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EFFECTS OF THE INCORPORATION OF CLAY ON PROPERTIES OF THE BIODEGRADABLE COPOLYESTER/PLA FLEXIBLE FILM*

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Abstract

Nowadays, population growth and the interest of food industry, makes the research and applications of biodegradable polymers increase, because under favorable conditions its degradations may occur within weeks or in a few months, reducing the environmental impact. This work presents the processing and characterization of flexible films by the incorporation of 3 % (% wt) of modified bentonite light green clay in the Copolyester/PLA biodegradable blend. The clay incorporation was carried out by melt-mixing processing, using a twin screw extruder machine. The films were obtained by cast extrusion tape. The films obtained were submitted to tensile tests, SEM and XRD analysis, and the correlation between their properties was discussed. The XRD results of clay showed that the quaternary salt and sodium carbonate addition increased the interlayer distance of clay making it easier to intercalation of blend in the nanoclay. The XRD results of PBAT/PLA/Clay nanocomposite show no characteristic organoclay peaks. This result suggests intercalation between nanoclay and matrix (blend). The tensile test results showed an increase of around 30% in tensile strength at break of nanocomposite film when compared with blend film.

Keywords: Biodegradable polymer; Clay; Flexible films; Mechanical properties.

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1 INTRODUCTION

Due to environment and sustainability issues, this century has witnessed remarkable achievements in green technology in the field of materials science through the development of biocomposites. The development of high-performance materials made from natural resources is increasing worldwide. With the developments of biodegradable materials, other researchers are trying to use directly the biomass constituents to manufacture polymeric materials [1,2].

Increasing population, scarcity of raw materials coupled with global warming issues has governments and corporations looking for opportunities such as recycling and biodegradability to expand material performance [3].

Since plastic packaging materials are often contaminated by food materials and biological substances, recycling of these materials is often impractical and most of the time not economical [4].

Biopolymers should be used in those applications where biodegradability and/or the derivation of natural resources gives added value, particularly, where valuable petroleum-based plastics are used for applications with a short life time [5].

The term ‘‘biodegradable’’ materials is used to describe those materials which can be degraded by the enzymatic action of living organisms, such as bacteria, yeasts, fungi and the ultimate end-products of the degradation process, these being CO_2, H_2O, and biomass under aerobic conditions and hydrocarbons, methane and biomass under anaerobic conditions [6].

The recent incorporation of biological waste treatment (i.e., composting and biogasification) in an integrated approach to solid waste management has resulted in a growing commercial interest in the development of biodegradable materials for consumer products [4, 5]. On the market are a number of materials known as biodegradable plastics (i.e., starch-based materials, cellulose-derived polymers, bacterial polyesters and a range of synthetic polymers) [7]. Among commercial biodegradable plastics, aliphatic-aromatic copolyester (PBAT) is one of the most promising biodegradable materials because they are readily susceptible to biological attack [8]. PBAT has gained research and industry attention due to good processability in extrusion lines LDPE; besides PBAT begins to degrade after only few days in soil and enzymatic environments in contrast to petroleum derived polymers, such as polypropylene, polyethylene, that takes hundreds or even thousands of years to degrade [8,9].

The PBAT (butylene adipate-co-terepthalate) and the PLA (Poly(lactic acid)) , have been extensively investigated as biodegradable polyesters and have a large number of biomedical applications such as absorbable bone plates, some surgical fixation devices, bioabsorbable surgical sutures and carriers for the controlled release of drugs. These aliphatic polyesters are commercially produced either by microorganisms, ring-opening polymerization of lactones or ring-opening poly addition of cyclic dimmers [10-12].

The combination of these two materials in a blend (PBAT/PLA), aims to bring the best characteristics for a biodegradable material, therefore aliphatic polyesters are the most promising biodegradable materials because they are readily susceptible to biological attack [13,14].

Polymer blending is a well-used technique whenever modification of properties is required, because it uses conventional technology at low cost. The usual objective for preparing a novel blend of two or more polymers is not to change the properties of

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the components drastically, but to capitalize on the maximum possible performance of the blend [15]

The modification of polymers, through the incorporation of additives in the micrometer range, can either improve modify the modulus and the strength (carbon black, silica beads and fibers, clay, mica) [16]. Recently the application of the nanocomposite concept has proven to be a promising option in order to improve mechanical and barrier properties [5].

