"Effect of different compatibilizers on environmentally friendly composites from poly(lactic acid) and diatomaceous earth"

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Abstract

Environmentally friendly composites from poly(lactic acid) (PLA) and diatomaceous earth (DE) were successfully manufactured by extrusion, followed by injection molding. Diatomaceous earth was used as a filler; several compatibilizer/coupling agents, namely silane (3-glycidyloxypropyl) trimethoxysilane, epoxy-styrene-acrylic oligomer (ESAO) and maleinized linseed oil (MLO) were used to improve polymer-filler interactions. Mechanical characterization was carried out by standard tensile, impact and hardness tests while morphological characterization of the fractured surfaces was conducted by field emission scanning electron microscopy (FESEM). The effect of diatomaceous earth was evaluated by differential scanning calorimetry (DSC) and dynamic mechanical thermal behavior (DMTA). Results show that diatomaceous earth addition provides improved tensile modulus and induces more brittle composites due to stress concentration phenomena. The addition of compatibilizers on PLA/DE positively contributes to improve ductile properties thus leading to high environmental efficiency materials with balanced mechanical properties. Specifically, the compatibility improvement between the PLA and diatomaceous earth was good with maleinized linseed oil (MLO) which contributed to improve the impact strength, which is a key factor in PLA-based composites due to the intrinsic brittleness of neat PLA.

Keywords: poly(lactic acid); diatomaceous earth; composites; natural fillers.

1. Introduction

Currently, the so-called active packagings are becoming very important in the packaging industry. An active packaging system does not act only as a container/protective barrier of the food, but also can provide additional features such as increased shelf-life, improved integrity and increased product quality. But the most important thing is that all these features can be provided without adding any substance to the food. According to Tornuk *et al.* "active packagings" are made with materials that incorporate specific components that provide some antimicrobial and/or antioxidant activity, which lengthen the foodstuff shelf-life [1]. Packaging must prevent the entry or exit of moisture, prevent contamination by microbial growth and act as a barrier against the diffusion of oxygen, carbon dioxide, etc.[2-4] . Active packaging systems use active components which are embedded into a polymer matrix or encapsulated into diferent particles/microcapsules to control its release during the storage time of food. In addition, in the last decade, the food packaging industry has progressively introduced the use of biopolymers that contribute to minimize the environmental damage caused by petrochemical polymers. Nowadays, containers and plastic packagings represent around 39.9% of the total domestic waste [5]. To overcome this problem, one interesting approach is the use of biodegradable/disintegrable polymers and fully or partially biobased polymers. Biopolymers, besides being respectful with the environment, minimize the carbon footprint and represent high environmental efficiency materials for industry. One of the most used biopolymers is the polylactic acid (PLA)[6]. PLA is an aliphatic polyester obtained from the bacterial fermentation of vegetable biomass, rich in starch such as corn, wheat, sugar cane, etc. [7].

Functional properties of some biopolymers can be improved by the incorporation of particles which has led to the so-called bio-composites [8]. Basically, a bio-composite is

composed of a biopolymer matrix with particles, usually in the micro or nano scale range. This new generation of functional materials show improved properties as compared to the base biopolymers, due to the high surface area that micro and nanoparticles can provide. In general, these materials show better mechanical, thermal, rheological and barrier properties [9, 10]. Nanoparticles have been successfully introduced into polymer matrices in the form of platelets, nanowires, nanorods, nanotubes, whiskers, etc. and they are mainly formed by nanoclays, silicates, carbon, cellulose crystals, etc. Biodegradable PCL-based films with organo-modified Argelian montmorillonite has shown enhanced mechanical, barrier and antimicrobial properties [11]. Sodium montmorillonite has been incorporating to a thermoplastic starch (TPS)/polylactic acid (PLA) blends, obtaining a mechanically improved composite since nanoclay acts as compatibilizer between both matrix [11] Summarising, several research works have archived that silicates and nanoclays offer high relevance to this technology due to their abundance, low cost, natural origin and good processability, and, what is more important for the packaging industry, according to FDA (American Food and Drug Administration) and EFSA (European Food Safety Authority), they are suitable to be used in food packaging [12, 13].

Another interesting characteristics of the clays is the possibility of being used as carriers for controlled release of active agents during food packaging, extending its shelf-life. Some research groups have analyzed the proper use nanoclays in active packaging for various purposes. Montmorillonite (MMT) and halloysite nanotubes (HTNs) particles have been loaded with different active compounds and successfully added to films of linear low density polyethylene (LLDPE). These nanofillers showed good dispersion in the polymeric matrix, and contributed to improve the barrier properties of the material, thus allowing to extend the shelf-life of packaged fresh food. [14]. Halloysite nanotubes (HNTs), at 1-7 wt%, have also been successfully incorporated

into polyethylene terephthalate (PET) as nanocontainers of antimicrobial agents for active packaging [15]. PLA nanocomposites with 5 wt% of HNTs showed an increase of 43% in the tensile strength of PLA due to the formation of hydrogen bonds between the hydroxyl groups of PLA chains and the outer-surface siloxane groups of HNT [16]. Bendahou *et al.* [17] used zeolites as nanofillers into a PLA matrix, obtaining important improvements in barrier and antimicrobial characteristics as well as improved mechanical behavior (high modulus and high tensile strength). PLA/nanoclay composites are interesting materials for active packaging with environmentally-friendly performance as reported by Lorite *et al.* [18]. Jampilek *et al.* [4] suggested that bio-nanocomposites, using SiO_2, offer good packaging properties due to their fine dispersion, increased mechanical strength, reduced gas permeability and improved water resistance.

Another source of silica is diatomaceous earth (DE). Its size and geometry, characterized by the presence of a complex 3D-porous structure, make it a good candidate to be loaded with active compounds that can provide antimicrobial or antioxidant properties. Diatomaceous earth, or diatomite, is composed mainly of amorphous silica SiO_2. It is made by the sedimentation of the "micro-shells" of marine eukaryotic unicellular organisms that form phytoplankton. These silica shells have a series of porous patterns in their structure, and it is this what makes them suitable to carry low molecular weight substances. Their nanoporous structure gives them a high surface area, above 200 m^2 g^{-1}. Some of their features are low density, porous structure, abrasive character, chemically inertness, biocompatible, good absorption capacity, low thermal conductivity, high resistance to acids and permeability. Diatomites are a natural, abundant and cost-effective product. Currently, diatomite has applications as a filtration element, absorbent, natural pesticide, functional additive, dental filling, membranes or chemical sensors, among others. Diatomites can act as inorganic fillers

with dual functions in a bio-composite: as a reinforcement component, hampering the gas diffusion through the material and as carrier/container for a controlled release of active substances [19-23].

