Bionanocomposite Obtained from Poly (lactic acid)/ Biopolyethylene Blend and Clay

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Summary: The aim of this work is the development of a bionanocomposite from Poly (lactic acid)-PLA/Biopolyethylene (PE) blend and clay. The montmorillonite (MMT) clay was organically modified with an ionic surfactant to become organophilic (OMMT). The MMT and OMMT clays were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD) techniques. The blends and the biocomposites were prepared by extrusion followed by injection molding and characterized by XRD, mechanical properties and Scanning Electron Microscopy (SEM). XRD and FTIR results indicated that the MMT clay was sucessfully modified becoming OMMT. XRD results also indicated that for the PLA/PE/EMA-GMA biocomposite a bionanocomposite with an intercalated structure was obtained. SEM results showed that the addition of the OMMT clay to both PLA/PE and PLA/PE/EMA-GMA blends led to a substantial decrease in the PE dispersed phase domains size. This decrease was more pronounced in the PLA/EMA-GMA/OMMT bionanocomposite.

Keywords: bionanocomposite; organoclay; Poly (lactic acid); polymer blends

Introduction

Polymers derived from non renewable fossil resources (oil) have ben widely used by the industry in various applications due to their versatility and relatively low cost. However these polymers are resistant to degradation and when they are inappropriately discarded, specially in the form of plastic bottles and bags, can cause severe damage to the environment. An alternative is the use of biopolymers, which are polymers made of raw-materials derived from renewable resources like sugar cane, cellulose, corn, chitin, etc. Exemples of biopolymers include Poly (lactic acid) – PLA, biopolyethylene (PE), Poly (hydroxy butirate) – PHB, among others. PLA, a biodegradable polyester, has some limitations since it is brittle and has poor mechanical properties and cannot be used in many applications,[1–3] therefore needing to be modified. This modification may be done by mixing PLA with other polymers or biopolymers forming polymer blends and/ or with clay forming composites (micro or nanocomposites). Since most of polymer blends are immiscible due to the chemical incompatibility between the blends phases, the use of a compatibilizer is necessary. Polymer/clay nanocomposites have better properties than conventional composites using a small ammount of clay ($<5\%$ wt). These properties include high flexural and tensile modulus, high tensile strength, thermal and dimensional stabillity and gas impermeability.[4,5] In some cases the addition of a compatibilizer, as in polymer blends, is necessary to improve the interaction between the clay and the polymer matrix. The aim of this work is the development of bionanocomposites (nancomposites with biopolymer matrix) from PLA/PE blend and clay. PLA is an aliphatic polyester produced by chemical synthesis from lactic acid obtained by the bacterial fermentation of glucose extracted from

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corn, a renewable resource. It is a biocompatible, biodegradable and compostable thermoplastic polymer (semi-crystalline or amorphous).[6] The PE used in the blend is semi-crystalline and is made of raw-material derived from sugar cane, also a renewable resource.

Materials and Methods

Materials

Poly (lactic acid) – PLA, Nature Works™ 2002D, MFI = 4-8 g/10 min (190 °C / 2.16 Kg), was obtained from Cargill, Brazil. Ethylene-Methyl Acrylate-Glycidyl Methacrylate (EMA-GMA) terpolymer, Lotader® AX 8900 (MFI= 6 g/10min) was provided by Arkema, Brazil. Linear Low Density "Green" Polyethylene Hexene copolymer (PE), SLH 218, MFI = 2.3g/10min, from renewable resource, was provided by Braskem, Brazil. Brasgel® PA montmorillonite clay (MMT) from Northeast region of Brazil was provided by Bentonit União Nordeste (BUN). Praepagen® WB (dimethyl stearyl ammonium chloride) cationic surfactant, used to modify the MMT clay, was provided by Clariant, Brazil.

