohydr. Polym.* **2012**, *87*, 1596.
14. Morelli, C. L.; Belgacem, M. N.; Branciforti, M. C.; Bretas, R. E. S.; Crisci, A.; Bras, J. *Compos. A* **2015**, *83*, 80.
15. Jiang, L.; Morelius, E.; Zhang, J.; Wolcott, M. *J. Compos. Mater.* **2008**, *42*, 2629.
16. Bondeson, D.; Mathew, A.; Oksman, K. *Cellulose* **2006**, *13*, 171.
17. Chivrac, F.; Kadlecova, Z.; Pollet, E.; Averous, L. *J. Polym. Env.* **2006**, *14*, 393.
18. Herrera, R.; Franco, L.; Rodriguez-Galán, A.; Puiggali, J. *J. Polym. Sci. A: Polym. Chem.* **2002**, *40*, 4141.
19. Perry, R. H.; Green, D. *Perry's Chemical Engineer's Handbook*; McGraw-Hill: New York, **1997**.
20. Kvien, I.; Tanem, B. S.; Oksman, K. *Biomacromolecules* **2005**, *6*, 3160.
21. Menezes, A. J.; Siqueira, G.; Curvelo, A. A. S.; Dufresne, A. *Polymer* **2009**, *50*, 4552.
22. Siqueira, G.; Bras, J.; Dufresne, A. *Biomacromolecules* **2009**, *10*, 425.
23. Dufresne, A. *Nano-Cellulose: From Nature to High Performance Tailored Materials*. Walter de Gruyter GmbH: Berlin/Boston, **2012**.
24. Favaro, M. M.; Rego, B. T.; Branciforti, M. C.; Bretas, R. E. S. *J. Polym. Sci. B: Polym. Phys.* **2010**, *48*, 113.
25. Rego, B. T.; Ribeiro Neto, W. A.; de Paula, A. C. C.; Goes, A. M.; Bretas, R. E. S. *J. Appl. Polym. Sci.* **2015**, *132*, DOI: 10.1002/app.41748.
26. Roohani, M.; Habibi, Y.; Belgacem, N. M.; Ebrahim, G.; Karimi, A. N.; Dufresne, A. *Eur. Polym. J.* **2008**, *44*, 2489.
27. Paralikar, S. A.; Simonsen, J.; Lombardi, J. *J. Membr. Sci.* **2008**, *320*, 248.
28. Lotti, C.; Isaac, C. S.; Branciforti, M. C.; Alves, R. M. V.; Liberman, S.; Bretas, R. E. S. *Eur. Polym. J.* **2008**, *44*, 1346.
29. Beatrice, C. A. G.; Branciforti, M. C.; Alves, R. M. V.; Bretas, R. E. S. *J. Appl. Polym. Sci.* **2010**, *116*, 3581.
30. De Paoli, M. A. *Degradação e Estabilização de Polímeros*, Editora Artliber: Brazil, **2009**.
31. Domb, A. J.; Kost, J.; Wiseman, D. *Handbook of Biodegradable Polymer*; CRC press: **1997**.