However, a possible structural limitation of bio-composites is the poor (or lack of) particle/polymer interaction. Some investigations have been developed in this regard, which have optimized the addition of coupling agents and/or compatibilizers that improve the formation of an interface between particles and the olymeric matrix, with the subsequent positive effect on mechanical properties [24, 25].

In this work, bio-composites based on polylactic acid (PLA) matrix and diatomaceous earth (DE) were manufactured by injection moulding. The effect of different coupling agents/compatibilizers on the mechanical, thermal, thermomechanical and biodegradation (disintegration in controlled compost) properties of PLA/DE bio-composites is studied. The efficiency of a glycidyl silane, *i.e.* (3-glycidyloxypropyl) trimethoxysilane, is compared with a petroleum-derived compatibilizer, *i.e.* acrylic styrene-acrylic oligomer (ESAO) and a vegetable oil-derived compatibilizer obtained from linseed oil, *i.e.* maleinized linseed oil (MLO).

2. Experimental.

2.1. Materials.

A polylactic acid (PLA), aliphatic polyester grade Ingeo Biopolymer 6201D from Nature Works LLC (Minnetonka, USA) was used as the matrix for bio-composites. This grade has a melt flow rate (MFR) comprised between 15 and 30 g/(10 min) (measured at 210 °C). This particular MFR makes this grade suitable for injection moulding.

Diatomaceous earth (DE) was supplied by Sigma-Aldrich Quimica S.L. (Madrid, Spain), CAS 68855-54-9 and chemical composition 89% SiO_2, 1.88% Na_2O+K_2O, 6.73% CaO, 1% Al_2O_3 and 0.46% Fe_2O_3. This kind of diatomaceous earth is characterized by showing a wide variety of particle sizes and geometric shapes, predominating disk and tubular forms as well as a high characteristic porosity (**Figure 1**).

To improve particle/polymer interactions different strategies were followed. The first one was a previous treatment of DE with a coupling agent. A glycidyl silane, namely (3-glycidyloxypropyl) trimethoxysilane, CAS 2530-83-8 supplied by Sigma-Aldrich with a molecular weight of 236.34 g mol^{-1} and a density of 1.07 g cm^{-3} was used at a concentration of 1.3 wt% in aqueous dissolution. In addition to the silanization approach, two compatibilizers were used during the extrusion/compounding process. The first one is a petroleum-derived compatibilizer, consisting on an epoxy styrene-acrylic oligomer (ESAO), Joncryl ADR 4368-C was provided by BASF S.A. (Barcelona, Spain) in the form of solid flakes. Its molecular weight is 680 g mol^{-1}, glass transition temperature (T_g) is 54 °C, and the epoxy equivalent weight (EEW) is 285 g mol^{-1}. The recommended dosage by manufacturer is 0.1–1 wt% for appropriate processability with biodegradable polyesters. The second compatibilizer is a vegetable oil-derived compound, maleinized linseed oil (MLO) from Traquisa S.L. (Barcelona, Spain). This maleinized oil possesses an iodine index between 109–120 g/(100 g) and a density of 0.92 g cm^{-3}.

2.2. Sample preparation

PLA pellets and diatomaceous earth were dried at 60 °C for 18 h to remove the residual moisture. **Table 1** summarizes the compositions and coding of the developed formulations.

Table 1. Composition and code of the different PLA/DE composites formulations.

Reference	PLA (wt%)	DE (wt%)	GLYMO* pretreament	ESAO** (phr)	MLO** (phr)
PLA	100	-	-	-	-
PLA-DE	90	10	-	-	-
PLA-DE-GLY	90	10	yes	-	-
PLA-DE-ESAO	90	10	-	1	-
PLA-DE-MLO	90	10	-	-	5

* Silanization was carried out on DE in an aqueous solution containing 1.3 wt% GLYMO. The solution was subjected to stirring for 1 h and filtered. After filtration, DE was subjected to a drying process at 40 °C for 24 h.

** Both ESAO and MLO were added during the extrusion/compounding process at the recommended dosage in phr (parts of compatibilizer per hundred parts of PLA/DE composites).

The selected amounts of the different compatibilizing systems is not arbitrary. Regarding silanization with GLYMO, typical concentration of the silane in the solution is comprised between 1 – 1.5 wt% to obtain the best polymer/particle interaction[26, 27]. With regard to the use of ESAO, the manufacturer recommends this amount since higher loadings, lead to undesired effects such as gel formation which, in turn, leads to a decrease in mechanical properties This behavior has also been reported by Torres-Giner[24]. Finally, regarding MLO; it is a relatively new compatibilizer and previous results suggest 5 wt% offers comparable results to the other compatibilization systems[28, 29].

All four compositions were extruded in a twin screw co-rotating extruder from DUPRA S.L. (Castalla, Spain). The temperature profile in the extruder was set to 165 $^{\circ}$C, 170 $^{\circ}$C, 175°C and 180 $^{\circ}$C (from the hopper to the die) and the rotating speed was set to 40 rpm. After extrusion, the different compounds were pelletized for further processing by injection molding in a Meteor 270/75 from Mateu & Solé (Barcelona, Spain). The profile temperature, from the feeding zone to the injection nozzle, was set as follows: 170-180-190-200 $^{\circ}$C. Testing pieces with a thickness of 4 mm were obtained for further characterization.

2.3. Testing and characterization.

Mechanical Testing.

Tensile properties PLA/DE bio-composites were obtained as indicated in ISO 527-1 using a universal test machine ELIB 30 from S.A.E. Ibertest (Madrid, Spain). The selected load cell was 5 kN and the crosshead speed was set to 2 mm min^{-1}. The main parameters obtained from the tensile tests were the tensile modulus (E_t), the tensile strength (σ_t) and the elongation at break in percentage (%ε_b). The impact strength was tested in a 6 J Charpy pendulum from Metrotec S.A. (San Sebastián, Spain) following the guidelines of ISO 179. Finally, the hardness of PLA/DE bio-composites was measured in a Shore D durometer mod. 673-D from J. Bot S.A. (Barcelona, Spain) following the ISO 868. At least five different samples were tested for each mechanical property and the average values of the different properties were calculated.