Clay Modification

To make the MMT inorganic clay compatible with PE, it was modified with the surfactant to become organophilic. In the organophilization process, the surface of the clay was modified via ion exchange reaction with the surfactant. The organically modified clay will be called OMMT.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis of the MMT and OMMT clays was carried out in a Perkin Elmer Spectrum 400 infrared spectrometer under Attenuated Total Reflectance (ATR) mode and wave number raging from 4000 to 650 cm^{-1}. The samples were characterized in powder form. This technique was used to evaluate if the surfactant was intercalated between the clay platelets.

X-Ray Diffraction (XRD)

To evaluate the degree of intercalation of the surfactant in the clay and the degree of dispersion (intercalation/exfoliation) of the clay in the blend a Shimadzu XRD-6000 X-Ray Diffractometer (Cu Kα radiation, $\lambda = 1.\ 5406$ Å), was used. For the clay analysis, 2θ ranging from 2 to 10° was used. To evaluate the degree of dispersion of the clay, 2θ ranging from 2 to 30° was used. The basal spacing (d) was calculated using the Bragg's law: $n\lambda = 2d\sin\theta$, where n is the diffraction order, λ is the wave length of the incident radiation, d is the crystal basal spacing and θ is the diffraction angle.

Biocomposites Preparation

The biocomposites containing 3 phr of OMMT clay were prepared in two steps: first a concentrate containing 1:1 of PLA and OMMT organoclay was prepared in a Rheomix 600 internal mixer, equipped with roller blades, attached to a Haake Buchler System 90 torque rheometer at 50 rpm and 180 °C during 10 min. In the second step this concentrate was diluted into either PLA/PE or PLA/EMA-GMA/PE blend in a Coperion Werner-Pfleiderer ZSK 18mm (L/D = 40) co-rotational modular twin screw extruder with screw speed of 250 rpm and feeding rate of 5 Kg/h. The thermal profile from hopper to die was 180:180:180:180:180:180:180 °C. The screw profile containing distributive and dispersive elements is shown in Figure 1.

The PLA/PE and PLA/PE/EMA-GMA blends were prepared under the same processing conditions. PLA was previously dried under vacuum at 80° for 4h. The extruded material was granulated and dried under vacuum for 15 h. The composition of the blends and the biocomposites are shown in Table 1.

Samples Preparation

Samples for tensile and impact strength tests were prepared by injection molding at 180 °C in a Fluidmec H30/40 injector. The mold temperature was 20 ± 02 °C.

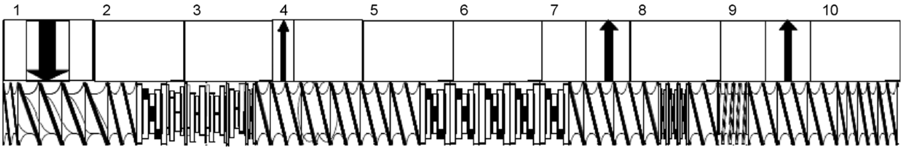

Figure 1.
Screw profile.

Table 1.
Composition of the blends and the biocomposites.

Material	PLA (%)	PE (%)	EMA-GMA (phr)	OMMT (phr)
PLA	100	---	---	---
PLA/PE	80	20	---	---
PLA/PE/EMA-GMA	80	20	10	---
PLA/PE/OMMT	80	20	---	03
PLA/PE/EMA-GMA/OMMT	80	20	10	03

Mechanical Properties

Tensile tests were carried out in a SHIMADZU AG-IS 100 kN Universal Testing Machine, according to ASTM-D 638, operating at crosshead speed of 50 mm/min. Izod impact strength tests were performed according to ASTM-D 256 in notched samples at room temperature using a CEAST Resil 5.5 apparatus. The results reported are the average of 6 samples.

Scanning Electron Microscopy (SEM)

For the morphology analysis, fracture surfaces of the samples subjected to the impact strength tests were coated with gold and analyzed using a SHIMADZU SS X550 Super Scan Scanning Electron Microscope.

