

# Nanocellulose: Effect on Thermal, Structural, Molecular Mobility and Rheological Characteristics of Poly(Butylenes Adipate-Co-Butylene Terephthalate) Nanocomposites

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# Abstract

The concern with environmental preservation is a very current and relevant topic. Regarding polymers, the search for potentially ecofriendly matters has been the subject of scientific research. In this context, this work aimed to study the effect of adding nanocellulose (nCE) with 1, 3, and 5 wt.% on poly(butylene adipate-co-butylene terephthalate) (PBAT). Thermal, structural, relaxometric, and rheological assessments were carried out. Quantitative evaluation of PBAT copolymer by high field NMR revealed 56.4 and 43.6 m.% of the butylene adipate and butylene terephthalate segments, respectively. WAXD measurement on the deconvoluted diffraction patterns identified that nCE was a mixing of Cellulose I and Cellulose II polymorph structures. At any composition, nanocellulose interfered with the PBAT crystallisation process. Also, a series of new PBAT crystallographic planes appeared as a function of nanocellulose content. PBAT hydrogen molecular relaxation varied randomly with nanocellulose content and had a strong effect on the hydrogen relaxation. PBAT cold crystallisation and melting temperatures (T<sub>cc</sub> and  $T_m$ ) were almost unchangeable. Although  $T_{cc}$  did not change during polymer solidification from PBAT molten state, the sample's degree of crystallinity varied with composition through the transcrystallization phenomenon. Nanocomposite thermal stability decreased possibly owing to the catalytic action of sulfonated amorphous cellulose chains. For the sample with 3 wt.% of nanocellulose, the highest values of complex viscosity and storage modulus were achieved.

## **Keywords**

Nanocellulose, Poly(Butylene Adipate-Co-Butylene Terephthalate), Molecular Relaxation, Nanocomposite