Microscopic characterization.

Fractured surfaces from impact tests of PLA/DE bio-composites were observed by field emission scanning electron microscopy (FESEM) in a ZEISS ULTRA 55 FESEM microscope from Oxford Instruments (Abingdon, United Kingdom), working at an acceleration voltage of 2 kV. Samples surfaces were coated, prior to analysis, with a gold-palladium alloy in a Quorum Technologies Ltd EMITECH model SC7620 sputter coater (East Sussex, UK).

Thermal characterization.

Thermal transitions of PLA/DE bio-composites were obtained by differential scanning calorimetry (DSC) in a Mettler-Toledo 821 calorimeter (Schwerzenbach, Switzerland). Samples with an average weight of 5-8 mg were subjected to a three step program with an initial heating cycle from 25 °C to 200 °C at 10 °C min^{-1} to remove thermal history, followed by a cooling to 0 °C at -10 °C min^{-1}. Finally, a second heating cycle from 0 °C up to 350 °C at 10 °C min^{-1} was used to evaluate all thermal transitions. All tests were run in nitrogen atmosphere at a constant flow of 30 mL min^{-1}. Standard aluminium sealed crucibles with a total volume of 40 µL were used to place the samples. In addition to above-mentioned temperatures, the degree of crystallinity (X_c) was calculated by using the following equation (**Equation 1**):

$$X_C = \left[\frac{\Delta H_m - \Delta H_{CC}}{\Delta H_m^0 \cdot (1-w)}\right] \cdot 100 \qquad \textbf{Equation 1}$$

Where ΔH_m and ΔH_{CC} (J g^{-1}) correspond to the melt and cold crystallization enthalpy respectively. ΔH_m^0 (J g^{-1}) is a theoretical value that corresponds to a fully crystalline PLA. This has been taken as 93.0 J g^{-1} as reported in literature [30], and w indicates the weight fraction of total additives and/or fillers in PLA formulations.

Thermogravimetric analysis (TGA) was used to evaluate thermal stability of PLA/DE bio-composites at high temperatures. The selected thermal program consisted on a single heating from 30 °C to 700 °C at a constant heating rate of 20 °C min^{-1} in air atmosphere. TGA characterization was carried out in a TGA/SDTA 851 thermobalance from Mettler-Toledo Inc. (Schwerzenbach, Switzerland).

Thermo-mechanical characterization.

Dimensional stability was assessed by obtaining the coefficient of linear thermal expansion (CLTE) in a thermomechanical analyzer (TMA) mod. Q400 from TA Instruments (New Castle, USA). Squared samples (10x10 mm^2) and a thickness of 4 mm were subjected to a temperature sweep from 0 °C up to 140 °C at a heating rate of 2 °C min^{-1} with a constant applied force of 20 mN.

Dynamic-mechanical thermal characterization (DMTA) was carried using an AR-G2 oscillatory rheometer from TA Instruments (New Castle, USA), equipped with a clamp system for solids working in a combination of torsion and shear. Rectangular samples (10x40 mm^2), with average thickness of 4 mm, were subjected to a temperature sweep from 30 °C up to 140 °C at a rate of 2 °C min^{-1}. The maximum shear deformation percentage (%γ) was set to 0.1%. The storage modulus (G') and the dynamic damping factor (tan δ) were obtained as a function of increasing temperature at a constant frequency of 1 Hz.

Disintegration tests

Disintegration in simulated composting conditions (controlled compost soil) was conducted at a temperature of 58 °C and a relative humidity (RH) of 55% as indicated in ISO 20200. Injection-molded pieces sizing 4x20x20 mm^3 were placed in a

carrier bag and buried in a controlled compost soil made of sawdust (40 wt%), rabbit-feed (30 wt%), ripe compost (10 wt%), corn starch (10 wt%), saccharose (5 wt%), cornseed oil (4 wt%), and urea (1 wt%). Samples were periodically unburied from the composting facility, washed with distilled water, dried and subsequently weighed in an analytical balance. The percentage mass loss during disintegration was calculated following **Equation 2.**

$$\text{Weight loss } (\%) = \left(\frac{W_0 - W_t}{W_0}\right) \cdot 100 \qquad \textbf{Equation 2}$$

Where W_0 is the initial dry weight of the sample and W_t is the weight of the sample after a bury time t. All tests were carried out in triplicate to ensure reliability. The reported values correspond to the average.

3. Results and discussion

3.1. Mechanical properties of PLA-diatomaceous earth composites.

Figure 2 shows the stress-strain curves and Table 2 resumes the changes in the mechanical behavior of PLA/DE bio-composites with different coupling agents. Neat PLA, used as matrix, is a brittle biopolymer with low elongation at break, 6.4%. Adding diatomaceous earth as fillers, the bio-composite presents a more rigid behavior. PLA-DE elastic modulus increases by 7.2%, while a slightly decrease in the tensile strength and elongation at break is observed, which is due to the stiffening caused by DE filler [9].

Table 2. Mechanical properties, tensile modulus (Et), tensile strength (σ_t) and elongation at break (%ε_b), of PLA-diatomaceous earth (DE) composites with different compatibilization systems.

