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Materiales

GLYCIDYL METHACRYLATE AS COMPATIBILIZER OF POLY(LACTIC ACID)/NANOCLAY/AGAVE FIBER HYBRID BIOCOMPOSITES: EFFECT ON THE PHYSICAL AND MECHANICAL PROPERTIES

GLICIDIL METACRILATO COMO COMPATIBILIZANTE DE BIOCOMPOSITES HÍBRIDOS DE POLI(ÁCIDO LÁCTICO)/NANOARCILLA/FIBRA DE AGAVE: EFECTO EN LAS PROPIEDADES FÍSICAS Y MECÁNICAS

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Abstract

This study evaluates the effect of agave fiber and nanoclay reinforcers over poly(lactic acid) (PLA) properties. Also, a compatibilizer based on glycidyl methacrylate and PLA was used to enhance the fiber-PLA interaction. The results showed that crystallinity of PLA was increased with nanoclay addition while fiber inclusion decreased it. Tensile and flexural moduli were increased by both reinforcements. The agave fibers affect negatively the tensile and flexural strengths, but they were importantly recovered by the used of the compatibilizer. Even though the nanoclay did not modify the impact strength, it was increased with agave fiber addition. The water absorption results showed that the coupling agent decreases the rate and maximum water absorption of the biocomposites. In general, it was concluded that with a proper combination of both reinforcers (hybridization) and the compatibilizer, it is possible to control the final characteristics of the biocomposite according to the desired or potential applications.

Keywords: PLA, agave fiber, nanoclays, biocomposites, mechanical properties.

Resumen

Este estudio evalúa los efectos de refuerzos de la fibra de agave y nanoarcilla sobre las propiedades del poli(ácido láctico) (PLA). Además, se utilizó un compatibilizante a base de glicidil metacrilato y PLA para mejorar la interacción fibra-PLA. Los resultados mostraron que la cristalinidad del PLA incrementó con la adición de nanoarcillas, mientras que la inclusión de fibras la disminuyó. Los módulos de tensión y flexión se incrementaron con ambos refuerzos. Las fibras de agave afectan negativamente las resistencias a la tensión y flexión, pero incrementaron de manera importante con el uso del compatibilizante. Aunque la nanoarcilla no modificó la resistencia al impacto, ésta se incrementó con la adición de fibra de agave. Los resultados de la absorción de agua mostraron que el compatibilizante disminuye la velocidad y la absorción máxima de agua de los biocompositos. En general, se concluyó que con una buena combinación de ambos refuerzos (hibridación) y el compatibilizante, es posible controlar las características finales del biocomposito de acuerdo con las aplicaciones deseadas o potenciales.

Palabras clave: PLA, fibra de agave, nanoarcillas, biocompositos, propiedades mecánicas.

1   Introduction

Nowadays one of the most important concerns in the world, is the reduction of oil-based products. This has motivated the interest in research related to the development of environmentally friendlier materials, using sustainable renewable resources such as lignocellulosic materials and biopolymers (Awal *et al*., 2015). Biopolymers can be produced from renewable resources such as corn starch and sugar beet (Gardette *et al*., 2011; Bolio-López *et al*., 2013); they can also be chemically synthesized from monomers produced biologically, like poly(lactic acid) for instance, or be directly synthesized by intracellular microorganisms pathways, like in the production of polyhidroxyalkanoates (Bordes *et al*., 2009).

Currently, the most used biopolymer is poly(lactic acid) (PLA), which is an aliphatic thermoplastic polyester. The typical common way for the industrial production of PLA, is the ring opening polymerization of lactic acid (Farah *et al*., 2016). PLA has interesting properties such as biocompatibility and biodegradability. Additionally, it is a polymer, which can be easily processed by different methods, e.g.: extrusion, injection or compression molding (Armentano *et al*., 2013). For its potential, it is important to overcome its limitations in some mechanical properties (e.g., high brittleness and low flexural strength, Farah *et al*., 2016), because PLA can be applied in surgical sutures, orthopedic implants, device management systems and disposable consumer products (Anaya-Reza and López-Arena 2018).

The use of nanoclays to modify PLA properties has been reported in some studies; for example: increased strength and moduli, degradability and heat resistance, as well as decreased gas permeability and flammability (Picard *et al*., 2011; Ojijo and Sinha Ray, 2013; Meng *et al*., 2015). Arroyo *et al*. (2010) found that the addition of 3-5 wt% of nanoclay (montmorillonite) to PLA, improved the thermal, tensile and flexural properties in comparison with pure PLA. Ligot *et al*. (2015) reported an increased crystallinity and a decrease in the crystallization temperature of PLA, with the addition of organically modified nanoclay (cloisite 20A and 30B).