# **1. Introduction**

Although efforts have been made to mitigate the effects of undue disposal of fossil-based pos-consumption plastics in the environment, recycling and the application of a circular economy in the field of plastics are still below expectations. The advent of nanotechnology brought insights into how to extract better material properties. In contrast to micrometric polymer composites in which high amounts of fillers were needed to achieve better properties, nanocomposites are composed of nanometric fillers with high surface area and reduced quantities and cost to achieve better performance. Inorganic and organic nanometric fillers have been incorporated into polymers in the search for the economy and upper properties. It is important to contextualise some aspects of the lignocellulosic matters regarding the botanical source, constitution, morphology, and yielding routes of nanocellulose. The main sources of lignocellulosic fibres are vegetables. Cellulose fibres are widespread around the world. They are natural composites in which cellulose fibres are the reinforcing element. Hemicellulose combines branched, amorphous polysaccharides with five and six-carbon sugar bonded to cellulose fibre through hydrogen bonds. Cellulose fibres and hemicellulose provided structural rigidity. Lignin is a branched, highly hygroscopic and complex polyphenols structure with functions of binding and barrier to microbial attacks [1]. The percentage of each component depends on the natural source. Sequential chemical and mechanical protocols are required to attain nanocellulose. For isolating the nanocellulose, acid hydrolysis must be carried out to remove the interspersed amorphous region from the crystalline domain. Commonly, hydrolysis is conducted by sulfuric acid and esterification reaction between cellulose hydroxyl and sulfate groups fashioning sulfonated ester groups  $(-OSO_3)$ . This procedure implicates lower nanocrystal thermal stability since sulfur catalyses the cellulose depolymerisation. Crystallinity degree is dependent on the vegetal sources, alkaline treatment, kind of acid for hydrolysis, and mainly the hydrolysis time. Therefore, there is no standard for nanocellulose, being each one with unique characteristics [1] [2] [3]. Recycled or not, lignocellulosic matters have been embedded as filler into polyolefins to produce a wood plastic composite. Decks, railings, fences, landscaping timbers, cladding, siding, park benches, frames, and furniture are examples of utensils for application indoor and outdoor. Since 2012, the industrial production of nanocellulose from chemically treated cellulose pulp has been rising. Features such as sustainable, surface active, and temperature resistant allow application in areas of drilling fluid, adhesives, paints, plastics, rubbers, etc. Delepierre et al. characterised five samples of cellulose nanocrystals from different suppliers. Significant differences were pointed out concerning the rheological, thermal stability, and self-assembly behaviour [4]. Ng et al. reported a review on the production of cellulose nanocrystals from empty fruit bunches. Aspects of the CNC properties related to the raw material pretreatment, isolation and post-treatment were highlighted [5]. Also, a review was published by Heise et al. comprised chemically modified cellulose nanocrystal end-groups. The authors stated that this modification applied to directed assembly provides huge possibilities for attaining new materials [6]. Bajwa et al. investigated the action of hybrid filler based on cellulose nanocrystal (CNC) and zinc oxide (ZnO) to improve mechanical, thermal, and flame resistance properties of melt-blending extrusion poly(lactic acid) (PLA) nanocomposites. The authors pointed out the increase in the mechanical, thermal, and flame retardancy properties [7]. Leite et al. studied the gelatin films incorporated with CNC. The control of pH and film-forming drying temperature on the properties was experienced. The properties were modulated as a function of CNC content, pH, and drying temperature showing prospective for packaging usage [8]. Antifungal and biodegradability characteristics were investigated in casting films of nanocomposite built from poly(vinyl alcohol) (PVA), chitosan nanoparticles, and CNC (from the byproduct of the mango industry). The inhibition against *C*. gloeosporioides was 70% while for dry soil, 88% of biodegradation was recorded [9]. Bionanocomposites based on polypropylene containing unbleached (with a high amount of lignin) and bleached cellulose nanocrystals (CNC), kenaf core and maleic anhydride grafted polypropylene were studied. The sample comprised of the CNC-containing high residual lignin showed better thermal and flammability properties, with the lignin action as compatibiliser [10]. Academia and industry are looking for alternative materials based on natural or synthetic polymers with biodegradable characteristics. In the plastic market for over two decades and produced from fossil starting matters—terephthalic acid, adipic acid and butylene glycol, poly(butylene adipate-co-butylene terephthalate) (PBAT) is a copolymer that meets the standards applied for a biodegradable polymer. Whether lonely, in polymeric composites, or blended with other polymers, there are many articles to render better its thermal, mechanical, flexibility, and decrease costs. Aiming to reduce costs, Bai et al. investigated the effect of thermoplastic starch on the PBAT matrix. Composite PBAT/TPS (60/40 wt/wt.%) was prepared by two-step extrusion in the presence of reactive epoxy compatibiliser (REC). The authors registered improvement in polymer interfacial region, no phase separation, formation of bicontinuous phase structure, and magnificent mechanical properties at high TPS content [11]. Qiao et al. proposed a study on the rejected plastic from agricultural films. They suggested the crystallinity control for adjusting the period of degradation of PBAT by adding polyethyleneimine (PEI) as a nucleating agent. They concluded that alteration of the degree of degradation was a function of the crystallinity degree [12]. For packaging, Bumbudsanpharoke et al. investigated blown-extruded films of binary blends of PBAT with linear low-density polyethylene (LLDPE) and poly(butylene succinate) (PBS). All systems presented immiscibility. PBAT/PBS blend showed good interface adhesion and diverse miscibility, molecular mobility, permeability, and shelf-life with composition [13]. In the search for better properties, Zhou et al. incorporated two phosphorous-containing ionic liquids in melting blends of PBAT and poly(lactic acid) (PLA). Due to the interaction among ionic liquids and polymers, the toughness, flame retardancy, and processability showed improvement [14]. Yap et al. developed a composite based on a blend of PBAT and PBS filled with rice rusk. A high level of biodegradability (92%), good mechanical properties, and competitive pricing were achieved [15]. As compatibiliser, glycidyl methacrylate-grafted poly(ethylene octene) (GPOE) was incorporated into PBAT/PLA blends. Blown-extruded films revealed that at a fixed amount of the GPOE, the molecular mobility, nucleation density, and size of spherulite, crystalline and thermal characteristics, water vapour barrier, and compatibility were influenced [16]. Rheological, crystallisation, morphological, thermomechanical, and mechanical characteristics were assessed in PLA/PBAT (75/25) blends filled with 1 - 5 wt.% cellulose nanocrystal (CNC). Composites by solution casting (SC) and twin-screw extruder (TSE) films were prepared. Divergent results were noticed according to SC or TSE preparation. SC film with 3 wt.% of CNC showed an increase in complex viscosity and storage modulus due to the formation of CNC network in PLA matrix but mechanical was not improved. About TSE films, better affinity was registered between PBAT/CNC. With 3 wt.% of CNC, the PBAT dispersed phase broken up enhanced PLA matrix viscosity. Neither improvement was found for rheological and thermal properties [17]. Mukherjee et al. incorporated 0.2 - 1 wt.% of nanofibrillated cellulose (NFC) to reinforce bionanocomposites based on PBAT. An increase in storage modulus, dynamic viscosity and crystallinity was achieved [18]. Hosseinnezhad studied the action of different shear rates on the crystallisation of biodegradable nanocomposites of poly(butylene adipate-co-succinate-co-glutarate-co-terephthalate) poly(butylene adipate-co-terephthalate) (PBAT) filled with cellulose nanofiber [19]. The authors reported induced nucleation upon shearing coexisting with quicker crystallisation, higher density nucleation sites, and thinner lamella stacks. PBAT, maleic anhydride grafted PBAT (mPBAT), and byproducts of the bast-hemp fibre production process, hemp powder, HP, were extruded to produce biocomposites. Meaningful improvement in tensile strength, toughness, impact resistance, and heat deflection temperature were detected [20]. At proportions comprising 25 - 75 wt.%, compression-moulded films of PBAT and PBS blends were studied. The authors pointed out that the stiffness raised as a function of PBS percentage but elongation at break and gas permeability lowered [21]. Lignocellulose fillers with different lignin content were incorporated into PBAT to build composites for replacing conventional fossil-based polymers. Filler's roughness notably affected the thermal properties, but filler's surface and

granulometry distribution influenced mechanical properties [22]. Li *et al.* studied the effect of low content of physical and chemical modification of the halloysite surface on PBAT crystallisation. Overall, the neat halloysite or modified ones provided heterogeneous nucleation, a decrease in spherulite dimension, and a lowering of the crystal growth rate [23]. PBAT/thermoplastic starch (TPS)/lignin ternary composites were investigated. The lignin provided compatibilization, higher thermal stability, reduced crystallisation temperature, and increased glass transition temperature. Additionally, reinforcement was imputed to lignin owing to the increase of elastic modulus, hardness, and yielding behaviour [24].

This work intended to investigate the action of adding cellulose nanocrystal (1, 3, and 5 wt.%) to biodegradable poly(butylene adipate-co-butylene terephthalate) (PBAT). Thermal, structural, relaxometric, and rheological were evaluated. Additionally, the effect of thermal rate on the samples' calorimetric and thermogravimetric behaviour was also assessed.

# 2. Experimental

# 2.1. Material

Poly(butylene adipate-co-butylene terephthalate)—PBAT, Basf, Ecoflex, F-Blend C1200 (Mw = 53,900 g/mol, Mw/Mn = 1.7, d = 1.25 - 1.27 g/cm<sup>3</sup>, MFR = 2.7 - 4.9 g/10 min<sup>-1</sup>, Tm = 110°C - 120°C) (de Matos Costa *et al.* 2020) was supplied by OEKO Bioplásticos, Brazil. Nanocellulose was purchase from Celluforce NCC Windsor, Quebec, Canada. Herein, it was named as nCE.

## 2.2. PBAT/Nanocellulose Masterbatch

To enable the homogenisation of the nCE in the PBAT matrix, a masterbatch of PBAT containing 20 wt./wt.% was prepared in a single-screw extruder with three heating zones 140°C, 150°C and 160°C, at 60 rpm. After that, the material was pelletised and mixed with the starting polymer.