Reference	Tensile properties			Impact Strength (kJ m^{-2})	Hardness Shore D
	Elastic modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)		
PLA	891 ± 76	65.8 ± 0.4	6.4 ±1.1	28.1 ± 3.4	80.0 ± 3.8
PLA-DE	955 ± 90	62.5 ± 0.7	4.9 ± 1.7	24.7 ± 1.1	82.4 ± 1.2
PLA-DE-GLY	1222 ± 59	60.8 ± 1.1	5.7 ± 0.7	30.3 ± 2.9	81.0 ± 0.8
PLA-DE-ESAO	1222 ± 54	59.3 ± 3.3	5.3 ± 1.4	33.5 ± 1.9	83.0 ± 2.7
PLA-DE-MLO	1122 ± 55	40.0 ± 0.8	13.8 ± 2.6	21.9 ± 1.2	82.0 ± 1.2

If DE is previously subjected to a silanization process (PLA-DE-GLY), the elastic modulus increases by 28%[31]. A slight coupling effect can be observed for these composites as the elongation at break increases from 4.9% (PLA-DE) up to 5.7% (PLA-DE-GLY), indicating a slightly decrease in brittleness. The addition of the ESAO as coupling agent has, practically, the same effect on the tensile properties of PLA-DE. Nevertheless, the use of the maleinized linseed oil (MLO), allows obtaining a much more ductile material due to several overlapping processes such as PLA plasticization, chain extension and compatibilization. Tensile strength decreases from 62.5 MPa of PLA-DE, without any coupling agent/compatibilizer, to 40 MPa for PLA-DE-MLO bio-composite. This is a direct consequence of the plasticization effect MLO can provide [28]. Accordingly, the elongation at break increases up to 13.8%, which is almost triple of PLA-DE value. PLA-DE-MLO bio-composite shows a less fragile behavior. Some

investigations have shown that this effect is a consequence of the maleinized vegetable oil dual function: on one hand, MLO acts as a compatibilizer between the polymeric matrix and the silica DE filler. This compatibilization effect is directly related to the reaction/interaction between the maleic anhydride pendant groups in MLO and the hydroxyl groups contained in both PLA (end-chains) and siloxane/silanol groups in DE as observed in other polyester composites [28]. On the other hand, MLO provides a plasticizing effect that allows chain motion with a slight decrease in T_g [29, 32].

On the other hand, **Table 2** shows the results obtained by the Charpy's impact test and Shore D hardness tests for PLA/DE bio-composites. The intrinsic PLA fragility is responsible for its low impact strength. The addition of diatomaceous earth particles reduces impact strength by 12%, which indicates an embrittlement of the composite. This is in total agreement with the tensile results as DE in uncompatibilized PLA-DE composite does not interact in a great extent with PLA. Generally, the addition of particle fillers in a thermoplastic matrix means a remarkable embrittlement in the composite due to poor particle/polymer interactions. These particles form a dispersed phase in the polymer matrix, PLA in this case, with a weak particle/matrix interaction. This lack of interaction, justifies the embrittlement in PLA-DE bio-composite. A previous treatment with glycidyl silane (PLA-DE-GLY), slightly improves the impact strength, reaching values of 30.3 kJ m^{-2}. Meanwhile, the use ESAO as compatibilizer achieved an interesting increase in the impact strength, superior to 35%, as compared to uncompatibilized PLA-DE composite. The ESAO (and, particularly, the glycidyl group contained in this oligomer) can chemically react with the end-chain hydroxyl groups of PLA, as well as with the hydroxyl groups in silica surface, thus favoring a compatibilizing effect [24, 32]. As suggested by results, both GLYMO pre-treatment and use of ESAO give an improvement on ductility on PLA-DE composites; these results

agree with the previous characterization by tensile test. However, the addition of MLO does not improve the impact strength on PLA-DE composite; in fact, the impact strength is slightly reduced. Although MLO provides an important increase in ductile properties (elongation at break), the impact strength is not only related to ductile properties but also on resistant properties such as tensile strength. As it has been described previously, the tensile strength decreases in a moderate way by the MLO addition. So that, the overall effect on impact strength is a slight decrease. Addition of MLO to PLA-DE bio-composite increases its ductile behavior with a remarkable increase in elongation at break, but the overall performance regarding impact strength is lower than that observed for PLA-DE-GLY and PLA-DE-ESAO which offer a better balance between both ductile and resistant properties and, consequently, they provide higher impact strength.

Regarding Shore D hardness, the results obtained show no significant variation, with values about 80 Shore D. Although slightly higher Shore D values can be observed for the uncompatibilized PLA-DE composite, the variation is within the standard deviation, so that, the variation is not significant.

The results obtained by mechanical tests, suggest that MLO is suitable as a compatibilizer in PLA-DE composites since it improves the ductility of these materials. The addition of MLO, increases the ductility (measured through $\%\varepsilon_b$) of PLA-DE composites, with a good balance on other mechanical resistant properties (E_t, σ_t, HS_D). This good mechanical performance can be due to the reaction of the hydroxyl groups on PLA end-chains and hydroxyl groups on DE silica with the anhydride groups contained in MLO that lead to several overlapping effects such as chain extension, branching and/or crosslinking [28, 33]. In addition to this phenomenon, MLO can also

provide slight plasticization effects on PLA-DE composites as observed in other polyester composites [28, 34].

3.2. Morphology of PLA-diatomaceous earth composites.

– a) & b), PLA-DE-GLY – c) & d), PLA-DE-ESAO – e) & f), and PLA-DE-MLO – g) & h). The images correspond to impact fractured surfaces.

The impact fracture surfaces of the samples are shown in **Figure 3**, in which the effect of the different compatibilization systems, *i.e.* previous silanization, addition of ESAO or MLO, on PLA-DE bio-composites is analyzed. In **Figure 3(a)** and **(b)**, the surface morphology of the uncompatibilizaed PLA-DE composite is observed at different magnifications. This fracture is characterized by a biphasic structure with a predominant matrix phase corresponding to PLA and a dispersed phase of embedded diatomite particles. The topography of the PLA matrix is characterized by a smooth and homogeneous morphology, typical of a brittle material. Diatomite particles appear embedded in the matrix. Somewhat lack of particle/matrix continuity is evidenced by the micro-gap existing around DE particles surroundings. **Figure 3(c)** and **(d)**, corresponding the silanized DE particles (PLA-DE-GLY) also shows a fracture morphology with two phases. PLA matrix seems to be smooth and homogeneous as well as in PLA-DE composites; nevertheless, a little better adherence between diatomite particles and the PLA matrix is observed, since the surrounding micro-gap has practically disappeared, thus indicating a more intense particle/matrix interaction. This same effect can be observed in **Figure 3(e)** and **(f)**, corresponding to bio-composite compatibilized with 1 phr ESAO (PLA-DE-ESAO). There is some interaction between the PLA matrix and the diatomaceous particles, having a smaller interface gap comparatively to uncompatibilized PLA-DE composites. These results corroborate