Alternatively, composite materials using natural fibers as reinforcement like hemp, kenaf, flax, bamboo, sisal or agave, have gained considerable commercial success in applications such as decking, fencing, docks landscaping, building and construction,

and the automobile industry (Mukherjee and Kao, 2011; Kovacevic *et al*., 2015). Characteristics such as biodegradability, low cost, low-density, non-toxicity, high mechanical properties and renewability of natural fibers offer advantages in comparison to inorganic fibers to produce composite materials (Torres-Tello *et al*., 2017). Furthermore, natural fibers application implicates a lower impact for the environment compared to the production and use of synthetic fibers. In addition, it is generally required a greater amount of natural fibers to match the performance of a synthetic fiber composite which would reduce the amount of polymer required for an application (Gutierrez *et al*., 2018). A composite that contains two or more different reinforcements in a polymeric matrix has been identified as a hybrid composite (Nguyen *et al*., 2017). The hybridization has the purpose to improve the matrix properties, combining the different characteristics of the reinforcements (Wang *et al*., 2008). The mechanical properties of composites reinforced with a natural fiber, can be increased with chemical modification of the fiber, but this modification causes a faster thermal degradation rate of the composite; however, the thermal degradation rate can be decreased by means of nanoclay addition to it (Sajna *et al*., 2017). Yusoff *et al*. (2016), mixed kenaf, bamboo and coir fibers to prepare PLA biocomposites, and they reported that the hybrid fiber combinations improved Young's modulus, and tensile and flexural strength of the biocomposites. Singh *et al*. (2015) observed an improvement in tensile strength of a high-density polyethylene composite hybridized with sisal and hemp fibers; the composite with 30 wt% of hemp or sisal fiber presented a tensile strength of 13 and 12 MPa respectively, but with the combination of those reinforcements (15 wt% of sisal and 15 wt% of hemp fiber), this property increased to 19 MPa. Sarasini *et al*. (2018) also noticed a positive effect in tensile properties by hybridization using hemp and basalt fibers in high-density polyethylene composites; the composite with hemp fiber (30 wt%) were improved up to 68% in comparison to the neat polymer in tensile strength, and the composite with basalt fiber (30 wt%) presented an increase, up to 140%, while with the combination of those fibers (15-15 wt%) an increase of 115% was obtained, comparing to polyethylene, which represents a positive hybridization effect. Sajna *et al*. (2017) reported that with the addition of a nanoclay (Cloisite 30B) to banana fiber/PLA biocomposites, the thermal degradation parameters like initial and maximum degradation temperatures increased from

286 to 295 ℃ and 380 to 387 ℃ respectively; those results demonstrated that the addition of a nanoclay to biocomposites can increase their thermal stability.

The use of natural fibers for polymers reinforcement requires a strong adhesion between the fibers and the matrix (Moreno *et al.*, 2018). This adhesion at the interface is an important issue because hydrophilic reinforcements are incompatible with hydrophobic thermoplastic matrices such as polyolefins or PLA, to a certain extent, and consequently it is important to improve the interfacial adhesion between the phases (Zhang, 2014; Essabir *et al.*, 2016). The importance of interfacial interactions is widely reported to improve the thermal stability and mechanical properties of polymer composites (Kuciel *et al.*, 2014). One of the most common methods to improve the interfacial adhesion is the use of coupling agents, like maleic anhydride (MA) or glycidyl methacrylate (GMA) grafted polymers (Khan *et al.*, 2018). Grafting routes often used to produce glycidyl methacrylate-grafted polyolefins (pol-g-GMA) are: reactive extrusion and solution copolymerization (Burton *et al.*, 2010; Xu *et al.*, 2012). The use of pol-g-GMA as coupling agent improved the mechanical properties of rice husk filled high-density polyethylene, as reported by Panthapulakkal *et al.* (2005), and for bamboo flour filled PLA biocomposites (Wang *et al.*, 2014). Sajna *et al.* (2017), using TGA measurements, reported that with the addition of GMA to a biocomposite prepared with banana fiber, nanoclay and PLA, the thermal stability of the material was increased; there, the maximum degradation temperature of the hybrid biocomposite with GMA was 403 ℃, while without the compatibilizer, for the biocomposite such temperature was 387 ℃.

In this sense, with the aim to prepare a biocomposite with competitive mechanical and thermal properties, in this study the combination of a modified montmorillonite and agave fiber in a PLA matrix was evaluated to produce hybrid biocomposites. Additionally, in order to enhance the matrix-reinforcement interfacial adhesion, the effect of the PLA-g-GMA inclusion to the system is reported. The hybrid biocomposites were characterized in terms of mechanical and thermal performance, as well as in water absorption capacity which is necessary due to the hydrophilic capacity of the natural fiber and the degradation susceptibility of the PLA chains by hydrolysis processes.

2 Materials and methods

2.1 Materials

PLA 3251-D was acquired by Nature Works LLC (USA) having a melt flow index of 80 g/10min (at 210 ℃ with a 2.16 kg weight), a density of 1.24 g/cm^3, and a melting temperature of 188-210 ℃. The nanoclay reinforcement used was montmorillonite 1.34MN (25-30 wt.%) with methyl dihidroxyethyl hydrogenated tallow ammonium with and average size $\leq 20\mu m$, acquired from Sigma Aldrich (USA). Agave fiber (Agave tequilana Weber var. Azul) was obtained from a local tequila company in Jalisco (México). Glycidyl methacrylate (GMA) and dicumyl peroxide (DCP) were purchased from Sigma Aldrich (USA).