Results and Discussion

Clay Characterization

Figure 2 shows the infrared spectra of the MMT and OMMT clays. Comparing the spectra of these two clays it may be observed that the OMMT clay presents three new bands: The first two bands at 2842 and 2916 cm^{-1} respectively, are related to the vibrations of an asymmetric axial deformation of CH_3 and CH_2 groups. The third band at 1470 cm^{-1} is related to the vibrations of the asymmetric and symmetric angular deformations of CH_3 and CH_2 groups. These bands are from Praepagen WB surfactant, indicating its presence in the OMMT clay. A broad band between ~3692 and ~3016 cm^{-1} may also be observed for the MMT clay, which may be related to hydroxyl (OH) groups due to the presence of water molecules in the clay. For the OMMT clay this band almost disappeared indicating that the clay became hydrophobic and that the MMT clay was successfully modified becoming organophilic (OMMT).

Figure 3 shows the XRD patterns of the MMT and OMMT clays. It may be observed that the MMT clay presents one peak at 2θ around 6.1° Corresponding to a

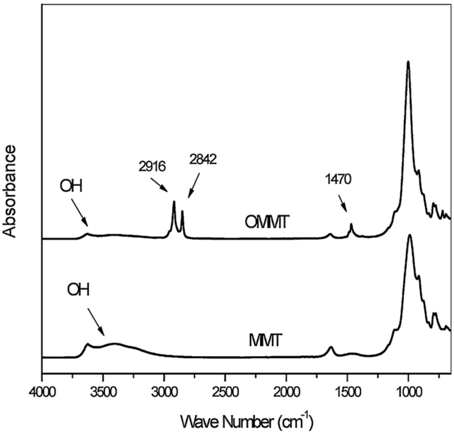

Figure 2.
FTIR spectra of MMT and OMMT clays.

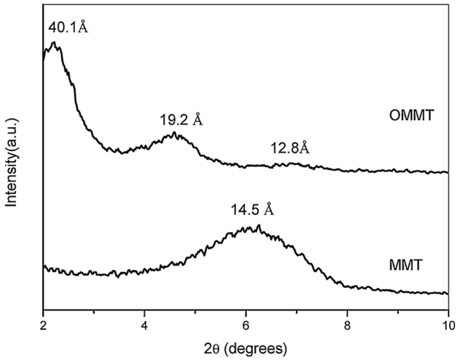

Figure 3.
XRD patterns of the MMT and OMMT clays.

$d_{(001)}$ basal spacing of ~ 14.5 Å. This peak is characteristic of the montmorillonite (MMT) clay. When the MMT clay was modified with the Praepagen WB surfactant the MMT characteristic 001 peak was shifted to lower 2θ angle (from 6.1 to 2.2°) corresponding to an increase in the $d_{(001)}$ basal spacing from 14.5 to 40.1 Å indicating that the surfactant molecules were intercalated between the clay platelets and that the clay was successfully modified becoming organophilic, corroborating the result obtained by FTIR.

Biocomposites Characterization

Figure 4 shows the XRD patterns of the neat PLA, the blends and the biocomposites. It may be observed that PLA presents a broad halo at 2θ between 8 and 26° indicating that it has an amorphous structure. For the PLA/PE blend two diffraction peaks at 2θ ~ 21.1 and 23.4° are observed. These peaks are associated with the (110) and (200) reflections of polyethylene.[7,8] The PLA/PE/EMA-GMA blend shows the same PE peaks, though the peak at 2θ ~ 21.1° is more intense. This increase in the PE peak intensity may be ascribed to the ethylene present in the EMA-GMA terpolymer which is miscible in PE. When the OMMT clay is added to the PLA/PE blend, the MMT peaks do not shift towards lower 2θ angles, indicating that a biomicrocomposite was obtained. When the EMA-GMA terpolymer is added to the PLA/PE/OMMT biocomposite, the MMT clay 001 peak is shifted towards lower 2θ angle (from 2.3 to 2.1°), corresponding to an increase in the d_{001} basal spacing from 38.4 to 42.0 Å, and its intensity is significantly decreased. Comparing with the OMMT clay (Figure 3), the d_{001} basal spacing is increased from 40.1 to 42 Å. These results indicate that a bionanocomposite with an intercalated structure was obtained.