those obtained in the mechanical characterization. The smaller micro-gap surrounding the diatomite particles, indicates an improvement in the particle/matrix interaction. This phenomenon enables load transfer between the matrix and the reinforcement filler, so that PLA-DE-GLY and PLA-DE-ESAO bio-composites offer a slight improvement on their elongation at break and an interesting increase in impact resistance, compared to uncompatibilized PLA-DE. Regarding the effect of the incorporation of MLO, in **Figure 3(g)** and **(h)**, a change in the PLA matrix morphology can be clearly distinguished. In this case, the matrix shows a high density of spherical cavities/voids. These microvoids are due to the formation of a new dispersed phase, rich in MLO, embedded in the PLA matrix. This is a consequence of the restricted miscibility between the maleinized vegetable oil and the polymer. This new phase has spherical shapes and it shows a droplike morphology with scattered spherical domains. Some of these microvoids correspond to MLO-rich zones that are pulled off during the deformation/fracture process. MLO can remain as a "dispersed phase" in the PLA matrix, affecting its homogeneity and, therefore, decreasing its impact resistance. This "dispersed phase" is formed as a consequence of plasticizer saturation as observed in similar systems [35-37]. Some research works show that the addition of natural-derived maleinized oils (MLO, for example) reach plasticizer saturation in PLA and other polyesters at a relatively low oil concentration. This leads to phase separation, which is visible as rounded shapes and hollows [33, 35, 38-41]. In addition, a certain decrease in the gap size between the PLA matrix and diatomite particles can be observed. This phenomenon positively contributes to improve the elongation at break as compared to uncompatibilized PLA-DE composite. Regarding some previous studies, it has been observed that epoxidized or maleinized vegetable oils, such as palm oil, cottonseed oil, flaxseed oil, among others, produce a plasticizing effect in thermoplastic matrices at relatively low concentrations [36, 40, 42, 43].

In an unexpected way, incorporating 5 phr MLO the PLA-DE bio-composite, an improvement of the impact resistance is not obtained. As indicated previously, the impact strength is not only linked to ductile properties (elongation at break) but also on mechanical strength (tensile strength). By analyzing in detail the internal structure of PLA-DE-MLO composites, and mainly due to the highly porous structure of diatomite particles, it can be observed that some part of the added MLO has been trapped inside the diatomite porous structure and, therefore, some MLO is not available as plasticizer/compatibilizer. This phenomenon is observed in **Figure 4**, in which, spherical shapes correspond, as previously indicated, to a MLO-rich phase, and are located in the interior of the diatomaceous shell.

3.3. Thermal properties of PLA-diatomaceous earth composites.

Thermal characterization by differential scanning calorimetry (DSC) allowed obtaining the characteristic thermograms as gathered in **Figure 5** for neat PLA, uncompatibilized PLA-DE and compatibilized PLA-DE with different strategies (silanizacion or compatibilization with ESAO or MLO). All the thermograms show the same thermal behavior. At moderate temperatures between 60-70 $^\circ$C temperatures, the a step change in the baseline can be detected, which corresponds to the PLA glass transition temperature (T_g); the exothermic peak located between 110-130 $^\circ$C is attributable to the cold crystallization temperature of PLA, (T_{cc}), and, finally, the endothermic peak comprised between 160-175 $^\circ$C stands for the melting process of crystalline PLA domains (T_m).

Table 3 gathers the main results obtained by DSC for PLA and its bio-composites with DE. First, it can be observed that the addition of diatomaceous earth does not change the T_g of neat PLA, remaining at around 63 °C as reported by Cacciotti *et al.* in PLA with functional diatomite loaded with coffee ground extracts [19]. The T_g of the compatibilized PLA-DE bio-composites, does not show any relevant changes. In fact, the T_g changes in the 60.4-62.4 °C range for all composites. Nevertheless, the plasticization effect of MLO is clearly evidenced by the highest T_g decrease down to values of 60.4 °C. Regarding the cold crystallization process, neat PLA shows a peak (maximum crystallization rate) at 119.4 °C. The only addition of diatomite, gives a slight decrease in T_{cc} down to 115.6 °C which is indicating a nucleant effect of diatomite particles. PLA-DE-GLY and PLA-DE-ESAO show a crystallization peak almost identical to neat PLA thus giving evidence of some particle/polymer interaction that affects the crystallization process (related to chain mobility). Once again, the effect of MLO is quite different as the PLA-DE-MLO composite shows a T_{cc} of 108.9 °C which is in total agreement with the above-mentioned MLO plasticizing effect. MLO molecules, provided improved mobility to PLA polymer chains and can crystallize at lower temperature. In general, a plasticizer increases the free volume and, subsequently, reduces polymer-polymer interactions, thus providing increased chain mobility and decreasing T_{cc} values [36, 44].

Table 3. Thermal properties obtained by differential scanning calorimetry (DSC) of PLA-diatomaceous earth (DE) composites with different compatibilization systems.

Reference	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J g^{-1})	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J g^{-1})	χ_c (%)
PLA	63.1±0.6	119.4±1.0	27.4±0.6	167.6±0.9	172.2±0.7	36.5±0.3	9.8±0.6

PLA-DE	62.9±0.7	115.6±1.4	26.5±0.7	164.8±1.0	172.4±1.2	32.7±0.5	7.3±0.7
PLA-DE-GLY	62.4±1.0	120.4±0.9	21.6±0.4	166.8±0.7	172.4±1.1	30.1±0.4	10.2±0.4
PLA-DE-ESAO	61.9±0.9	122.2±1.4	20.9±0.6	167.7±0.9	170.5±0.7	30.5±0.4	11.4±0.8
PLA-DE-MLO	60.4±0.8	108.9±1.2	20.7±0.7	--	169.7±1.1	35.6±0.5	17.7±0.7

DSC thermograms also show that neat PLA has two endotherm peaks for its melting, T_{m1} and T_{m2}, which correspond to a difference in the morphology of the PLA crystallites. These different crystalline structures differ, mainly, in the width of the sheets and size of the spherulites [19, 45]. The addition of 10 wt% diatomaceous earth to the PLA matrix (PLA-DE), practically does not modify T_{m1} and T_{m2} values, retaining the peak values at 165 °C and 172°C respectively. Both the silane pretreatment on DE (PLA-DE-GLY) and the use of 1 phr ESAO have the same effect with not relevant change in the melting process (peaks, and shape). Nevertheless, once again, the use of MLO as compatibilizer in PLA-DE-MLO composites, shows a different melting process, characterized by a single melting peak located at 170 °C, meaning that all crystalline zones have the same geometrical shape and melt temperature range.