Polymer nanocomposites are two-phase materials, in which the polymers are reinforced by nanoscale fillers [16]. Organoclay-based nanocomposites can be a potential candidate because of their mechanical, thermal, gas barrier, and optical properties at low clay content [17].

Since the creation of flexible films, the packaging industry has been propelled to astonishing heights. Through the development and utilization of these films, manufacturing practices, and continual innovations, the field of packaging has been able to grow and evolve to adapt to the needs of products around the globe.

The aim of this work is to produce biodegradable flexible film through a polymeric nanocomposite consisting of biodegradable copolyester, PLA and nanoclay, for the film to be used with dry foods.

1.1 Biodegradable Copolyester (PBAT)

The Poly (butylene adipate-co-terepthalate) (PBAT), an aliphatic-aromatic copolyester based on terephthalic acid, adipic acid, 1,4- butanediol and modular units is used in industrial applications [9]. This product was basically designed to meet the requirements of a biodegradable plastic; a combination of melt processability, end use performance and biodegradability. The films are tear-resistant and flexible, and also resistant to both water and fluctuations in humidity. The PBAT can be processed by conventional blown film lines for PELD. [4,9].

Typical applications of PBAT are compost bags for organic waste, films in the agricultural sector, household films, and coating or lamination (e.g., paper), and coating materials for starch-based products (e.g., plates, cups) within the fast food and catering industries [9]**.**

The PBAT is considered a good candidate for the toughening of PLA due to its high toughness and biodegradability and no indication of environmental risk (ecotoxicity) when are introduced into composting processes [18,19].

1.2 PLA

Poly(lactic acid) (PLA) is a linear, semicrystalline, aliphatic, biodegradable polyester that can be produced from lactic acid by the fermentation of renewable sources such as whey ,corn, potato, or molasses [20]. Polymerization of lactic acid into PLA produces a biodegradable thermoplastic polyester with good biocompatibility and physical properties, such as high mechanical strength, thermoplasticity, fabricability, and shows a number of interesting properties including biodegradability, high strength and high modulus [21].

The PLA is considered synthetic biodegradable polymer class, and this group of polymers has been widely used in biomedical uses, such as controlled-release capsules of drugs in living organisms, fasteners surgery (sutures, implants for bone pins) and special candidate for producing package materials [22,23].

PLA is a hydrolytically degradable aliphatic polyester which presents water vapor permeability that may have a significant influence on its rate of degradation [22]. Is considered a relatively brittle material, thus it needs to be plasticized to produce flexible packaging films by cast film extrusion or blown film extrusion [24,25].

1.3 Clay and Nanocomposites

Various inorganic nanoparticles have been recognized as possible additives to enhance the polymer performance such as the layered inorganic solids like nanoclay. Clay nanocomposites with biobased polymer matrices are of increasing scientific and industrial interest have attracted some attention by the packaging industry, due to their low cost, relative simple processability and improvements in some properties of polymers composites. Favorable characteristics include improved Young's modulus, reduced gas permeability, improved fire retardancy, chemical resistance, surface appearance, electrical and thermal conductivity and mechanical properties. In addition, the origin of the polymer matrix from renewable resources is an advantage as well as the biodegradable character of the organic components. Potential applications include melt-processed thermoplastic moulding, packaging films and coatings [22,26-28].

The most studied clay is montmorillonite (MMT), whose chemical general formula is $Mx(Al_4\text{-}xMgx)$ $Si_8O_{20}(OH)_4$ [29]. The imbalance of the surface negative charges is compensated by exchangeable cations (typically Na^+ and Ca^{2+}) [30].

This type of clay is characterized by a moderate negative surface charge (cation exchange capacity, CEC), which is an important factor to define the equilibrium layer spacing. The charge of the layer is not locally constant as it varies from layer to layer and must rather be considered as an average value over the whole crystal [31]. MMT clays have hydrophilic nature due to the presence of inorganic cations on the basal montmorillonite layer [32].