## 2.3. PBAT/Nanocellulose Nanocomposites

Nanocomposites based on PBAT filled with nCE were prepared with different proportions (99:1, 97:3 and 95:5). The masterbatch was added to attain the final amount of nCE for each composition. For comparative purposes, the precursor PBAT was processed without nCE. Melt extrusion was performed in a single-screw extruder at 140°C, 150°C and 160°C, at 60 rpm, and the extruded film was achieved. **Figure 1** shows a schematic representation of the experimental procedure for the nanocomposite preparation. The sample designation is summarized in **Table 1**.

#### 2.3.1. Nuclear Magnetic Resonance (NMR)

High and low field NMR technique was accomplished. The first one was performed to evaluate the PBAT chemical composition. The low one monitored the PBAT and nanocomposite's molecular mobility.



Figure 1. Schematic representation of nanocomposite preparation.

nCE wt.%
-
1
3
4

 Table 1. Sample designation.

#### • Hydrogen nuclear magnetic resonance (<sup>1</sup>HNMR)

PBAT copolymer constitution was carried by <sup>1</sup>HNMR technique in the Varian/Agilent model Mercury VX300. About 60 mg was dissolved in 0.8 ml CDCl3 with 20 transient numbers, time puls 10 seconds, spectral windows 0f 5000 Hz. The content of aliphatic and aromatic portions was determined.

#### • Hydrogen nuclear magnetic resonance in the time domain (<sup>1</sup>HNMRTD)

<sup>1</sup>HNMRTD was performed in a MARAN Ultra spectrometer with an electromagnet operating at 0.54 T (Larmor frequency corresponding to 23.4 MHz for the proton), probe with an internal diameter of 18 mm, at 27°C. The 90° excitation pulse was automatically calibrated to 7.5  $\mu$ s. The longitudinal (T1) relaxation time was fitted by inversion-recovery (IR). Inversion-recovery (T1) was accomplished in the time intervals, considering forty points spaced logarithmically at a range of 0.1 to 5000 ms, with a recycle interval of 3 s and 8 accumulations [25].

## 2.3.2. X-Ray Fluorescence Spectroscopy (EDX)

The elemental evaluation was performed by fluorescence in Shimadzu equipment, model EDX-720. The analysis was conducted in powder, free of water and under vacuum, for 320 seconds. The data were expressed in terms of oxides.

#### 2.3.3. Wide Angle X-Ray Diffraction (WAXD)

In Rigaku equipment, model Miniflex using CuK $\alpha$  radiation, wavelength 1.5418 Å, Ni filter, voltage 20 kV, current 20 mA, 2 $\theta$  between 2-700, at an interval of 0.05°, the WAXD analysis was performed. The diffraction pattern was considered.

## 2.3.4. Differential Scanning Calorimetry (DSC)

DSC was conducted in TA equipment model Q1000, at nitrogen atmosphere, according to the ASTM D3418 [26]. Five thermal cycles at three different thermal rates (5, 7.5 and  $10^{\circ}$ C·min<sup>-1</sup>) were performed. For each thermal rate, the experimental procedure was performed as described forward. In the first cycle, the sample was heated between  $-40^{\circ}$ C to  $160^{\circ}$ C, under a nitrogen atmosphere, remaining at about 1 minute to eliminate the thermal history. Next, a cooling cycle considering the equipment's maximum rate was applied. A second heating cycle was performed similarly to the first one. A second cooling cycle with a controlled thermal rate was carried out. Finally, a third heating cycle was conducted

like the first one. Glass transition temperature  $(T_g)$  was registered in the second thermal cycle. Melting crystalline temperature  $(T_m)$  was taken from the third heating cycle. The cooling crystallisation temperature  $(T_{cc})$  was captured from the second cooling cycle. The degree of crystallinity  $(X_c)$  was calculated considering the third heating cycle through the ratio between the enthalpy of fusion  $(\Delta H_m)$  of the sample and the enthalpy of fusion  $(\Delta H_m)^\circ$  of 100% crystalline PBAT (114 J/g) as described in Equation (1) where  $\Phi$  is the filler weight fraction in the nanocomposites [18] [27] [28].

$$X_c = \frac{\Delta H_m}{(1-\phi)\Delta H_m^0} \times 100 \tag{1}$$

#### 2.3.5. Thermogravimetry (TGA)

Thermogravimetry was performed in TA Instruments model Q500, between  $30^{\circ}$ C -  $700^{\circ}$ C, at 5, 7.5 and  $10^{\circ}$ C·min<sup>-1</sup> and with nitrogen as the carrying gas. Tonset (initial degradation temperature), Tmax (maximum degradation speed temperature), and mass loss were determined.

#### 2.3.6. Rheology

The rheological evaluation was carried out in a TA rheometer, model AR-2000, fitted with a geometry of parallel plates, 25 mm in diameter, at 250°C, in an inert atmosphere, both in continuous shear and in an oscillatory (or dynamic) regime. The variation of storage modulus *versus* deformation was performed at a frequency of 1 Hz to determine the linear viscoelasticity region. The storage modulus, loss modulus and complex viscosity as a function of frequency were monitored.

#### 3. Results and Discussion

## 3.1. High Field Hydrogen Nuclear Magnetic Resonance (<sup>1</sup>HNMR)

This technique was experienced to assess the chemical constitution. As known, the PBAT is a kind of random copolymer constituted by aliphatic and aromatic moieties. **Figure 2** shows the <sup>1</sup>HNMR spectrum. The chemical shifts of each moiety were identified following the peak areas calculation. The relationship of each fraction with the sum of the fractions enabled us to attain the fractions's percentage. The PBAT consists of 56.4% butylene adipic (BA) and 43.6 m.% butylene terephthalic (BT) segments.

