The Effects of Henequen Cellulose Treated with Polyethylene Glycol on Properties of Polylactic Acid Composites

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Cellulosic henequen fibers were subjected to steam explosion and impregnated with polyethylene glycol (PEG) to improve fiber-matrix compatibility in polylactic acid (PLA) composites. Through Fourier-transform infrared spectroscopy (FTIR) it was shown that the hydroxyl, methyl, and ether functional groups were increased after the steam explosion treatment. Changes in the cellulose morphology caused by the steam explosion and impregnation with PEG were observed *via* scanning electron microscopy (SEM). Good adhesion of the treated cellulose and the PLA matrix was observed through improvement of the tensile strength and Young's modulus of the PLA composite. The PEG impregnated into the fiber plasticized the PLA matrix and reduced the T_g from 59 °C to 52 °C. The increase in crystallinity confirmed the cellulose fibers induced nucleation of the PLA, which resulted in greater rigidity of the PLA composites.

Keywords: Biodegradable; Biopolymers; Composites; Polylactic acid; Polyethylene glycol; Henequen fibers

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INTRODUCTION

In recent years, great emphasis has been given to the development of composites with biodegradable thermoplastic matrices and fillers from renewable resources; a goal of these efforts is to decrease the contributions of plastics to environmental pollution (Ibrahim *et al.* 2014; Jia *et al.* 2014; Bourmaud *et al.* 2015; Rubio-López *et al.* 2017). The use of cellulosic or lignocellulosic materials (cellulose fibers, wood fibers, nut flour, sisal or jute fiber, *etc.*) as fillers or reinforcement for polymeric matrices has been increasing (An and Ma 2017; Chaitanya *et al.* 2017; Moustafa *et al.* 2017). Advantages of these materials are their low density, flexibility in their processing, reduced equipment wear, and their biodegradability. Lignocellulosic materials are relatively inexpensive and obtained from

renewable natural resources (Canché-Escamilla *et al.* 1999). Cellulose is the most abundant natural biopolymer on Earth and is renewable, biodegradable, and nontoxic. It is a natural polymer composed of units of β -D-glucopyranose, which contains three hydroxyl groups per anhydroglucose unit (AGU) (Peng *et al.* 2011). The attractive mechanical properties of cellulose fibers, *i.e.*, high strength in combination with low weight, are desirable to utilize in more sophisticated applications beyond conventional paper and board.

Early reports on the use of natural fibres in composites date back to 1970 and 1980 (Huber *et al.* 2012). Since then, modern advances in the development of cellulose fiber reinforced polymer composites have been the subject of several hundred studies. Due to the independence of cellulosic fibers of crude oil and their vast availability, an improved CO_2 balance compared with composites made from industrially made fibers and fillers and good mechanical properties, cellulose-containing composites have generated much interest amongst various industries, especially the automotive industry (Huber *et al.* 2012). Lignocellulosic fiber, such as that obtained from henequen (*Agave fourcroydes*), is an unconventional source of cellulose. *Agave fourcroydes* belongs to the family Asparagaceae and is native and cultivated mainly in the state of Yucatán, Mexico for the use of the fiber contained in the leaves of the plant. It is used to make ropes, carpets, and sacks to pack and transport seeds, as well as for the manufacture of fabrics. It has been reported that henequen fiber has a high cellulose content (60%) compared to wood (40%) used in the production of cellulose from henequen fibers, it is not yet a commercial source.

Different biodegradable polymers, such as polylactic acid (PLA) (Pracella *et al.* 2014), poly(ɛ-caprolactone) (PCL), polyhydroxybutyrate (PHB), and poly(hydroxylbutyrate-co-hydroxyvalerate) (PHBV), have been used as matrices in composites with natural fibers (Csikós *et al.* 2015), such as cellulose microfibers or nanofibers as reinforcement. The total production capacity of bioplastics in 2017 was 2.05 million tons. PLA occupied the 10% of the raw material used for bioplastics production (Gaille 2018). Polylactic acid, a biodegradable polymer, has entered the market quite rapidly due to its advantageous properties. It is produced from natural feedstock, is compostable, and has good stiffness and strength. The world PLA market was \$1.49 billion dollars in 2013 and in 2016 was 3.74 billion dollars. The United States is the major exporter of PLA; in 2016 it exported PLA worth US\$ 116.47 million, while other countries are exporting very small quantities. The price of PLA in 2017 in the USA was \$2.04 per ton in January, and by October it was \$1.91 per ton (Baron 2018). The demand for PLA is increasing along with the production capacity.