2.2 Preparation of poly(lactic acid) grafted glycidyl methacrylate

The grafting of GMA in the PLA chains was carried out by reactive extrusion. Before being used, PLA pellets were dried at 50 ℃ for 48 h. In accordance with Nguyen *et al.* (2016), 10 wt% of GMA in the presence of 0.2 wt% of DCP as initiator, were mixed with PLA in a twin-screw extruder (Thermo Scientific Process 11), with a temperature profile set to 165/170/175/180/180/180/170/165 ℃, using a screw speed of 70 rpm. PLA-g-GMA was cooled in water and pelletized, and later oven-dried for 48 h at 60 ℃. In order to achieve a minimum residence time (10 minutes) in the extrusion process, the PLA-g-GMA was passed twice by the extruder.

2.3 Biocomposites preparation

First, the agave fibers were cleaned to remove the fiber pith and impurities. For this purpose, the fibers were placed in a water bath for 24 h and passed throughout a Sprout-Waldron refiner (D2A509NH). Afterwards, the fibers were dried, milled and sieved to keep particles between 40 and 50 mesh. The formulation code of the different biocomposites is presented in Table 1. The biocomposites were prepared in a twin-screw extruder Leistritz Micro 27 GL/GG 32D with a temperature profile set from 150/160/165/165/170/170/180/180/160℃ and a screw speed of 50 rpm. The biocomposites were cooled in a water bath and then pelletized.

Table 1. Sample codes of PLA and the prepared biocomposites. Numbers indicate wt.%.

Sample	PLA	Agave fibers	Nanoclay	PLA-g-GMA
PLA0	100	—	—	—
PLA3	97	—	3	—
PLA5	95	—	5	—
PLA0AF	70	30	—	—
PLA3AF	67	30	3	—
PLA5AF	65	30	5	—
PLA0AF/GMA	60	30	—	10
PLA3AF/GMA	57	30	3	10
PLA5AF/GMA	55	30	5	10

The biocomposite pellets were oven-dried for 48 h at 60 °C and then injection molded on a NISSEI ES 1000 machine, with a temperature profile of 170/180/185/190 °C and a mold temperature of 30 °C. All the samples were prepared in a rectangular mold cavity with dimensions of $128 \times 40 \times 2.5$ mm^3.

2.4 Characterization of PLA-g-GMA

In order to observe the characterization of GMA, grafted samples of PLA-g-GMA and PLA were scanned by Fourier transform infrared (FTIR) in a Nicolet iS5 spectrometer with a resolution of 2 cm^{-1} and 24 scans in a range of 4000 to 400 cm^{-1}.

2.5 Morphology

The dispersion and adhesion of fibers in the matrix was observed by scanning electron microscopy (SEM). For this purpose, samples fractured by tensile testing were used, after transversal depth surface coating with Au/Pd under vacuum during 120 s, using a SPI module sputter coater. The samples were observed using a TESCAN MIRA3 LMU equipment. An image analysis to calculate the fractal dimension and the exposed or identified fibers at the biocomposites surface was carried out using Matlab® software.

2.6 Mechanical properties

Mechanical properties evaluation was performed according to the following analyses: tensile tests were carried out according to ASTM D638 (type IV with 7 specimens), using a crosshead speed of 5 mm/min. Flexural tests were carried out according to ASTM D790. Six samples of each polymeric material were tested at a crosshead speed of 2 mm/min. A universal testing machine Instron model 3345 at room temperature (23 °C) was used for tensile and flexural tests. Charpy impact strength was determined according to ASTM D6110, and each reported value represents the average of 10 notched samples. This test was performed in an Instron Ceast model 9050 impact tester.

2.7 hermal properties and density

The glass transition (T_g), crystallization (T_c), specific heat (C_p) and melting (T_m) temperatures were measured by differential scanning calorimetry (DSC) using a TA instruments model Discovery Q100 equipment. The samples used were cut from injected specimens (2 - 5 mg) to perform a scan between 40 and 180 °C at a heating rate of 10 °C/min under a nitrogen flow of 50 mL/min. The crystallinity after molding processing (X_0) was determined using the following equation:

$$X_0 = \frac{\Delta H_m - \Delta H_c}{\Delta H_{ref}} \times \frac{1}{x} \times 100 \qquad (1)$$

where ΔH_m and ΔH_c are the experimental heat of fusion and crystallization respectively; ΔH_{ref} is the theoretical heat of fusion for 100% crystalline PLA (93 J/g, (Mathew *et al.*, 2006), and x is the weight fraction of PLA in the biocomposites. To evaluate the thermal stability of PLA and its biocomposites, a thermogravimetric analysis (TGA) was used. The tests were performed in a TA instruments TGA Discovery equipment. The samples (5-10 mg) were heated from 25 to 600 °C with a heating rate of 10 °C/min under nitrogen atmosphere. The bulk density (ρ_b) of the biocomposites was determined according to ASTM D2395, measure the length, width, and thickness of the specimen in a sufficient number of places to ensure a precise indication of volume and mass of the specimen with a gravimetric balance.