MMT clays must be submitted to treatments which play an important role in the preparation of nanocomposites since it can affect their final properties. The most widely used treatments are the diverse functionalizations of clay by various organic cations through ion exchange where the inorganic cations are replaced by organic cations intercalated into the silicate layers. Its hydrophilic nature and ionic exchange capacity allow the silicate mineral to be intercalated by organic cations, which in most cases are alkylammonium ions, to make the clay organophilic and compatible with polymer matrices, preferably with polymers with polar groups which exhibit a higher affinity towards the alkylammonium ion-modified clays [33].

In the immiscible structure the polymer does not penetrate between the clay platelets and the interlayer space of the clay gallery does not expand due to its poor affinity with the polymer, so this structure is also known as phase separated morphology or tactoid morphology. Intercalation is attained when polymer chains slightly penetrate within the gallery space and induce moderate expansion of the clay platelets. Exfoliation is characterized by a random distribution of the clay platelets due to extensive penetration of the polymer chains, resulting in the delamination of the clay platelets and the loss of the crystalline structure of the clay. This is due to a high affinity between polymer and clay [22].

Processing conditions have significant influence on the delamination and dispersion of clay additive in the matrix. The intercalated nanocomposites result from the penetration of polymer into the interlayer region of the clay, resulting in an ordered multilayer structure with alternating polymer/inorganic layers at a repeated distance

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of a few nanometers. The exfoliated nanocomposites involve extensive polymer penetration, with the clay layers delaminated and randomly dispersed in the polymer matrix [30,34,35].

Bentonites are defined as a sedimentary rock consisting of a large portion of expandable clay minerals with three-layer structures (smectites) such as montmorillonites (80%), beidellite, nontronite etc with minor amounts of non-clay minerals such as quartz, calcite, dolomite and feldspar [36].

Bentonite, clay composed essentially of one or more of the smectite group clay minerals especially montmorillonite is the most commonly clay used in obtaining nanocomposite polymer/clay. However, bentonite clay should be organically modified with quaternary ammonium salts to improve their interaction with the polymer matrix. Therefore, this work presents the preparation and characterization of nanocomposite based on blend of PBAT/PLA and a natural Brazilian bentonite light green clay [37,38]. In the present work, PBAT/PLA/organoclay with 3% (wt) of organoclay was prepared by direct melt intercalation method. The addition of 3% (wt) of organoclay was selected thus in the previous work, it was found that the optimum loading of nanoclay in others polymers was attained at 3% (wt) [39,40].

2 MATERIALS AND METHODS

2.1 Materials

The materials used in this work were biodegradable Aliphatic-aromatic copolyester (PBAT) with biodegradable Poly(lactic acid) (PLA), producing a blend with MFI = 8,59 g/ 10 min at 190°C / 2.16 Kg, and natural Brazilian bentonite light green clay from Boa-Vista, PB, Brazil.

2.2 Preparation of Nanoclay

The light green clay extracted from nature, presents calcic character (Ca^{2+}) then undergoes processes for its modification. The first step consists in dispersing the clay in deionized water under constant stirring for 30 min. The second phase is to turn it into sodium clay by adding sodium carbonate (Na$_2$CO$_3$) and keeping under constant stirring for 1h, so there is exchange of Ca^{2+} by Na$^+$ in the interlayer spaces of the clay. After this time, add quaternary ammonium salt and keep stirring for another 30 min. The organoclay is then filtered, washed with deionized water and dried at 60°C for 48h. After this time the clay is sieved and characterized by XRD to verify the interlayer distance obtained after the process, compared with the XRD clay before modification.

2.3 Preparation of blend and composite

PLA and PBAT pellets and the nanoclay were dried at 60 ± 2 ºC for 4 h to reduce its moisture content to less than 2%. The PBAT/PLA blend (80%/ 20% based on wt%) and PBAT/PLA with 3% (wt%) modified clay nanocomposite were prepared by melting extrusion process, using a co-rotating twin screw “extruder AX 16LD40” made by AX Plásticos Máquinas Técnicas Ltda. A temperature profile was 80/90/95/100/110/120/130/130 ºC. Screw speed was 70 rpm. The extrudates coming out of the extruder were cooled down for a better dimensional stability, pelletized by a

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pelletizer, dried again at 60 ± 2 ºC for 4 h and fed into extrusion tape to obtain the film samples.