## 3.2. X-Ray Fluorescence Spectroscopy (EDX)

X-ray fluorescence showed the elemental composition of nanocellulose expressed in terms of oxides. The major components were sulfur trioxide (SO<sub>3</sub>, 79%) and sodium oxide (Na<sub>2</sub>O, 18%). Phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>), calcium oxide (CaO), iron trioxide (Fe<sub>2</sub>O<sub>3</sub>) and potassium oxide (K<sub>2</sub>O) were in an amount lesser than 1%. The presence of sulfur came from the process of nanocellulose yielding due to the sulfuric acid as a hydrolysis agent to remove the amorphous cellulose portion as reported by Mandal and Chakrabarty [29].



Figure 2. Hydrogen nuclear magnetic resonance spectrum of PBAT.

#### 3.3. Wide Angle X-Rays Diffraction (WAXD)

Figure 3 depicts the deconvoluted X-ray diffraction patterns of the PBAT, nanocellulose and nanocomposites. Table 2 displays the deconvoluted diffraction angles. Deconvoluted X-ray diffraction of nanocellulose depicted a broadened and low intense diffraction peak centred around 16.0°, a lesser intense diffraction peak at 21° and a higher intense one at 23.0°. Tenrite et al. published an article on the comparison between measurement techniques of native and microcrystalline cellulose. They reported that a maximum intensity peak centred between 22° - 24° represented the crystalline plane with the Miller indices 200 while the diffraction angle around 18° was the non-crystalline contribution [30]. Gong et al. studied the impact of cellulose polymorphs on the characteristics of cellulose nanocrystals. For Cellulose I, the X-ray analysis revealed  $2\theta$  angles at 14.5 (110), 16.5 (1 - 10) and 22.5 (200) [31]. In their work on the yielding of nanocellulose from Imperata brasiliensis grass, Beninia et al. reported the appearance of two diffraction peaks at 16° and 22°. The lower one denoted the overlapping of (1 - 10) and (110) crystalline planes characteristic of semicrystalline material, such as lignocellulose fibres. The one at a higher angle was correlated to the (200) plane, representing the crystalline cellulose polymorphism I $\beta$  [32].



Figure 3. WAXD deconvoluted diffractograms of nanocellulose, PBAT and nanocomposites.

Sample	$2\theta$ diffraction angle									
nCE		16	21	23						
PBAT	12.3	18	21	22	23.5	24.4	25			
PBAT-nCE1	17.3	17.9	20.6	21.6	23.5		25			
PBAT-nCE3	16.2	17.5	20.5	20.6	23.2	24.8				
PBAT-nCE5	10.1	12.3	16.3	17.7	20.6	21.1	23.3	24	24.9	27.3

**Table 2.**  $2\theta$  diffraction angles from deconvoluted diffractograms.

From ten types of natural fibres, Poletto et al. studied the cellulose crystalline arrangement after extraction of the lignocellulosic portion and its implication on the physical properties [33]. Deconvoluted diffraction pattern showed  $2\theta$  reflection in the range of 14.5° - 15.3° (crystalline plane 1 - 10), 15.7° - 16.3° (crystalline plane 110), 18.3° - 18.4° (amorphous plane) and 21.9° - 22.2° (crystalline plane 200). Herein, the nanocellulose presented three diffraction peaks. The results indicated the mixing of polymorph structures. We attributed the first one to the amorphous plane of Cellulose I. The intermediate one was associated with the crystalline plane of Cellulose II [34]. The last one was attributed to the crystalline plane of Cellulose I. The calculated degree of crystallinity was 73.3% quite higher and quite lower than cellulose nanofiber (63%) and cellulose nanocrystal (85%), respectively, as reported by Ouna et al. [3] in their article on multifunctional nanocellulose-based hybrid nanomaterials. We agreed that the presence of polymorph structures is related to the cellulose source and the nanocellulose yielding process. The deconvoluted PBAT diffraction pattern presented six peaks. The enlarged and low intense peak at 12.3° was attributed to an amorphous fraction. The diffraction angles at 18, 21, 23.5, 24.4 and 25 designated as representative of PBAT crystalline planes showed variable width and intensity. The more significant was centred at 25°. Ordinarily, the current works reported PBAT  $2\theta$  reflections at 16.1°, 17.3°, 20.2°, 23.1° and 25.0° correlated to the crystallographic planes (0 - 11), (010), (-111), (100) and (1 - 11), respectively [12] [13] [14] [23] [35]. We credited this variation solely or jointly to the factors such as different manufacturers and grades, little technical information on copolymer composition, melt flow rate, density, and processing conditions (temperature window, residence time, screw rotation and others). The incorporation of nanocellulose brought changes in the crystalline arrangement of PBAT. The alterations were random concerning the nanocellulose content. The nanocomposite with 1 wt.% of nCE exhibited five diffraction peaks. That one around 17.3° arose from the combination of the amorphous portion of the cellulose and PBAT. The diffraction peaks at 17.9° represented the PBAT crystalline plane while at 20.6° expressed the PBAT and Cellulose II crystalline planes. The  $2\theta = 23.5^{\circ}$  was enlarged and understood as the manifestation of PBAT and Cellulose I crystalline arrangement. The last one at 25° was attributed to PBAT crystalline ordering. It must be emphasized that the PBAT crystalline plane at 24.4° disappeared. Also,

the nanocomposite embedded with 3 wt.% of nCE showed five diffraction peaks. The lowest one at 16.2° was associated with that observed at 17.3° in the sample with 1 wt.% of nCE. We understood that the displacement to a lower angle was owing to the increase of amorphous cellulose matter. Also, a narrowing peak baseline was noticed and interpreted as being likely some action of cellulose chain on the PBAT crystallisation process. The other diffraction peaks at 17.5°, 20.5°, 23.2° and 24.8° received the same attributions as those of the sample with 1 wt.% of nCE. Multiple diffraction peaks appeared at 10.1°, 12.3°, 16.3°, 17.7°, 20.6°, 23.3°, 24.0°, 24.9° and 27.3° when 5 wt.% of nCE was added.