2.8 Water absorption

Water absorption tests were conducted in accordance to ASTM D570. Five samples per composition with dimensions of $4 \times 3 \times 0.25$ cm^3 were dried and weighed. Then, the samples were immersed in distilled water at 55 °C for 28 days (672 h). Samples were removed after specific time periods to follow absorption kinetics. After a sample was removed, its surface water was wiped off with a dry cloth, and the sample was immediately weighed before being returned to the water bath. The amount of water absorption (M_t) was calculated as follows:

$$M_t = \frac{w_i - w_0}{w_0} \times 100 \tag{2}$$

where w_i is the weight of the sample after immersion and w_0 is the initial weight.

3 Results and discussion

3.1 Characterization of PLA-g-GMA

The infrared spectra of pure PLA and PLA-g-GMA are shown in Fig. 1. The peaks observed at 1747 cm^{-1} and 1080 cm^{-1} corresponds to the link C=O and C−O presented in the PLA. Compared with the spectrum of PLA, a new signal appeared around 910 cm^{-1} in the spectrum of PLA-g-GMA which corresponds at the asymmetric stretching of the epoxy group of the GMA. This small signal has been reported in the literature as a demonstration that GMA is successfully grafted onto PLA chains via reactive extrusion (Xu *et al.*, 2012; Wang *et al.*, 2014; Sajna *et al.*, 2017; Khan *et al.*, 2018).
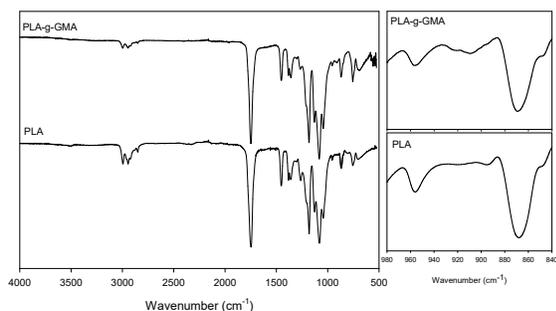
Fig. 1. FTIR spectra of PLA and PLA-g-GMA.
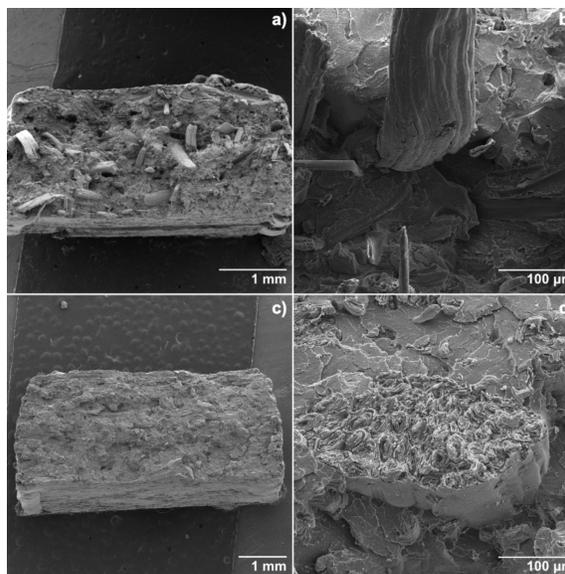
Fig. 2. SEM micrographs of: PLA3AF (a, b), and PLA3AF/GMA (c, d) biocomposites after tensile testing.

3.2 Morphology

In Fig. 2, SEM micrographs of PLA3AF and PLA3AF/GMA biocomposites can be observed. In samples without compatibilizer (Fig. 2 a-b), due to the low compatibility and poor adhesion between agave fiber and PLA (Chen and Yan, 2013; Pérez-Fonseca *et al.*, 2015), it can be noticed that fibers were pulled-out from the matrix. On the contrary, in the biocomposite with PLA-g-GMA (Fig. 2 c-d) such fiber pulling does not occur, indicating that the compatibility and interfacial adhesion were successfully reached with the compatibilizer used. This improvement in compatibility is due to the reaction bond formed with the epoxide ring of the GMA in the compatibilizer with the hydroxyl groups of the agave fibers (Khan *et al.*, 2018). Xu *et al.* (2012) also observed this situation when they added GMA to bamboo flour/PLA biocomposites. Fig. 3 shows the micrographs and image analysis of the biocomposites surface (45x), where the fractal dimension (FD) was quantified and the fraction of the depictions of identified fibers was obtained. The PLA3AF presents a fractal dimension of 1.60 with 25.1% of the surface with exposed or identified fibers, while for PLA3AF/GMA the value of the fractal dimension shows 1.46 with 14.5% of the surface with exposed or identified fibers.
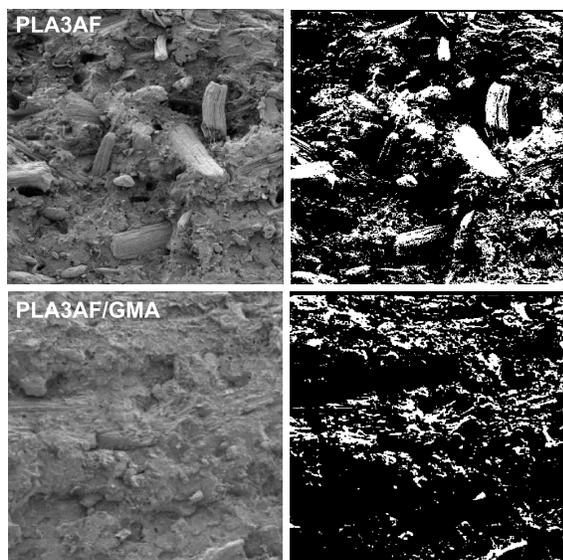
Fig. 3. Micrographs and image analysis of PLA3AF and PLA3AF/GMA biocomposites.