2.4 Analyses

X-rays diffraction (XRD): XRD is most commonly used to probe the nanocomposites structure and occasionally to study the kinetics of the polymer melt intercalation owing to its ease and availability. XRD, in this study was used to evaluate the modification of bentonite light green clay and the intercalation in the PBAT/PLA blend. XRD patterns were recorded on a Simens - D5000 diffractometer operated at 40 kV and 40 mA, with $CuK\alpha$ radiation ($\lambda = 15.4$ Å).
Cation Exchange Capacity –CEC: CEC of bentonite light green clay determination was carried out by ammonium acetate method [41].
Wavelength Dispersive X-Ray Fluorescence (WDXRF): the main components of bentonite light green clay were determined by using a Rigaku RIX 3000 analyzer.
Melt flow index (MFI) measurements: MFI measurements for PBAT/PLA blend were determined with a microtest extruder plastometer at 190°C/2.16 kg conditions (ASTM 1238-04).
Thermogravimetric analysis (TG): were carried out using Mettler-Toledo – TGA/SDTA 851. A sample with 10.0 ± 1.0 mg of the samples were weighed and then the samples were kept in a platinum sample pan, weighed and heated to 600°C starting from room temperature (25°C), at a heating rate of 10°C/min (in an oxygen atmosphere).
Differential scanning calorimetry (DSC): analyses were carried out using a Mettler Toledo DSC 822e from 25 to 250°C at a heating rate of 10°C/min under oxygen atmosphere. DSC analyses of the materials were performed on four samples of the irradiated and non-irradiated materials.
Mechanical tests: Tensile tests were determined using an INSTRON Testing Machine model 5564, according to ASTM D 882-91 in order to evaluate the mechanical behavior of the materials studied. Each value obtained represented the average of five samples.
Scanning Electron Microscopy (SEM): were carried out using a LX 30 (Philips). The samples were cryofractured under liquid nitrogen, and then the fractured surface was coated with a fine layer of gold and observed by SEM.

3 RESULTS AND DISCUSSION

3.1. Bentonite Light Green Clay Characterization Results

X-rays diffraction (XRD) analysis results: the XRD patterns of natural bentonite light green clay and after be modified by quaternary ammonium salt are showed in Figure 1. The results show that the natural bentonite light green clay presented an interlayer distance (d_{001}) of 1.55 nm and after modification the interlayer distance increased to (d_{001}) of 2.17 nm. This increase confirms the major intercalation of the quaternary ammonium cation in the interlamellar spacings of the bentonite light green clay took place. These results are also consistent with others clays results [37].

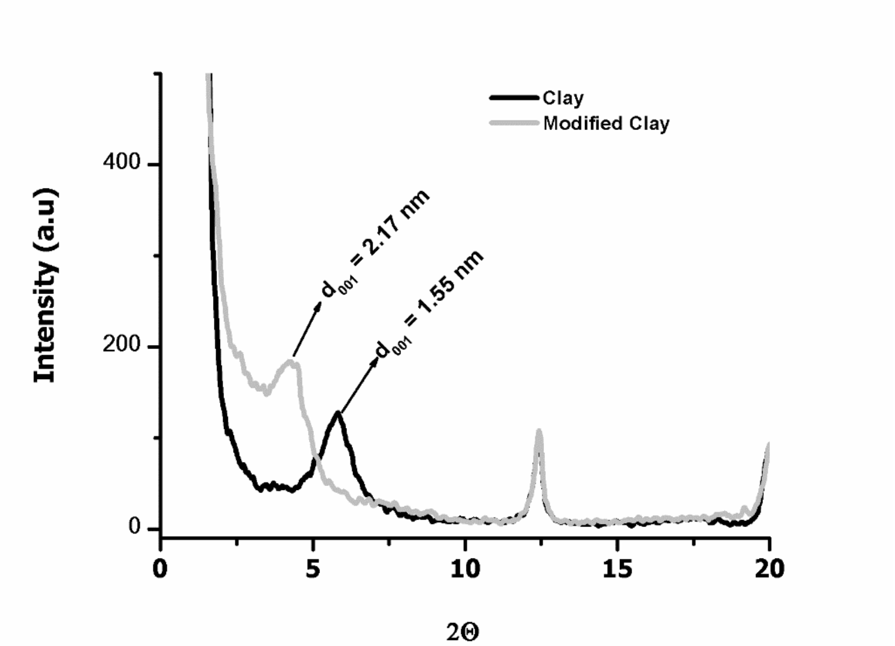

Figure 1. X-rays diffraction patterns of natural bentonite light green clay and after modification with quaternary ammonium salt.