The normalized enthalpies corresponding to the cold crystallization and melting processes, ΔH_{cc} and ΔH_m, respectively, allowed estimating the degree of crystallinity of the PLA phase in PLA-DE composites. **Table 3** shows that the PLA has a degree of crystallinity of 9.8%, which is reduced down to 7.3% by the addition of 10 wt% diatomaceous earth. The DE particles embedded in the PLA matrix hinders the formation of crystallites. On the other hand, bio-composites with any compatibilization process show increased crystallinity. Firstly, both silanized (PLA-DE-GLY) and ESAO-compatibilized (PLA-DE-ESAO) composites exhibit a considerable increase in crystallinity, up to 39% and 55% respectively compared to the uncompatibilized PLA-

DE composite. Regarding MLO-compatibilized composites (PLA-DE-MLO), it is worthy to note a decrease in crystallinity regarding the previous compatibilizing approaches but the overall degree of crystallinity is still higher than neat PLA, with a value of 17.7%. This greater crystallinity of the PLA-DE-MLO composite is due to the improved chain mobility caused by the addition of MLO, which enables crystallization [38].

Results obtained by the TGA analysis are gathered in Figure 6 for neat PLA, PLA with diatomaceous earth and PLA-DE with different compatibilizing systems. TGA thermograms indicate that all developed materials undergo degradation / decomposition in a one-step process. **Table 4** shows how the beginning of thermal degradation process, $T_{5\%}$ (temperature measured for a mass loss of 5%) is slightly retarded with the addition of diatomites, as well as the maximum degradation temperature, T_{max}.

Table 4. TGA properties of PLA-diatomaceous earth (DE) composites with different compatibilization systems.

Reference	$T_{5\%}$ (°C)	T_{max} (°C)	Residual mass (%)
PLA	336.8±1.3	365.3±1.0	1.5±0.2
PLA-DE	342.3±0.9	368.4±1.1	14.4±0.5
PLA-DE-GLY	332.7±1.1	370.7±1.3	9.4±0.7
PLA-DE-ESAO	333.4±1.3	360.4±0.9	7.8±0.4
PLA-DE-MLO	325.1±0.8	346.1±1.2	7.6±0.5

3.4. Thermomechanical properties of PLA-diatomaceous earth composites.

The variation of the storage modulus (G') and the damping factor (tan δ) as a function of temperature for neat PLA, PLA with diatomites and PLA-DE with different compatibilizing systems, can be seen in **Figure 7(a)**, and in **Figure 7(b)**, respectively.

The G' values obtained for neat PLA and, in particular, with the incorporation of diatomaceous earth, indicate high stiffness at moderate temperatures. This high storage modulus decreases rapidly when temperature increases, specifically when approaching T_g (around 65 °C). This is due to the change in the vitreous-plastic behavior of the polymer. The low values of storage modulus (around 2 MPa, between 70 and 90 °C) correspond to the visco-plastic behavior of PLA.

Table 5 shows the T_g and storage modulus (G') values at different temperatures. With regard the storage modulus, it can be observed that adding diatomaceous earth (PLA-DE) provides increased stiffness. In particular, G' changes from 604 MPa (neat PLA) up to 1733 MPa by the only addition of 10 wt% DE to PLA. This represents a percentage increase of 287% in the overall stiffness at moderate temperatures of 40°C. Singh *et al.* have shown that increasing nanoclay loading on PLA, gives an increase in the storage modulus throughout the temperature range [46]. However, in this work, nanoclay particles did not provide any significant change in damping factor curves. This increased rigidity may occur due to the reinforcing effect that stiffer clay silicate layers produce in nanocomposites [47].

The different compatibilizing systems used in this work, show a remarkable change in the thermomechanical behavior. There is a clear decrease in the stiffness, as a consequence of the ductility improvement that ESAO and MLO provides to PLA-DE composites. This same behavior is observed for the silanized approach (PLA-DE-GLY),

nevertheless, this decrease is slightly more pronounced in the case of MLO and ESAO. Pluta *et al.* suggested how the incorporation of a compatibilizer improves the compatibility between PLA and an organic clay, thus reducing the rigidity of the composite and increasing the ductility [48]. As it can be seen in Table 5, G′ changes from 1733 MPa (PLA-DE) to 1293 and 978 MPa for PLA-DE-MLO and PLA-DE-ESAO respectively. Note that at temperatures above 100 °C, ESAO and MLO contribution allows composites with lower storage modulus (G′), even below PLA characteristic values. In all samples, the increase by G′ in the 75-90 °C range is due to the cold crystallization process in the biopolymer.[40]

Table 5. Summary of glass transition temperature, Tg, and storage modulus, (G ′), values obtained from solid samples by dynamic mechanical thermal characterization (DMTA) of PLA-diatomaceous earth (DE) composites with different compatibilization systems.

Reference	T_g (°C)	Storage modulus (MPa) (40 °C)	Storage modulus (MPa) (110 °C)
PLA	68.1±1.2	604±25	42.6±2.1
PLA-DE	67.1±1.4	1733±21	49.1±1.7
PLA-DE-GLY	65.8±0.9	1687±14	79.2±1.2
PLA-DE-ESAO	67.8±1.3	978±17	35.3±1.4
PLA-DE-MLO	65.4±1.2	1293±15	29.5±1.0

3.5 Biodegradability characterization of PLA-diatomaceous earth composites.

Finally, disintegration tests in controlled compost soil were carried out in order to ascertain the effect of diatomaceous earth and different compatibilizers on PLA compostability. The weight loss of the injection-molded pieces during the

disintegration process can be observed in **Figure 8**. In addition, **Figure 9** shows the visual aspect of the samples during the disintegration process.

It can be seen how until week 2-3, the weight loss is constant as this is the induction period. In particular, the sample PLA-DE-MLO reaches a weight loss of 12%, while the sample of PLA-DE-ESAO does not lose almost mass. This factor is closely related to the difference between the MLO and the ESAO. The MLO, due to the plasticizing effect, facilitates the disintegration of the sample. On the contrary, the ESAO, since it is a chain extender, it allows the sample to maintain a greater stability against degradation.