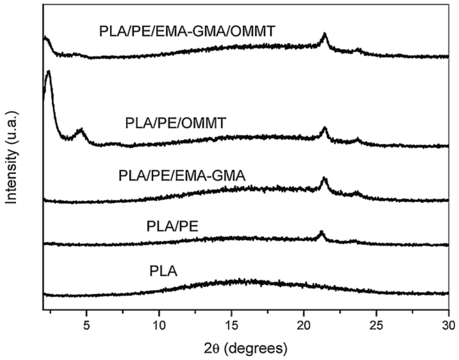

Figure 4.
XRD patterns of the blends and the biocomposites.

Table 2 shows the mechanical properties results of the blends and the biocomposites. It may be observed that the addition of PE to PLA decreases the mechanical properties. This may be related to the immiscibility between PLA and PE phases. Immiscible polymer blends are characterized by high interfacial tension, lack of adhesion between the phases, unstable morphology and coalescence of the dispersed phase particles, thereby leading to poor mechanical properties. It is also observed that the addition of EMA-GMA terpolymer to PLA/PE blend leads to a decrease in the modulus and tensile strength. This may be ascribed to the low modulus of EMA-GMA terpolymer (0.008 MPa). On the other hand, the impact strength is substantially increased. This may be attributed to the reaction of the epoxy ring present in EMA-GMA with both hydroxyl and carboxyl groups present in PLA[9] forming a copolymer *in-situ* at the interface between PLA and PE phases. The addition of the OMMT clay increases the impact strength of PLA/PLE blend. It is known in the literature that

Table 2.
Mechanical properties of the blends and the biocomposites.

Sample	E^a (GPa)	TS^b (MPa)	IS^c (J/m)
PLA	3.06 ± 0.15	58.8 ± 1.4	28.2 ± 0.9
PLA/PE	2.26 ± 0.03	35.4 ± 1.0	26.2 ± 2.3
PLA/PE/EMA-GMA	1.72 ± 0.08	28.8 ± 0.4	56.5 ± 5.7
PLA/PE/OMMT	2.16 ± 0.12	29.1 ± 2.4	34.6 ± 3.2
PLA/PE/EMA-GMA/OMMT	1.66 ± 0.03	25.1 ± 1.3	54.1 ± 6.7

a) Modulus
b) Tensile Strength
c) Impact Strength

the organoclay, when present at the interface, decreases the dispersed phase domains size by suppressing the coalescence of the particles.[10] In this case the decrease in the PE dispersed phase domains size may have resulted in the increase in the impact strength of the PLA/PE blend. The presence of the clay in the PLA/PE/EMA-GMA blend decreases the modulus and tensile strength while the impact strength is slightly decreased. A possible interpretation is that some clay agglomerates present in the PLA/PE/EMA-GMA/OMMT bionanocomposite, with an intercalated structure, act as stress concentrators, decreasing the mechanical properties. This bionanocomposite shows higher impact strength than the PLA/PE/OMMT biomicrocomposite. This result may be ascribed to the presence of the EMA-GMA terpolymer, which has polar groups that may interact with OMMT clay.[11]

Figure 5 shows the SEM micrographs of the blends and the biocomposites. It may be observed that the PLA/PE blend (Figure 5a) is characterized by a high PE dispersed phase domains size and lack of adhesion between the PLA and PE phases, since many PE particles were pulled out from the PLA matrix, leading to a poor impact stregnth (Table 2). The addition of the EMA-GMA terpolymer to the PLA/PE blend (Figure 5b) leads to a substantial decrease in the PE domains size and to an improvement in the adhesion between the PLA and PE phases, resulting in higher impact strength. The presence of the OMMT clay in the PLA/PE blend (Figure 5c) also leads to a significant decrease in the PE domains size, though the adhesion between the PLA and PE phases is not improved. However the decrease in the PE domains size was suficient to increase the impact strength of the PLA/PE blend. This decrease in the PE dispersed phase domains size is more pronounced in the PLA/PE/EMA-GMA/OMMT bionanocomposite (Figure 5d). This may be related to the combining effect of EMA-GMA terpolymer and OMMT clay when present together.[12]