To the diffraction peaks at 16.3°, 17.7°, 20.6°, 23.3°, 24.9°, the same imputations implemented for the sample with 1 wt.% of nCE were considered. Slim and broadened diffraction peaks appeared at 10.1 and 12.3, respectively. The first could probably be attributed to a new PBAT crystalline plane, while the second represented an amorphous plane that arose from the contribution of cellulose and PBAT amorphous matter. Surprisingly, the PBAT crystalline plane around 24° resurged. Also, a new crystallographic plane around 27.3° emerged. In summarising, the deconvolution of the WAXD curves brought insight into the effect of nanocellulose on the PBAT crystallisation process. Regardless of nanocellulose content, in all nanocomposites, meaningful changes in PBAT  $2\theta$  reflection peaks were noticed. Some PBAT diffraction planes were maintained, but, to some extent, nanocellulose regulated the PBAT crystallisation process. It could be hypothesised that likely transcrystallisation of PBAT on nanocellulose surface occurred leading to alterations of PBAT crystallisation process. The nanocellulose crystalline matter showed intervention on the PBAT crystalline arrangement. Nanocellulose amorphous portion aggregated to low molar mass and/or amorphous portion of PBAT could be associated with the appearing of new diffraction planes. Finally, it must be emphasised that PBAT/nCE constituted a multiphase system.

# 3.4. Hydrogen Nuclear Magnetic Resonance with the Time Domain (<sup>1</sup>HNMRTD)

Molecular relaxation by nuclear magnetic resonance describes the evolution of magnetisation in two distinct directions. It emerges from magnetic field fluctuations caused by modulation of the magnetic dipole-dipole interaction or other magnetic interactions. The longitudinal relaxation of a nucleus, also called spin-net relaxation, with a time constant called T1 is associated with the recovery (return) of magnetisation to the ground state (equilibrium) after a radiofrequency pulse. The longitudinal relaxation time (T1) describes faster material movements in which its magnetisation occurs parallel to the external magnetic field, with frequencies in the order upper 10 MHz. Figure 4 shows the longitudinal relaxation domain curves of PBAT and nanocomposites. Table 3 records data on longitudinal relaxation analysis. PBAT domain curve showed two relaxation intervals. The first one between 6 - 20 ms likely comprised the hydrogen



Figure 4. Longitudinal relaxation domain curves: PBAT (-----), PBAT-nCE1 (-----), PBAT-nCE3 (------), PBAT-nCE5 (------).

Table 3. Longitudinal	relaxation ti	ne of PBAT and	I nanocomposites.
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Sample	T1H (ms)	Area (u²)	Peak (starting/finishing) (ms)
PBAT	9/58	467/41,933	20/(90 - 100)
PBAT-nCE1	56	40,830	30/115
PBAT-nCE3	59	56,007	30/146
PBAT-nCE5	58	28,447	40/(90 - 100)

molecular relaxation of PBAT amorphous matter. The second one occurred at 20-(90-100) ms and encompassed the hydrogen molecular relaxation of the PBAT crystalline structures. For all nanocomposites, the lowest PBAT relaxation peak disappeared. The highest relaxation peak was shifted along the time axis; the peak started at higher times, but the finishing varied randomly. Some domain curves exhibited enlargement or narrowing with nCE content. The domain curve of the sample with 1 wt.% of nCE showed little or no disturbance concerning the presence of nanocellulose. As the lowest relaxation domain vanished, we understood that the mixing of PBAT low molar mass and the amorphous portion of nanocellulose happened to lead to a homogeneous system. With 3 wt.%, the domain curve depicted the strongest disturbance. The peak relaxation was shifted to a higher value and enlarged. We believe that peak enlargement could be attributed to the contribution of the hydrogen molecular mobility comprising a cluster of amorphous cellulose portions and PBAT amorphous chains plus and hydrogen motion in the crystalline cellulose and PBAT crystalline structures. None of the domains has a predominance over sample mobility. For the sample with 5 wt.%, the peak started at 40 ms, but the peak finishing remained as the neat PBAT. Also, the baseline of the domain curve was sharply reduced. We could speculate that the narrowing likely indicated some difficulty in the PBAT hydrogen relaxation. As seen in the WAXD section, the action of nanocellulose surface as a probable nucleating agent of the PBAT chains crystallisation was hypothesised. Thus, the mobility of PBAT hydrogen was linked to the hydrogen mobility into the nanocellulose crystalline structure. In the latter, the hydrogens had more restricted mobility and appeared dominant in the sample molecular relaxation. The results showed a relevant effect of the nanocellulose structure on the PBAT chain's molecular relaxation. This effect was random with respect to the nCE content and could be understood as a kind of reinforcement owing to the rigidity of the crystalline nanocellulose structure.

# 3.5. Differential Scanning Calorimetry (DSC)

Figure 5 shows the DSC curves at different thermal rates. Table 4 displays the calorimetric data. At the first heating cycle, all calorimetric curves exhibited two broad endothermic peaks. The first peak was located around 40°C - 60°C, and the second one was near 90°C - 140°C. A single melting peak was noticed in the second and third scan heating (90°C - 140°C). For the second cooling cycle, a unique peak was registered (60°C - 90°C). The tendency of  $T_{co}$  Tm and  $X_c$  versus nCE content are plotted in Figures 6-8, respectively. At any rate, the glass transition temperature ( $T_{e}$ ) remained constant. Li *et al.* investigated the action of thermoplastic starch (TPS) and lignin (LG) in PBAT matrix. Mixing of TPS/LG shifted the  $T_g$  of PBAT to the upper value [24]. PBAT was embedded with treated fibres from wheat straw. The authors registered an increase in  $T_g$  [22]. For application as food packaging, Moustafa et al. filled PBAT matrix with coffee grounds. They detected the  $T_g$  around  $-30^{\circ}$ C, but the sample with 30 wt.% of torrefied matter  $T_g$  increased [36]. For all samples, the cold cooling temperature  $(T_{cc})$  varied according to the thermal rate. The latter and  $T_{cc}$  showed opposite behaviour, meaning that the thermal rate increased while  $T_{cc}$  decreased. Independent of the nCE content and for each thermal rate, the  $T_{cc}$  values were analogous to the PBAT precursor. The crystallisation behaviour of PBAT filled with halloysite-neat, calcinated and organo-modified-was studied by Li et al. [23]. The presence of filler provided a progressive increase in the crystallisation temperature. For the authors, the filler had a role of a heterogeneous nucleating agent during the PBAT crystallisation process. Five and ten percent of layered silicate clays were added to the PBAT matrix. DSC thermal measurement indicated that the filler promoted a slight reduction of the crystallisation temperature. The authors explained that on cooling, the filler could slightly hinder kinetics and the extent of crystallisation of PBAT. Also, provide imperfect crystals with melting temperatures lesser than neat PBAT crystals. They concluded that the phenomena were ascribed to the increase of the molten viscosity by the addition of clay [35]. Generally, Tm revealed a tendency to decrease with the increase of thermal rate. Also, for either thermal rate, Tm practically did not vary with the nCE content. It