Over 3 weeks, all the materials undergo a fast mass loss and a clear embrittlement in their structure. Neat PLA disintegrates faster than its composites with diatomaceous earth. The incorporation of diatomite delays the degradation rate. Paul *et al.* reported that the addition of nanoclays to PLA led to higher disintegration rates of PLA in compost, which was attributed to the high relative hydrophilicity of the clays, allowing an easier permeability of water into the polymer matrix and activating the hydrolytic degradation process [49]. Diatomaceous earth seems to delay the degradation due to its structure and adherence, thus avoiding hydrolytic degradation more directly. With the use of the different compatibilizers (ESAO and MLO), this degradation is further reduced. In particular, ESAO-compatibilized PLA-DE composites show the lowest disintegration rate among all the developed composites. This reduction in the degradation of the material is due to the chain extender, which in general due to the more complex structure delay the degradation.[50] The improved polymer/particle interactions than can be achieved by the different compatibilizing systems, leads to a delayed disintegration process.

4. Conclusions.

Injection-molded pieces based on PLA and 10 wt.% of diatomaceous earth (DE) with different compatibilizers, presented a potential solution for active packaging, due the DE particles porosity and cavity, and showing interesting mechanical behavior and good biodegradability.

Subjecting previously the DE particles to a silanization process (PLA-DE-GLY), an increase in stiffness and hardness is achieved, gently reducing tensile and impact strength as compared to uncompatibilized PLA-DE. The silanized DE particles show greater adherence to the PLA matrix, thus indicating a better matrix/particle interaction, enabling a better internal loads transfer. This is reflected in an improvement in ductility and impact strength. In addition to the silanization, additive (ESAO) and a vegetal oil-derived (MLO) were used. Compatibilized PLA-DE-ESAO shows similar tensile results, but on impact test, a remarkable impact resistance increase is obtained, a 35% upper to PLA-DE. Regarding the use of linseed oil as a compatibilizer, adding MLO the most interesting results are obtained. PLA-DE-MLO bio-composite presents an elongation at break of 13,8%, that is almost triple that PLA-DE value. The addition of MLO also affects thermally, decreasing Tg and Tcc values 3°C and 11 °C respectively. The results obtained corroborate the dual effect exerted by MLO; on the one hand, the maleic acid reacts with the hydroxyl and silanol groups present on PLA and DE, performing as a compatibilizing agent; and on the other hand, as a plasticizer, increasing the free volume and mobility of PLA chains. This is reflected in the thermal behavior, as well as in a crystallinity increase. By increasing the free volume the hydrophobicity is affected, favoring hydrolytic degradation, and consequently, PLA-DE-MLO shows a similar biodegradability of neat PLA. Concluding, compatibilizing PLA- DE with MLO lead to a good mechanical balance,

offering an improved ductility and a slight resistance loss without compromise the good environmental performance of the bio-composite.

Acknowledgements

References

1   F. Tornuk, M. Hancer, O. Sagdic and H. Yetim, *LWT-Food Science and Technology* **64:**540-546 (2015).

2   B. Kuswandi, A. Restyana, A. Abdullah, L. Y. Heng and M. Ahmad, *Food Control* **25:**184-189 (2012).

3   B. Kuswandi, *Environmental Chemistry Letters* **15:**205-221 (2017).

4   J. Jampílek and K. Kráľová, *Ecological Chemistry and Engineering S* **22:**321-361 (2015).

5   O. Horodytska, F. J. Valdés and A. Fullana, *Waste Management* (2018).

6   T. Trongsatitkul and S. Chaiwong, *Polymer International* **66:**1456-1462 (2017).

7   M. Sanyang, S. Sapuan, M. Jawaid, M. Ishak and J. Sahari, *Carbohydrate polymers* **146:**36-45 (2016).

8   A. Brandelli, L. F. W. Brum and J. H. Z. dos Santos, *Environmental chemistry letters* **15:**193-204 (2017).

9   J.-W. Rhim, H.-M. Park and C.-S. Ha, *Progress in Polymer Science* **38:**1629-1652 (2013).

10   S. Kumar and P. Maiti, *Polymer* **76:**25-33 (2015).

11   F. Yahiaoui, F. Benhacine, H. Ferfera-Harrar, A. Habi, A. S. Hadj-Hamou and Y. Grohens, *Polymer Bulletin* **72:**235-254 (2014).

12   C. Ibarguren, P. M. Naranjo, C. Stötzel, M. C. Audisio, E. L. Sham, E. M. F. Torres and F. A. Müller, *Applied Clay Science* **90:**88-95 (2014).

13   B. Kuswandi, Nanotechnology in food packaging, in *Nanoscience in Food and Agriculture 1*. Springer, pp. 151-183 (2016).

14   (!!! INVALID CITATION !!! [1, 5, 6]).

15   G. Gorrasi, M. Tortora, V. Vittoria, E. Pollet, B. Lepoittevin, M. Alexandre and P. Dubois, *polymer* **44:**2271-2279 (2003).

16   P. Pasbakhsh, R. De Silva, V. Vahedi and G. J. Churchman, *Clay Minerals* **51:**479-487 (2016).

17   D. Bendahou, A. Bendahou, Y. Grohens and H. Kaddami, *Industrial Crops and Products* **72:**107-118 (2015).

18   G. S. Lorite, J. M. Rocha, N. Miilumäki, P. Saavalainen, T. Selkälä, G. Morales-Cid, M. Gonçalves, E. Pongrácz, C. M. Rocha and G. Toth, *LWT-Food Science and Technology* **75:**305-315 (2017).

19   I. Cacciotti, S. Mori, V. Cherubini and F. Nanni, *International journal of biological macromolecules* **112:**567-575 (2018).

20   S. Davoudizadeh, M. Ghasemi, K. Khezri and S. Bahadorikhalili, *Journal of Thermal Analysis and Calorimetry* **131:**2513-2521 (2018).

21   M. S. Aw, S. Simovic, Y. Yu, J. Addai-Mensah and D. Losic, *Powder technology* **223:**52-58 (2012).

22   Đ. P. Medarević, D. Lošić and S. R. Ibrić, *Hemijska industrija* 69-69 (2016).

23   İ. Özen, S. Şimşek and G. Okyay, *Applied Surface Science* **332:**22-31 (2015).