The higher value of FD in the biocomposite without compatibilizer is related to a rougher fracture surface compared to the surface of the PLA3AF/GMA biocomposite (Quiang and Yu, 2012). That is, the decrease in the amount of fibers that can be identified at the surface of the compatibilized biocomposite and smaller FD is due to the improved fiber-matrix interaction and consequently a better wettability of the fibers by the biopolymer.

3.3 Tensile properties

In Fig. 4 (a), an increase in tensile modulus with agave fibers or nanoclay particles for the different

concentrations can be observed. The increase in tensile modulus was expected due to the higher modulus of either reinforcement, comparing each one of them with the polymer matrix (Shumigin *et al*., 2011; Rajesh and Patna Prasad, 2014). Wootthikanokkhan *et al*. (2013) reported that tensile modulus increased and tensile strength decreased in PLA/kenaf fiber and PLA/nanoclay (cloisite 30B); this behavior might be related to different compatibility levels between PLA and the fillers. However higher increments were obtained with the hybrid reinforcement, being the PLA5AF the formulation that presented the higher improvement (70% in comparison to the PLA sample (1290 MPa)).

When the PLA-g-GMA is added, the tensile modulus remains at the same level or with a slightly decrease probably due to a plasticizing effect of the compatibilizer which causes a reduction of the biocomposite stiffness in combination with a lower dispersion of the nanoclays. These results are similar to the ones reported by Pérez-Fonseca *et al*. (2014), where tensile modulus decreased by the presence of a compatibilizer in hybrid composites of high-density polyethylene with agave/pine fibers.

The tensile strength is shown in Fig. 4 (b). There, it can be observed that the addition of nanoclay improves the tensile strength, with an increment of 12% (PLA3) in comparison to PLA0 sample. Jandas *et al*. (2013) observed that tensile strength increased up to 19% with the addition of montmorillonite to PLA. Araújo *et al*. (2014) reported that incorporation of 3 and 5 wt% of two types of nanoclays (cloisite 30B and 15A) in PLA, motivated agglomeration in the polymeric matrix that caused a decrease in tensile strength.
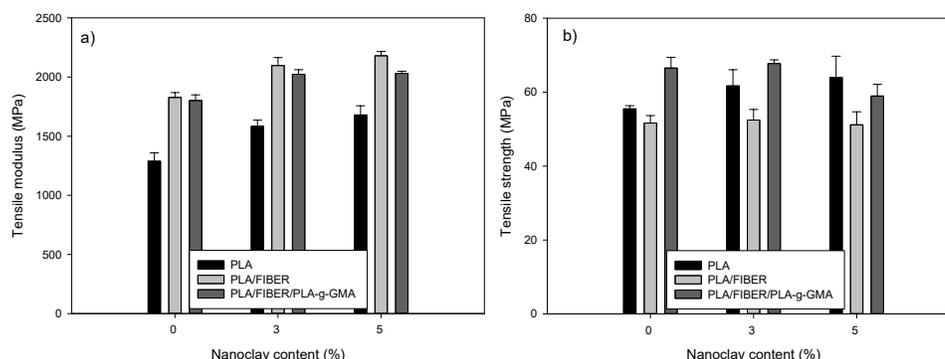
Fig. 4. Tensile properties of PLA, PLA/agave fiber and PLA/agave fiber/ PLA-g-GMA biocomposites with different amounts of nanoclay: (a) Young modulus and (b) strength.

According to Alexandre and Dubois (2000), when a composite shows agglomeration, its properties stay in the same range, and can even decrease, with respect to the neat polymer. In contrast, when the structure is laminated/exfoliated, the polymer chains are strained by the nanoclay particles due to their large interfacial area. Conversely, the incorporation of agave fibers showed a decrease in the tensile strength values and the hybridization (i.e. nanoclay and agave addition) did not show a significant modification. Nevertheless, when the PLA-g-GMA is added and consequently the compatibility in the system is improved, the tensile strength of the hybrid biocomposites increased from 51, 52 and 51 MPa (for PLA0AF, PLA3AF and PLA5AF respectively), to the correspondent 66, 68 and 59 MPa (denoting increments of 29, 31 and 16% respectively) with the addition of PLA-g-GMA. Khan *et al.* (2018) reported an increase of 22% with the addition of GMA to 20 wt.% of hemp hard/PLA biocomposites.