**Figure 5.** DSC curves of PBAT and nanocomposites as function of thermal rates: (a) first heating, (b) second heating, (c) second cooling, and (d) third heating.

Sample	Rate	<i>T<sub>g</sub></i> (°C)	<i>T</i> <sub>cc</sub> (°C)	<i>T</i> <sub>m</sub> (°C)	$\Delta H_m$ (J/g)	X <sub>c</sub> (%)
	2.5	-32	93	120	19	16.7
	5	-31	83	123	9.2	8.1
PBAI	10	-31	76	122	12.3	10.8
	2.5	-31	93	126	8	7.1
	5	-31	83	121	16	14.2 (75%)*
PBAT-nCEI	10	-31	76	121	13.6	12.1 (12%)*
	2.5	-30	93	126	8	7.2
	5	-30	84	125	8.7	7.9
PBA1-nCE3	10	-31	75	122	12.3	11.1
	2.5	-30	93	126	10.5	9.7
	5	-30	85	125	9.6	8.9
PDAI-IICE5	10	-31	77	121	12.4	11.5 (6.5%)*

Table 4. Calorimetric properties of the samples at different thermal rates.

\*Increase of the crystallinity degree.



**Figure 6.** Behavior of the  $T_{cc}$  against nCE content at three different thermal rates.

must highlight that for PBAT on the first thermal scan two melting peaks were observed. The first peak was related to the PBAT melting temperature of crystal domains of the aliphatic portion (butylene adipate). In contrast, the second one was associated with the PBAT melting temperature of crystalline segments related to the aromatic portion (butylene terephthalate). At other thermal cycles, only one melting peak was detected. We understood that the aromatic portion is



**Figure 7.** Behavior of the  $T_m$  against nCE content at three different thermal rates.



**Figure 8.** Behavior of the  $X_c$  against nCE content at three different thermal rates.

planar due to the terephthalic units. It stiffened butylene moiety, decreasing the degree of freedom to chain conformation, and its crystallisation was enabled. On the contrary, the aliphatic portion is constituted by a sequence of 10 carbon atoms allowing a higher degree of freedom for chain conformation. This higher

degree of freedom spoils its ability to crystallise. Poly(butylene succinate) (PBS) and PBAT blends were studied. The presence of PBS shifted the PBAT melting peak to a slightly higher value [21].  $X_c$  changed randomly with the thermal rate and nCE content. PBAT had the highest degree of crystallinity at the thermal rate of 2.5°C/min. The values were reduced at the highest thermal rates. In fact, at slower thermal rates, the PBAT chains had more time to access the crystallisation centres raising the  $X_c$ . For the nanocomposite, the behaviour of  $X_c$  was compared to the neat PBAT at each thermal rate. The sample embedded with 1 wt.% of nCE showed a random variation of  $X_c$ . At 2.5°C/min., the  $X_c$  was relatively lesser, while at 5 and 10°C/min were upper. Xc had an increment of 75 and 12%, respectively. As there was no change in the  $T_{cc}$  during the PBAT solidification from the melting, we postulated that  $X_c$  variations could be likely attributed to the transcrystallization phenomenon between PBAT chains onto cellulose-ordered structures. Transcrystallization could be associated with the surface morphology's adhesiveness [37]. Thinking about transcrystallization, Wang et al. studied composites of isotactic polypropylene (iPP) with bacterial cellulose (BC) as a fibre-reinforcing agent. For better compatibilisation, maleic anhydride grafted polypropylene (MAPP) was used. The authors reported that BC fibre provided transcrystallization of iPP, improving the mechanical properties with the additional contribution of MAPP as an interfacial agent [38]. In situ generation of biodegradable copolyester nanocomposites filled with 5, 10 and 20 wt.% of cellulose nanofibers (CNFs) was experienced by Hosseinnezhad. The shear-induced and cellulose-nanofiber nucleated crystallisation were investigated. The author reported that the addition of CNFs did not influence the PBAT crystallinity degree but contributed to the strong increase in the crystallisation temperature [19]. Active packaging films based on nanocomposites of PBAT and cellulose nanofibers (CNS, 5 wt.%) encapsulated with eugenol and linalool were studied. The slight increase in crystallinity degree was imputed to the modified nanocellulose as a nucleating agent [39]. Nanofibrillated cellulose (NFC, 0.2 - 1.0 wt.%) from the regenerated wood fibre was incorporated into the PBAT matrix. Overall, an increase in the crystallinity degree was registered [18]. 2014). For the samples filled with 3 and 5% nCE, the behaviour was similar. Again, at 2.5°C/min., the presence of cellulose prevented the diffusion of the chains to the crystallisation centres, decreasing the  $X_{c}$ . At other thermal rates, the  $X_c$  was almost constant, except at 10°C/min, where the sample embedded with 5 wt.% showed an increase of about 6.5%. In short, the protocol experienced for  $T_g$ ,  $T_{cc}$  and  $T_m$  virtually did not affect them. Any variation noticed on  $X_c$  could be ascribed to the transcrystallization phenomenon enabled owing to the nanocellulose crystalline surface. The result agreed with the NMR and WAXD ones.