Conclusion

In this work a montmorillonite (MMT) clay from Northeast region of Brazil was used in the development of bionanocomposite from PLA/PE blend. The MMT clay was modified with a inonic surfactant to become organophilic (OMMT). FTIR and XRD analyses indicated that the clay was sucessfully modified by the surfactant becoming organophilic (OMMT), with the surfactant molecules intercalated between the MMT platelets. XRD analysis also indicated that for the PLA/PE/OMMT biocomposite a biomicrocomposite was obtained, since no shift in the MMT peaks towards lower 2θ angles was observed. For the PLA/PE/EMA-GMA/OMMT biocomposite, a bionanocomposite with an intercalated structure was obtained. The presence of the EMA-GMA terpolymer in the PLA/PE blend led to a significant increase in the impact strength, decreasing the PE phase domains size and improving the adhesion between PLA and PE phases. The addition

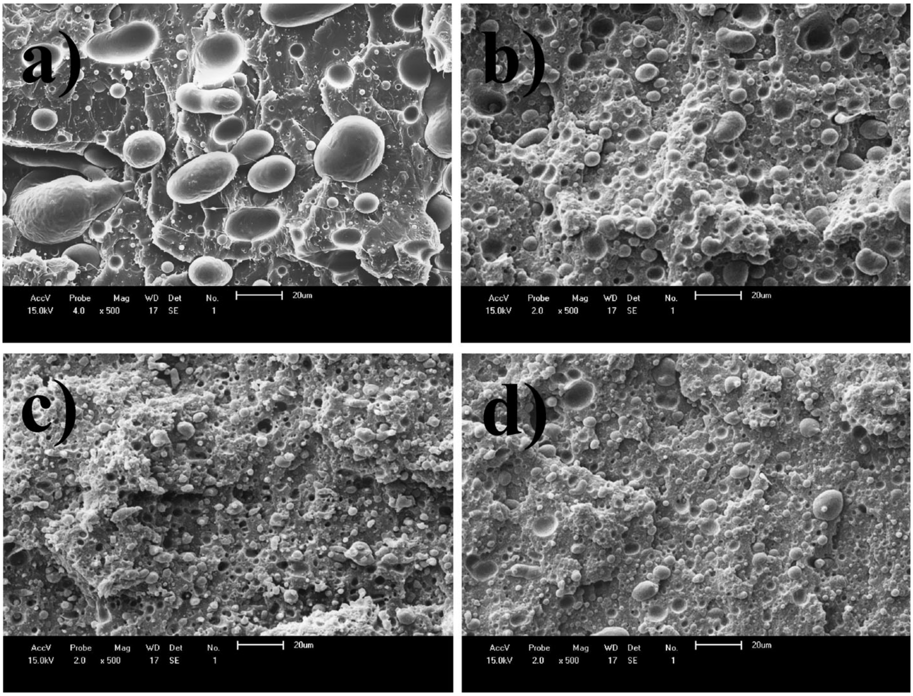

Figure 5.
SEM micrographs of the blends and the biocomposites: a) PLA/PE; b) PLA/PE/EMA-GMA; c) PLA/PE/OMMT; d) PLA/PE/EMA-GMA/OMMT.

of the OMMT clay slightly decreased the impact strength of the PLA/PE/EMA-GMA blend. The presence of the OMMT clay in the PLA/PE/OMMT and PLA/PE/EMA-GMA/OMMT biocomposites subtstaintially decreased the PE dispersed phase domains size. This decrease was more pronounced in the PLA/PE/EMA-GMA/OMMT bionanocomposite.

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