3.4 Flexural properties

For flexural modulus (Fig. 5 a), starting with 3585 MPa for pure PLA, the highest value obtained using nanoclay particles was 4730 MPa with PLA5 (which represents an improvement of 32%). Besides, flexural modulus of the biocomposites increased with the hybridized reinforcements up to 5486 MPa with PLA5AF (a total improvement of 53%). Way *et al.* (2013), reported that with the addition of 50 wt.% of maple wood to PLA, the flexural modulus increased 120%. Shibata *et al.* (2003) observed a similar trend with flexural modulus of PLA/abaca fiber biocomposites, reporting an increase of 60% with 20 wt.% of fiber loading. Furthermore, flexural

modulus increased from 4117 MPA for PLA0AF to 4346 MPa for PLA0AF/GMA, once again due the improved compatibility. Khan *et al.* (2018) attained a significant increase of this property with the addition of GMA to hemp hard/PLA biocomposites. However, a small decrease on this property is observed here in the case of the PLA3AF/GMA sample, and more particularly for PLA5AF/GMA; this can be attributed to the increase in interfacial adhesion between agave fibers and PLA, which hinders the dispersion of the nanoclay particles in the composite material.

Flexural strength (Fig. 5 b) was also increased with nanoclay inclusion, with a maximum value of 106 MPa for PLA3, while for PLA0, it was 86 MPa. The increment of this property can be explained in terms of the organic modification of montmorillonite that allows interaction with PLA carbonyl group (Jandas *et al.*, 2013). In the case of PLA5 samples, a reduction in the flexural strength was observed, probably due to a low dispersion and agglomeration of the nanoclay particles. Similarly, Armentano *et al.* (2013), observed an enhancement in mechanical properties with low nanoclay content (attributed to the high interfacial area), but reported a reduction in those properties when the nanoclay content was increased, due to particles agglomeration. Prakalathan *et al.* (2012), reported an increase in flexural strength, from 82 MPa for pure PLA to 97, 105 and 131 MPa, using 5 wt.% of different nanoclays (C15A, C25A and 93A respectively). Sinha Ray and Okamoto (2003) reported that with the addition of montmorillonite organically modified with octadecyltrimethylammonium, the flexural strength presented an increment of 55%, with 4 wt.% of nanoclay content; then, the flexural strength gradually decreased with higher nanoclay content.
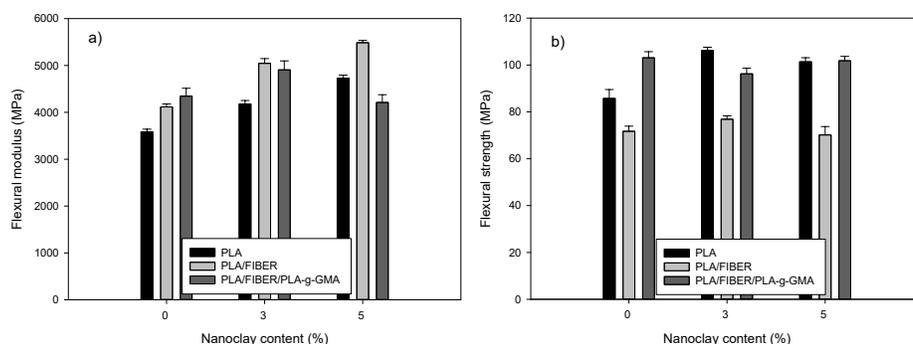
Fig. 5. Flexural properties of PLA, PLA/agave fiber and PLA/agave fiber/ PLA-g-GMA biocomposites with different amount of nanoclay: (a) modulus and (b) strength.

Table 2. Static mechanical properties of some thermoplastics and composites.

Composite	wt.(%)	TS (MPa)	TM (MPa)	FS (MPa)	FM (MPa)	IS (J/m)	Reference
PP/coir/banana	80/10/10	30	694	30	683	73	Bujjibabu *et al.* (2018).
PP	100	39	375	50	734	-	
PP/agave	70/30	26	500	46	1458	-	Pérez-Fonseca *et al.* (2014).
PP/pine	70/30	27	580	55	1690	-	
HDPE	100	28	295	22	566	45	
HDPE/agave/MAPE	67/30/3	26	475	30	1150	55	Pérez-Fonseca *et al.* (2016).
HDPE/coir /MAPE	67/30/3	25	485	32	1205	45	
PLA	100	57	1250	86	3500	30	This
PLA/agave/GMA	60/10/30	65	1750	104	4200	40	work

PP: polypropylene; HDPE: high density polyethylene; MAPE: Maleic anhydride grafted polyethylene; TS: tensile strength: TM: tensile modulus; FS: flexural strength; FM: flexural modulus; IS: impact strength (Charpy).

With the addition of agave fibers, the flexural strength decreased 16, 10 and 19 % for the samples PLA0AF, PLA3AF and PLA5AF respectively, in comparison to PLA0. This reduction of the flexural strength is due to the poor interfacial adhesion between the fibers and the PLA matrix (Jiang *et al.*, 2016). Kim *et al.* (2012) observed that flexural strength decreased 40% with the addition of pineapple flour to PLA. This reduction in flexural strength was attenuated with the addition of PLA-g-GMA. In that way, the values for PLA0AF, PLA3AF and PLA5AF changed from 72, 77 and 70 MPa respectively, to 103, 96 and 102 MPa for the correspondent compatibilized hybrid biocomposites (PLA0AF/GMA, PLA3AF/GMA and PLA5AF/GMA). The higher flexural strength of biocomposites using PLA-g-GMA in comparison with non-compatibilized biocomposites, can be attributed to the increase in the interfacial adhesion. Xu *et al.* (2012) reported increments at flexural strength up to 28% in biocomposites of bamboo fiber in PLA matrix with the addition of PLA-g-GMA.