#### 3.6. Thermogravimetry (TGA)

TGA analysis was performed at 5 and 10°C/min. For illustrative purposes, Figure 9 shows the mass loss and derivative curves. Table 5 depicts the degradation



Figure 9. TGA mass loss and derivative curves of precursors and nanocomposites.

temperatures (Tonset and Tmax) and residue content for both heating rates. For nCE, the thermogravimetric data were only registered at 10°C/min. There are three steps of degradation. Tonset were 45°C, 289°C and 349°C. The corresponding Tmax were 53°C, 304°C and 357°C being the mass loss of 5, 55, and 21 wt.%, respectively. Deepa *et al.* yielded nanocellulose extracted from five different

Rate (°C/min)	Sample	Tonset (°C)	Tmax (°C)	Residue (%)
	PBAT	359	324/382/596	4
	PBAT-nCE1	361	388	5
5	PBAT-nCE3	358	382/574	4
	PBAT-nCE5	364	384/387	4
	nCE	289/349	304/357	20
	PBAT	360	386	4
	PBAT-nCE1	357	384	3
10	PBAT-nCE3	268/360	281/383	3
	PBAT-nCE5	268/361	274/385	3

Table 5. Thermogravimetric data of the precursors and nanocomposites at 5 and 10°C/min.

plant fibre sources (banana rachis, sisal, kapok, pineapple leaf and coir). Different chemical treatments such as alkaline treatment and bleaching were conducted. Hydrolysis was experienced with oxalic acid to isolate the nanocellulose [40]. Thermogravimetric analysis was performed at 25°C - 700°C, 10°C/min and nitrogen as carrying gas with a 100 mL/min rate. Two decomposition steps appeared. The first (around 100°C) was attributed to the water release. For all, the second step was steep, showing Tmax at 351°C, 348°C, 360°C, 347°C, 348°C for banana rachis, sisal, kapok, pineapple leaf and coir, respectively. The coir sample presented a slight shoulder around 320°C and lesser thermal stability due to the higher percentage of lignin content (45% - 50%). Mandal and Chakrabarty [29] used waste sugarcane bagasse (SCB) as raw material for yielding nanocellulose. Grounded bagasse lesser than 0.250 mm in size was submitted to delignification and isolation of cellulose. The latter, free of lignin and hemicellulose, was hydrolysed with 60% sulfuric acid aqueous solution, at 50°C, for 5 hours, under stirring. Thermogravimetric analysis was conducted at a temperature interval of 30°C - 750°C, 10°C/min, at a nitrogen carrying gas rate of 20 ml/min. The authors registered two decays of degradation. The lower stage of the cellulose decomposition (Tmax = 311°C) was attributed to the degradation of more accessible and highly sulfonated amorphous regions. The higher Tmax (345°C) was associated with the collapse of unsulfonated cellulose crystals. They concluded that the insertion of sulfonated groups into the crystals of cellulose reduced its thermal stability. Herein, the initial step of decomposition was related to the breakage of residual inter and intramolecular hydrogen bonds, according to reported by Souza et al. [41]. We could conjecture that the two degradation peaks, in which Tmax was at 304 (mass loss of 55%) and 357°C (mass loss of 21%), would be associated with the presence of amorphous cellulose matter including portions with sulfonated groups and intact crystalline nanocellulose, respectively. The peak at lower temperatures was dominant. It depicted lesser thermal stability, and that the sulfonated groups could be an inductor of cellulose depolymerisation. Then, the nCE applied is a mixing of cellulose amorphous and crystalline structures. At 5°C/min, PBAT revealed three degradation decays with Tmax at 324, 382 and 590°C. Herein, PBAT is a random copolymer with higher content of adipic segments. We could speculate that the first decay was possibly related to the low molar mass chains richer in adipic segments, representing 5% of the neat sample; the intermediate one depicted the main portion of the sample (88%); the last one could likely be associated to PBAT chains richer in terephthalic segments, constituting about 2%. At 10°C/min, only one degradation step was noticed being Tonset and Tmax around 360 and 386°C, respectively. At this heating rate, the thermal events occurred faster and simultaneously building solely one on degradation decay. Regardless of the thermal rates, the presence of nCE modified the sample thermal behaviour. At 5°C/min, the number of degradation steps changed with nCE content. With 1 wt.% of nCE, a single degradation decay was registered, showing Tonset at 361°C and Tmax at 388°C. For the samples incorporated with 3 and 5 wt.% of nCE, two degradation steps occurred. Tonset was higher for the sample with 5 wt.% of nCE. Tmax at 382°C (mass loss of 90%)/574°C (mass loss of 5%) and 284°C (mass loss of 5%)/389°C (mass loss of 91%) were recorded for sample with 3 and 5 wt.% of nCE, respectively. At 10°C/min, Tonset remained practically unaltered. The addition of nCE regulated the number of degradation steps and Tmax assignments. A unique decay was noticed for the sample with 1 wt.% of nCE ( $T_{max} = 386$ °C). Sharply, there is a great difference on the  $T_{\text{max}}$  assignment to the first decay for the samples embedded with 3 and 5 wt.% of nCE. T<sub>max</sub> were 281°C and 274°C, respectively, both with a mass loss of around 5% (2% and 3%, respectively). Mukherjee et al. investigated the effect of the nanofibrillated cellulose (NFC, 0.2 - 1 wt.%) embedded into the PBAT matrix. TGA analysis was conducted between 3°C - 850°C, 10°C/min and nitrogen was the carrying gas (20 mL/min). They pointed out that Tonset and Tfinal occurred at 320°C and 465°C, respectively. For the composites, Tmax changed in no linear fashion around 400°C - 397°C. Also, only one deflection appeared, suggesting that NFC was well dispersed into PBAT or it was out of equipment detection limit [18]. Independent of the heating rates, the thermal behavior was similar for each nanocomposite. The sample with 1 wt.% of nCE exhibited better dispersion into the PBAT matrix since only single degradation decay occurred. Above this content, an additional degradation step arose. It could be supposed that PBAT is amorphous, has low molar mass and is rich in adipic segments incorporated mainly sulfur-containing nanocellulose. The PBAT ester group degradation plus nanocellulose depolymerisation were assisted by sulfonated groups taking the decrease of thermal stability of the nanocomposites. Finally, the findings induced to conjecture that the nanocomposites comprised a multiphase system. The results agreed with the NMR, WAXD and DSC ones.