Cation Exchange Capacity –CEC results: CEC determination of the bentonite light green clay showed a value of 37meq/100g.

Wavelength Dispersive X-Ray Fluorescence (WDXRF): In order to determine the composition of the bentonite light green clay, samples undergone the wavelength dispersive X-ray fluorescence analysis (WDXRF). Table 1 presents the list of components that constitute the light green clay. Silica is the clay major component, corresponding to 55.44 % of its total. Table I also shows that aluminum oxide, besides iron oxide, is another important component of the light green clay.

Table 1. Inorganic components of the bentonite light green clay by WDXRF

Component	(%)	Component	(%)	Component	(%)	Component	(%)
SiO_2	55.44	MgO	1.78	ZrO_2	0.06	ZnO	0.03
Al_2O_3	17.81	K_2O	1.35	P_2O_5	0.05	NiO	0.02
Fe_2O_3	7.15	TiO_2	0.92	CuO	0.04	Y_2O_3	0.02
CaO	5.04	SO_3	0.07	SrO	0.04	FL [(a)]	10.14

(a) Fire Loss (FL)

3.3 PBAT/PLA Blend and PBAT/PLA/Clay Nanocomposite Characterization

Melt flow index (MFI) measurements: the MFI values of PBAT/PLA blend measurements was 8.59 g/ 10 min at 190°C / 2.16 Kg, and for PBAT/PLA/Clay nanocomposite was 6.96 g/ 10 min at 190°C / 2.16 Kg. These results shows a reduction in original blend MFI due to clay addition.

X-Rays Diffraction (XRD): the XRD patterns of PBAT/PLA blend and PBAT/PLA/Clay nanocomposite in the range of 2θ between 3° to 30° are showed in Figure 2.

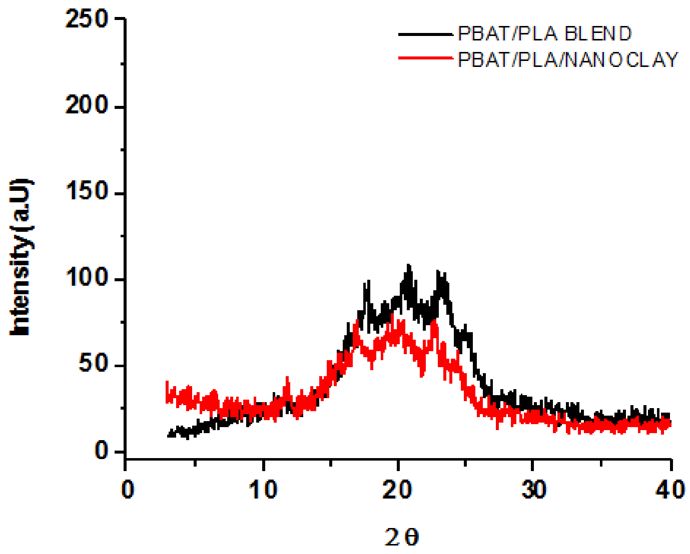

Figure 2. X-rays diffraction patterns of PBAT/PLA Blend and PBAT/PLA/Clay nanocomposite.

It can be seen in Fig. 2, the XRD pattern for PBAT/PLA/Clay nanocomposite show no characteristic organoclay peaks in the range of $2\theta = 4.05^{\circ}$; that is, the peak corresponding to the basal spacing modified bentonite light green clay (d_{001}) of 2.17 nm has disappeared. This indicates that PBAT/PLA chains have diffused into the gallery of the clay and that the clay has been successfully intercalated in the PBAT/PLA matrix leading to the formation of exfoliated structures.

Thermogravimetric analysis results (TG): The onset temperature of degradation (T_{onset}), temperature of maximum loss (T_{max}), temperature corresponding to 50 % loss ($T_{50\ \%}$), and overall weight loss have been calculated from the DTG curves (10°C/min) and are presented in Table 2.