3.5 Impact strength properties

Impact strength results are presented in Fig. 6. The inclusion of nanoclay in the PLA did not show any significant effect in the impact strength, as it was reported before by Robledo-Ortíz *et al.* (2019) probably due to the low amount of nanoclay content which is not significant in comparison to the high values of absorbed energy supported by the neat PLA. Jandas *et al.* (2013) reported that impact strength decreased with the addition of modified montmorillonite to PLA.
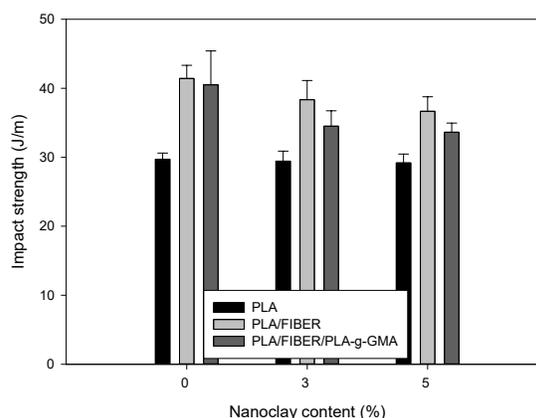
Fig. 6. Impact strength of PLA, PLA/agave fiber and PLA/agave fiber/ PLA-g-GMA biocomposites with different amounts of nanoclay.

Nevertheless, an increase in impact strength of 42% was achieved here, with the agave fiber incorporation (from 29 J/m for PLA0 to 41 J/m to PLA0AF). The strain energy that is released by the fiber detaching and fracture in this type of test is proportional to the fiber length and diameter (Virk *et al.*, 2010). A much higher amount of energy will be absorbed when there is a poor adhesion between the matrix and the fiber (Sawpan *et al.*, 2011). This can also be related with the FD value that was obtained, Quian and Yu (2011) reported that high fractal dimension values are due to rougher fracture surfaces and can be related to higher impact resistance, implicating that the free volume between fibers and polymer is contributing to such resistance.

Table 3. Thermal analysis by DSC and density of PLA and its biocomposites.

Sample	T_g (ºC)	T_c (ºC)	C_p (J/g°C)	ΔH_c (J/g)	T_m (ºC)	ΔH_m (J/g)	X_0 (%)	ρ_b (g/cm³)
PLA0	58	85	1.1	27	161	48	23	1.1
PLA3	59	82	1.3	23	160	48	27	1.1
PLA5	59	84	1.4	23	160	46	27	1.1
PLA0AF	60	88	1	17	162	29	19	1.2
PLA3AF	60	87	1	16	161	27	17	1.2
PLA5AF	60	88	1	15	161	26	18	1.2
PLA0AF/GMA	57	85	1.2	17	160	26	14	1.2
PLA3AF/GMA	57	86	1.2	15	159	26	17	1.2
PLA5AF/GMA	55	89	1.2	15	160	25	18	1.2

That situation can explain why with the addition of PLA-g-GMA to the biocomposites, there were no significant changes, although agave fiber shows high elongation at break due to its high cellulose content, which is in turn related to impact resistance (Torres-Tello *et al*., 2017). Such phenomenon could be the dominant parameter involved as a whole in this test, because the applied force travels in all direction in an impact test. Table 2 shows the mechanical properties of the prepared biocomposites, commercial polymers (polyethylene and polypropylene) and their composites. There, it can be observed that the higher values for flexural and tensile properties belong to the used PLA/agave biocomposites. Only for impact strength the conventional polymers, presented higher value (especially HDPE). Nevertheless, the inclusion of agave fibers to PLA contributed to the nearness of the impact strength value of the biocomposite to that of neat HDPE. This comparison allows to elucidate the potential applications of these PLA based biocomposites.

Besides, the incorporation of PLA-g-GMA leaded to an increase in T_c, these results indicate that the interfacial adhesion between PLA and agave fiber was enhanced by the presence of PLA-g-GMA because PLA chains were more susceptible to line up over the surface of the agave fibers and crystallize; similar results were observed by Xu *et al*. (2012) and Zhang *et al*. (2009). The Tm value of pure PLA 161°C remained similar for all the biocomposites. In comparison to PLA, the ΔH_m of the biocomposites decreased from 48 to 29 J/g for biocomposites reinforced with agave with the inclusion of PLA-g-GMA; this can be related to the motion restriction of the PLA chains due to the agave fibers presence, which contributes to a decrease in crystallization (Jandas *et al*., 2011). It has been reported that nanoclay particles act as nucleating agents, promoting the extent of PLA crystallization during heating (Araújo *et al*., 2014); that effect was also observed in this study; nevertheless, as it was mentioned previously, with the addition of agave fibers the amount of crystallinity decreased.