24   S. Torres-Giner, N. Montanes, T. Boronat, L. Quiles-Carrillo and R. Balart, *European Polymer Journal* **84:**693-707 (2016).

25   L. Quiles-Carrillo, N. Montanes, J. M. Lagaron, R. Balart and S. Torres-Giner, *Polymer International* **67:**1341-1351 (2018).

26   M. Samper, R. Petrucci, L. Sánchez-Nacher, R. Balart and J. Kenny, *Polymer Composites* **36:**1205-1212 (2015).

27   M. A. Khan and M. M. Hassan, *Journal of applied polymer science* **100:**4142-4154 (2006).

28   L. Quiles-Carrillo, N. Montanes, C. Sammon, R. Balart and S. Torres-Giner, *Industrial Crops and Products* **111:**878-888 (2018).

29   J. Ferri, D. Garcia-Garcia, L. Sánchez-Nacher, O. Fenollar and R. Balart, *Carbohydrate polymers* **147:**60-68 (2016).

30   T. Tábi, A. Z. Égerházi, P. Tamás, T. Czigány and J. G. Kovács, *Composites Part A: Applied Science and Manufacturing* **64:**99-106 (2014).

31   G. L. Re, S. Benali, Y. Habibi, J.-M. Raquez and P. Dubois, *European Polymer Journal* **54:**138-150 (2014).

32   M. J. Garcia-Campo, L. Quiles-Carrillo, J. Masia, M. J. Reig-Pérez, N. Montanes and R. Balart, *Materials* **10:**1339 (2017).

33   S. C. Mauck, S. Wang, W. Ding, B. J. Rohde, C. K. Fortune, G. Yang, S.-K. Ahn and M. L. Robertson, *Macromolecules* **49:**1605-1615 (2016).

34   J. M. Ferri, D. Garcia-Garcia, N. Montanes, O. Fenollar and R. Balart, *Polymer International* **66:**882-891 (2017).

35   V. Silverajah, N. A. Ibrahim, N. Zainuddin, W. M. Z. W. Yunus and H. A. Hassan, *Molecules* **17:**11729-11747 (2012).

36   B. W. Chieng, N. A. Ibrahim, Y. Y. Then and Y. Y. Loo, *Molecules* **19:**16024-16038 (2014).

37   H. Liu and J. Zhang, *Journal of polymer science part B: Polymer Physics* **49:**1051-1083 (2011).

38   A. Carbonell-Verdu, L. Bernardi, D. Garcia-Garcia, L. Sanchez-Nacher and R. Balart, *European Polymer Journal* **63:**1-10 (2015).

39   A. Carbonell-Verdu, M. D. Samper, D. Garcia-Garcia, L. Sanchez-Nacher and R. Balart, *Industrial Crops and Products* **104:**278-286 (2017).

40   L. Quiles-Carrillo, S. Duart, N. Montanes, S. Torres-Giner and R. Balart, *Materials & Design* **140:**54-63 (2018).

41   F. Ali, Y.-W. Chang, S. C. Kang and J. Y. Yoon, *Polymer Bulletin* **62:**91-98 (2009).

42   Y. Q. Xu and J. P. Qu, *Journal of applied polymer science* **112:**3185-3191 (2009).

43   D. Garcia-Garcia, J. M. Ferri, N. Montanes, J. Lopez-Martinez and R. Balart, *Polymer International* **65:**1157-1164 (2016).

44   M. P. Arrieta, M. d. M. Castro-Lopez, E. Rayón, L. F. Barral-Losada, J. M. López-Vilariño, J. López and M. V. González-Rodríguez, *Journal of agricultural and food chemistry* **62:**10170-10180 (2014).

45   S. Pilla, A. Kramschuster, L. Yang, J. Lee, S. Gong and L.-S. Turng, *Materials Science and Engineering: C* **29:**1258-1265 (2009).

46   S. Singh, A. K. Ghosh, S. N. Maiti, S. Raha, R. K. Gupta and S. Bhattacharya, *Polymer Engineering & Science* **52:**225-232 (2012).

47   B. Ayana, S. Suin and B. Khatua, *Carbohydrate polymers* **110:**430-439 (2014).

48   M. Pluta, J. Jeszka and G. Boiteux, *European Polymer Journal* **43:**2819-2835 (2007).

49   M.-A. Paul, C. Delcourt, M. Alexandre, P. Degée, F. Monteverde and P. Dubois, *Polymer degradation and stability* **87:**535-542 (2005).

50   P. A. Palsikowski, C. N. Kuchnier, I. F. Pinheiro and A. R. Morales, *Journal of Polymers and the Environment* **26:**330-341 (2018).

Figure captions

Figure 1. Images FESEM of diatomaceous earth (DE) a) shapes dispersion, 700X ; b) disc shape detail, 2000X; c) tubular shape detail, 3000X.

Figure 2. Typical stress-strain curves of PLA and uncompatibilized and compatibilized PLA-DE composites.

Figure 3. Field emission scanning electron microscopy (FESEM) images at different magnifications (1000x, left column and 2000x, right column) corresponding to PLA-DE – a) & b), PLA-DE-GLY – c) & d), PLA-DE-ESAO – e) & f), and PLA-DE-MLO – g) & h). The images correspond to impact fractured surfaces.

Figure 4. Field emission scanning electron microscopy (FESEM) image at 2000x, corresponding to PLA-DE-MLO. The image corresponds to impact fractured surface.

Figure 5. DSC thermograms corresponding to PLA-diatomaceous earth (DE) composites with different compatibilization systems.

Figure 6. Thermogravimetric analysis of PLA-diatomaceous earth (DE) composites with different compatibilization systems, a) TGA thermograms and b) first derivative TGA thermograms (DTG).

Figure 7. Comparative plot of dynamic mechanical thermal properties of PLA-diatomaceous earth (DE) composites with different compatibilization systems as a function of temperature. a) Storage modulus, G′ and b) Dynamic damping factor (tan ∂).

Figure 8. Percentage weight loss as a function of the elapsed time during disintegration test in controlled compost soil of PLA-diatomaceous earth (DE) composites with different compatibilization systems.

Figure 9. Visual aspect during the disintegration test in controlled compost soil of PLA-diatomaceous earth (DE) composites with different compatibilization systems.