Table 2. TG analysis results for PBAT, PLA, PBAT/PLA blend and PBAT/PLA/Clay nanocomposite

Materials	**T_{onset}[(a)] (ºC)**	**$T_{(50\ \%\ degrad.)}$[(b)] (ºC)**	**T_{max}[(c)] (ºC)**	**Weigh Loss[(d)] (%)**
PBAT	253.2	375.4	449.1	98.82
PLA	255.4	317.2	370.2	97.22
PBAT/PLA	307.7	380.1	447.8	98.08
PBAT/PLA/CLAY	310.2	363.6	439.5	96.64

(a) onset temperature of degradation; (b) temperature of maximum loss; (c) temperature corresponding to 50 % loss; (d) overall weight loss

It was observed in Table 2 an increase of around 50ºC for PBAT/PLA blend T_{onset} in comparison with neat PBAT and neat PLA. On the other hand, the clay addition not causes significant changes at PBAT/PLA blend T_{onset}. The temperature corresponding to 50 % loss ($T_{50\%}$), and T_{max} were higher for blend than nanocomposite.

Differential Scanning Calorimetry (DSC): Figure 3 shows the curve of DSC analysis of neat PBAT, neat PLA, PBAT/PLA blend and PBAT/PLA/CLAY nanocomposite.

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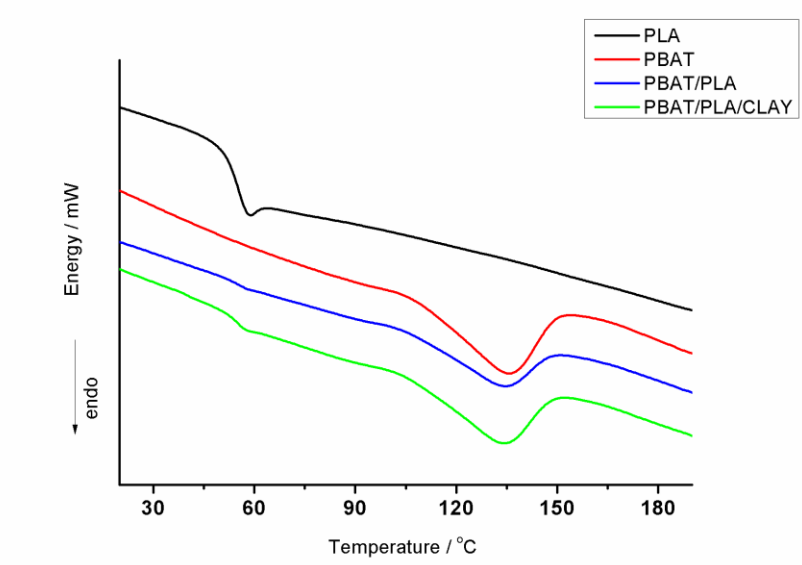

Figure 3. DSC analysis of neat PBAT, neat PLA, PBAT/PLA blend and PBAT/PLA/CLAY nanocomposite.

From figure 3, it could be inferred that compared with the neat PLA the endothermic melting enthalpy of PBAT/PLA blend increased considerably due to blending with PBAT. The addition of clay (3 % in wt) in PBAT/PLA blend leads to obtaining of new material with higher melting enthalpy than original blend. The increases in the melting enthalpy can be attributed to the increase in crystallinity of material. It indicated that blending PBAT with PLA, followed by organophilic Clay addition caused structural changes in the polymeric chains of blend component. It means that blend processing and clay addition had a capability to reorient the polymeric molecules presents in crystal form in order to obtain a composite material with high melting enthalpy and, consequently, high crystallinity percentage.

Table 3. DSC analysis results of materials studied

Materials	**Melting Temperature (T_m, ºC)**	**Melting Enthalpy (ΔH_m,Jg^{-1})**
Neat PBAT	135.7	298.8
Neat PLA	58.9	43.5
PBAT/PLA blend	134.4	218.8
PBAT/PLA/CLAYnanocomposite	134.05	296.2

The average values of melting enthalpy (ΔHm) and melting temperature (Tm) of the materials studied are given in Table 3. As it can be seen, the melting temperature and enthalpy of blend and composite were higher than of PLA and lower than of PBAT indicating good miscibility between the components of the blend and also suggesting a good incorporation and dispersion of clay nanoparticles in the final composite.