3.6 Thermal properties

The results of DSC are shown in Table 3, where it can be seen that the thermograms of all the biocomposites are very similar to neat PLA. T_g values of the biocomposites with nanoclay and nanoclay/agave fiber are practically the same; such behavior is similar to the results reported by Piekarska *et al*. (2016). However, the T_g value of the biocomposites decreased with the addition of PLA-g-GMA; such behavior indicates higher flexibility of PLA-g-GMA chains, compared to neat PLA (Thanh *et al*., 2015). In contrast, the values of C_p are very similar in all the prepared biocomposites and they are consistent with the values reported by Pyda *et al*. (2004) for pure PLA.

Fig. 7. Water absorption of the biocomposites.

In other studies, the PLA-g-GMA inclusion also promoted a reduction in the degree of crystallinity of the materials (Araújo *et al*., 2008; Sarasini *et al*., 2018); this can be explained by the decrease in regularity of the PLA chains with the addition of agave fibers (Yu *et al*., 2014). In Table 3, the bulk density of the polymeric materials is also shown, where an average density value of 1.2 g/cm^3 for all the biocomposites can be observed. This small increase in the density of the biocomposites in comparison with pure PLA is due to the higher density of agave fiber (1.4 g/cm^3 and 1.1 g/cm^3 respectively).

3.7 Water absorption

The weight increment of PLA0 due to water absorption can be seen in Fig. 7, reaching a maximum at 168 h; the decrement that occurs after that, is generally attributed to the hydrolysis of PLA ester bonds in the presence of water (Ma *et al*., 2014), while for the biocomposites that contain nanoclay particles such decrement is not observed. The latter behavior is due to the increase in crystallinity of the biocomposites caused by those particles, as it was explained in the former section, and as a consequence the water absorption process was modified. Chen and Yan (2013) reported that by the addition of nanoclay, the water absorption at equilibrium was reduced in clay/kraft fiber/HDPE composites. In another study, it was shown that with nanoclay addition to starch, the composite presented higher water adsorption stability than the material without nanoclay, due to the intercalated/exfoliation nanoclay (Chiou *et al*., 2007). On the contrary, with the incorporation of agave fibers to the biocomposites, the water absorption increased. This is due to the hydrophilic character of agave fiber, as it happens with natural fiber composites (Chavooshi *et al*., 2014). Nevertheless, the addition of PLA-g-GMA caused a decrease in water absorption capacity of the biocomposites, equivalent to 37, 27 and 18% (for PLA0AF/GMA, PLA3AF/GMA and PLA5AF/GMA respectively) in comparison with uncompatibilized biocomposites. The main reason for this decrease is the higher hydrophobicity of the biocomposites, due to the adhesion increment between the fibers and the polymeric matrix (Chavooshi *et al*., 2014), as it was shown with the SEM micrographs (Fig. 2).

Conclusions

The results obtained in this study show how the preparation of hybrid biocomposites provide special characteristics in a polymeric material; on one side, the inclusion of nanoclay to PLA originates increments in several mechanical properties (tensile and flexural properties), while the inclusion of agave fibers provides high impact strength, added to the fact that a low-cost agro-industrial waste fiber is being used. In this sense, the effect of the hybridization reinforcement proposed here leads to a fine combination of mechanical properties. Although agave fibers caused a certain reduction in flexural and tensile strength, such effect was overcome using here an efficient compatibilizer (PLA-g-GMA), for the preparation of the biocomposites, displaying an excellent capacity to increase the compatibility between PLA and the fibers. That compatibilizer caused increments in tensile and flexural strength, as well a reduction in water absorption of the biocomposites, which is important for wood-like products.

The replacement in the short term of conventional polymers by biopolymers in common applications is difficult to achieve due to the present cost of biopolymers which nowadays are processed on a smaller scale. However, in recent years, many companies have been working in the development and production of biopolymers; in that way the expectancy to reduce their price and make them more competitive in the market is growing. Currently, the price of 1 kg of PLA is $3.25 USD while for HDPE is $1.39 USD and $1.77 USD for PP. The idea of the inclusion of waste natural fibers (e.g. agave fibers) to the base polymer, is to give an option to reduce the cost of the final material by at least 30%. Besides, if a very high rigidity is required for a specific application, the hybrid biocomposite of PLA/agave fiber/nanoclay would be a better option than conventional polymers or their composites.

Acknowledgements

Nomenclature

X_0	crystallinity degree, %
ΔH_m	experimental heat of fusion, J g^{-1}
ΔH_c	experimental heat of crystallization, J g^{-1}
ΔH_{ref}	theoretical heat of fusion for 1005 crystalline PLA, J g^{-1}
x	weight fraction of PLA in the biocomposites, g g^{-1}
M_t	amount of wáter absorption, %
w_i	weight of the sample after immersion, g
w_0	initial weight of the sample, g
T_g	glass transition temperature
T_c	crystallization temperature
C_p	specific heat
T_m	melting temperature
ρ_b	bulk density

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