## 3.7. Rheological Evaluation

**Figure 10** displays the curve of storage modulus (G') as a function of strain. The curves of storage modulus, loss modulus (G') and complex viscosity ( $\eta^*$ ) as a



Figure 10. Storage modulus as function of percent of strain, at 1 Hz, 250°C: PBAT (\_\_\_\_\_), PBAT-nCE1 (\_\_\_\_\_), PBAT-nCE3 (\_\_\_\_\_), PBAT-nCE5 (\_\_\_\_\_).

function of angular frequency are allocated in Figures 11-13, respectively. Table 6 arranges the G' and G" at 10° Hz besides the relationship G"/G'. The curve of G' versus strain allowed us to notice which strain range the materials had behaviour as a Newtonian fluid. The maximum strain value was around 10<sup>2</sup>. G' versus frequency curves did not show linear behaviour. Below  $10^{\circ}$  Hz, the G' curve of the nanocomposite embedded with 1% nCE had a higher storage modulus. The others seem to be overlapping. Above 10° Hz and along the frequency axis, the curves presented a new hierarchy. There was an increase in G' with the frequency but no connection with the nCE content. The highest value of G' was noticed for the sample with 3 wt.% of nCE, indicating a slight reinforcement action on PBAT matrix probable due to the rigidity of cellulose structure. The samples embedded with 0 and 5 wt.% of nCE alternated values upper and down along the frequency axis. In the sample incorporated with 1 wt.% of nCE, the cohesion between the cluster formed by amorphous cellulose plus PBAT low molar mass and crystalline structures of cellulose and PBAT was disrupted due to likely some shearing degradation process. With respect to G", for all samples, although there was no direct relationship with the nCE content, was observed an increase along the frequency axis. The tendency of G" values followed this hierarchy concerning nCE content: 3 > 5 > 0 > 1. G"/G' relationship gives information on the predominance of elastic or viscous components. Except for the sample with 1 wt.% of nCE, the value of the G"/G" increased with nanocellulose content. Based on the G"/G' values, it could be deduced that the viscous component predominated for the samples with 3 and 5 wt.%. All complex viscosity curves presented stability up to 10<sup>-1</sup> Hz, and then a continuous drop was observed.  $\eta^*$  showed no linear tendency regarding the n-CE content following this



Figure 11. Storage modulus *versus* frequency: PBAT (\_\_\_\_\_), PBAT-nCE1 (\_\_\_\_\_), PBAT-nCE3 (\_\_\_\_\_), PBAT-nCE5 (\_\_\_\_\_).



Figure 12. Loss modulus versus frequency: PBAT (\_\_\_\_), PBAT-nCE1 (\_\_\_\_), PBAT-nCE3 (\_\_\_\_), PBAT-nCE5 (\_\_\_\_).

hierarchy: 3 > 5 and 0 >1. The behaviour of the sample curves with 0 and 5 wt.% of nCE was like those observed for G' and G". They are superimposed until 4 ×  $10^{-1}$  Hz and after separated showing the sample with 5 wt.% higher values of  $\eta^*$ . As was observed in other analyses, the viscosity results were random. We understand the rheological behaviour of each sample could be related to the dispersion



Figure 13. Complex viscosity *versus* frequency: PBAT (——), PBAT-nCE1 (——), PBAT-nCE3 (——), PBAT-nCE5 (——).

Sample	G' (MPa)	G" (MPa)	
	(10º Hz)	(10º Hz)	G"/G'
PBAT	2.2	6.1	2.8
PBAT-nCE1	1.3	3.3	2.6
PBAT-nCE3	2.7	8.5	3.1
PBAT-nCE5	1.9	6.8	3.5

Table 6. G', G" and G"/G ratio at frequency 10<sup>o</sup> Hz.

of the nanocellulose into the PBAT matrix for each system studied. At 3 wt.% of nCE, the nanocellulose crystalline portion formed clusters hampering the flow of the polymer chains. The greater resistance to polymer flow denotes an increase in viscosity. For the sample with 1 wt.% of nCE, we deduced that the clusters of PBAT low molar mass and amorphous cellulose portions were aligned with polymer chains acting as plasticisers and then, decreasing flow resistance. For the sample with 5 wt.% of nCE, no preferential arrangement between PBAT and nanocellulose arose, meaning PBAT viscosity was not perturbed.

# 4. Conclusion

Nowadays, when climatic variations are worrying the planet, it is of uppermost importance to search for eco-friendly materials. In this context, the work aimed to study an ecological and biodegradable nanocomposite based on PBAT with nanocellulose. Different proportions of nanocellulose were embedded into the PBAT matrix. According to the NMR, the aliphatic segments (butylene adipate) predominated in the copolymer constitution. Glass transition, cold crystallisation, and melting temperatures remained unchangeable. As cold crystallisation did not change, the enhancement of PBAT crystallisation degree for some nCE content was ascribed to the transcrystallisation process. The evaluation of molecular relaxation showed complexity and a strong influence of nanocellulose in the PBAT molecular mobility. The nanocellulose amorphous and crystalline portions presented a strong impact on the PBAT amorphous and crystalline planes as seen in the calorimetric and crystallographic analysis. The rheological evaluation indicated that a reinforcing effect was noticed in the sample with 3 wt.% of nCE. The nanocomposites were considered multiphase systems.

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# **Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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