3.4 Flexible Film Characterization

Mechanical Tests Results of PBAT/PLA blend and PBAT/PLA/Clay Flexible Film: Table 4 summarizes the mechanical tests results for the flexible film from PBAT/PLA Blend and PBAT/PLA/Clay nanocomposite. These results shown the average values calculated from the data obtained in tests, with standard deviations less than 10 % for all tests.

Table 4. Mechanical tests results for the flexible film from PBAT/PLA Blend and PBAT/PLA/Clay nanocomposite

Test	PBAT/PLA Blend	PBAT/PLA/Clay	Variation (%)
Tensile strength at break (MPa)	10,88	14,43	+ 30
Elongation at break (%)	890	1051,8	+ 18
Young´s Modulus (MPa)	40,7	29,5	- 28

The results presented in Table 4 shows that the addiction of clay in PLAT/PLA blend improved the tensile strength at break (of around 30%) and also improved the elongation at break. These changes should be associated with the interfacial interaction between the PBAT and PLA component of blend and Light Green Clay. As it can be seen, the Yong´s Modulus has been reduced (of around 28%).
Figure 4 shows the diagram stress (MPa) X strain (%) for tensile tests results of Flexible Film from PBAT/PLA blend and from PBAT/PLA/Clay.

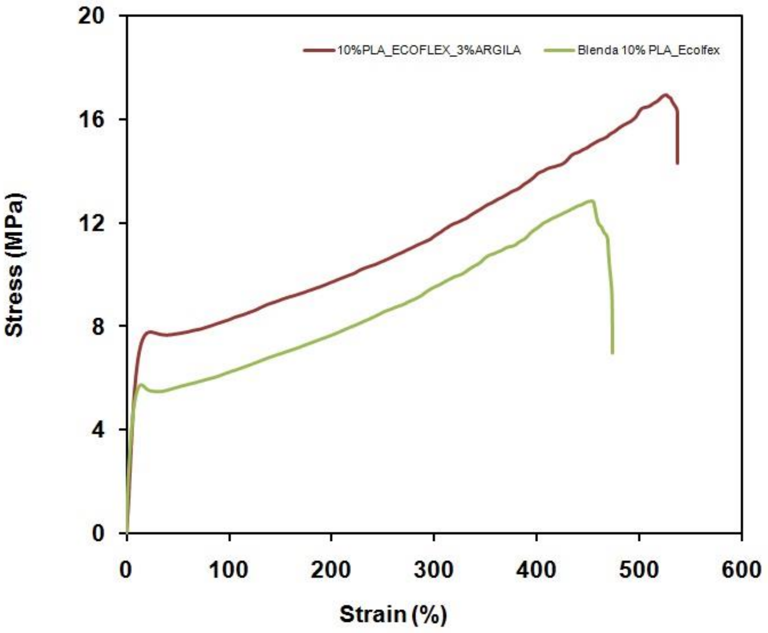

Figure 4. Diagram Stress (MPa) X Strain (%) for both, PBAT/PLA Blend and PBAT/PLA/Clay

From of stress–strain curve it is possible observed that the addition of modified light green clay makes the PBAT/PLA blend more ductile than original PBAT/PLA blend. This is evident from the elongation at break values of the nanocomposite.
Scanning Electron Microscopy (SEM): SEM micrographs of cryo-fractured surfaces of blend PBAT/PLA and PBAT/PLA/Clay nanocomposite are compared in Figure 5. As it can be seen, PBAT/PLA/Clay nanocomposite, Figure (5b), showed a slightly rough cryo-fractured surface, when compared with cryo-fractured surface of blend

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PBAT/PLA Figure (5a). However, from Figure (5b), it can be revealed that some small particles dispersed in the PBAT/PLA matrix. The voids observed in PBAT/PLA blend are considered to be created by debonding at interfaces between PLA and matrix.

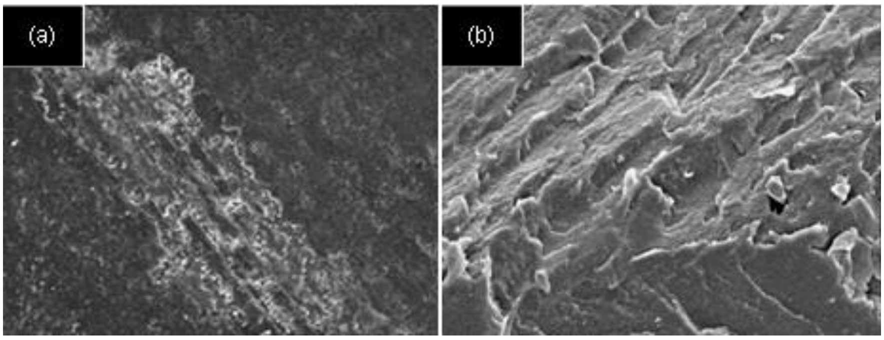

Figure 5. (a) PBAT/PLA blend; (b) PBAT/PLA/Clay nanocomposite

The SEM micrographs of the nanocomposite in the Figures (6a; 6b; 6c; 6d), showed an interaction between matrix and nanocomposite. It is possible to view some brighter points representing the clay in the Figures (6c) and (6d). This is probably a consequence of the some agglomeration of clay particles, and suggests that some of the light green clay particles remain unexfoliated. More direct evidence for the formation of a true nanoscaled composite.

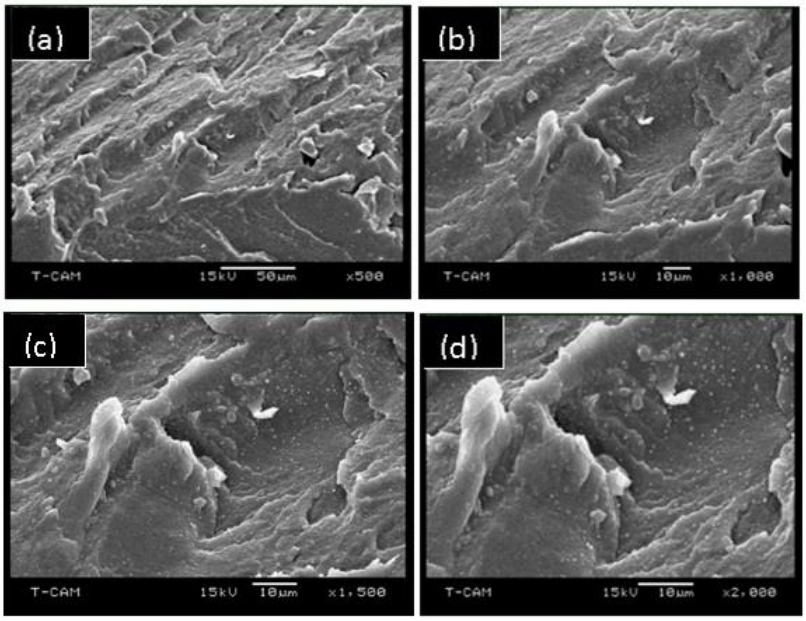

Figure 6. (a; b; c; d) showed PBAT/PLA/Clay nanocomposites

4 CONCLUSIONS

The aim of this study was to process and evaluate the changes in the mechanical and morphological properties of the biodegradable film due to the incorporation of clay yielding a nanocomposite. Results showed that incorporation of 3% (wt %) of light green clay in the blend matrix of PBAT/PLA, resulted in a gain of mechanical properties of the film. Although the addition of light green clay in the polymer matrix resulted in a rough surface with some voids between fiber and matrix, the mechanical gains outweigh the morphological differences. The addiction of clay in the PBAT/PLA

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blend improved the thermal degradation temperature increasing the thermal resistance of material as shown in TG results. The peaks of DSC analysis indicated that blending PBAT with PLA, followed by organophilic Clay addition caused structural changes in the polymeric chains of blend component and leads to obtain a composite material with high melting enthalpy and, consequently, high crystallinity percentage. The superior mechanical properties of PBAT/PLA/Clay nanocomposite observed in this study can be attributed to the stiffness of Brazilian bentonite light green clay, reinforcing effects, to the degree of the intercalation and good dispersion of the clay layers in the PBAT/PLA matrix. From the results of XRD and SEM micrographs, is possible claim that the morphology at PBAT/PLA/Clay presents a mixture of intercalated and partially exfoliated structures. This result indicates that PLA and PBAT chains have diffused into the gallery of the clay and the clay has been successfully intercalated in the PBAT/PLA matrix leading to obtain flexible films with improved tensile strength and elongation at break properties when compared with the flexible film prepared from PBAT/PLA blend.

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