Despite its advantages, PLA also has some drawbacks for its application in composite materials. Due to its hydrophobicity, PLA has poor compatibility with hydrophilic reinforcements such as cellulose; therefore, remedies are necessary to improve this compatibility. Different types of reactions can be applied for the covalent modification of cellulose, including etherification, acetylation, silylation, amidation, and urethane formation as a method to introduce small molecules compatible with PLA (Chaitanya *et al.* 2017). Apart from small molecules, it is possible to graft polymers on a cellulose surface. The grafting of polymers allows increased compatibility between cellulose and a polymer matrix due to decreased surface energy and the possible formation of entanglements between the grafted polymers and the matrix (Carlsson 2014). However, there are simple non-covalent methods, such as filling the porous fiber structure with polymers (pre-impregnation) (De Cuadro *et al.* 2015). Steam explosion is a promising technology that may have wide applications for lignocellulosic materials (Boonterm *et al.*

2016; Feng *et al.* 2017). Steam explosion is an efficient physical-chemical method that can destroy the structure and separate the components of fibers (Deepa *et al.* 2011) by increasing superficial area and accessibility to functional modification. Polyethylene glycol (PEG) is a water-soluble polyether polymer that can be used in biodegradable PLA-cellulose composites due to its good compatibility with PLA and its capacity to impregnate the cellulose fiber. Researchers have used steam explosion as a means to study biomass (Deepa *et al.* 2011), and other researchers have been blending polymers using biocompatible plasticizer and incorporation of filler materials. Chemical incompatibilities between reinforcement and matrix phases can also be removed by utilizing cellulose for both components (Mohapatra *et al.* 2014).

The aim of this study was to use PEG, as a modifier of the surface of henequen cellulose fibers subjected to steam explosion treatment, to improve cellulose-matrix compatibility in the PLA composite, and to study the effects on mechanical and thermal properties. The cellulose composites were analyzed *via* scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), thermal analysis, differential scanning calorimetry (DSC), and their mechanical properties.

EXPERIMENTAL

Materials

Cellulose extracted from the henequen fiber (*Agave fourcroydes*) was obtained using a method developed at the Scientific Research Center of Yucatán (CICY), Mexico (Canché-Escamilla *et al.* 2005). The process consists of four steps: (1) mild acid hydrolysis with 0.4% H₂SO₄ at boiling temperature, (2) treatment with 3.5% NaClO at 30 ° C, (3) an alkaline extraction with 20% NaOH at room temperature, and (4) bleaching with 0.5% NaClO at room temperature. After each step, the material was washed until neutral pH was obtained. The cellulose was dried at room temperature. The cellulose content was not determined in this work. However, when the same method was used by Cazurang-Martínez *et al.* (1990), they reported that the henequen cellulose obtained had a content of 96% cellulose and 4% hemicellulose. Polyethylene glycol 400 from Sigma-Aldrich (St. Louis, MO, USA) and deionized water were used for all of the impregnation experiments. The reagents were used as received without any additional purification. Polylactic acid (IngeoTM Biopolymer 2003D, specific gravity: 1.24, melt flow rate: 6 g/10 min (210 °C, 2.16 kg), extrusion grade was supplied by NatureWorks (Minnetonka, MN, USA) and used as received without further purification.

Henequen cellulose treated by steam explosion and PEG impregnation

The boiler was filled with double-distilled water until reaching 10 lbf/in² (psi) of generated steam pressure. The henequen cellulose was loaded in a tank, hermetically closed, and the valves that conduct the steam to the deposit were opened. The cellulose was allowed to stand for 5 min at a constant 10 psi steam pressure. Once this time elapsed, the valve located in the lower part of the tank was immediately opened, creating a sudden change in pressure and violently expelling the cellulose towards a container located in the lower part of the equipment. This procedure was repeated once. The wet cellulose was placed in a 70 °C oven until a constant weight was obtained.

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Impregnation of PEG into steam-exploded cellulose

A solution of PEG/water with a 1:1 ratio was prepared. Afterwards, the PEG/H₂O solution and cellulose were deposited in the reactor to prepare the cellulose/PEG required. The mixture was agitated for 2 h at room temperature. The resulting mixture was filtered, poured into a vessel open, and placed in a 150 °C oven for 2 h to evaporate the water. Then, the materials were removed and dried at room temperature. Subsequently, the cellulose with PEG was placed in a beaker with 1 L of double-distilled water and stirred for 2 h to remove the remaining PEG. This procedure was performed three times, replacing the old water and adding new. After removing the largest amount of residual PEG, the cellulose was placed in an oven to dry at 105 °C for 5 d, to finally obtain material at a constant weight with its chemical treatment. The calculations determined that approximately 92% by weight of the PEG was added to the cellulose, when it was realized the chemical treatment. Figure 1 shows a photograph of the cellulose subjected to steam explosion, without PEG (CEST) and with PEG (CETQ), accordingly.



Fig. 1. Cellulose subjected to steam explosion without PEG (CEST) and with PEG (CETQ)

Elaboration of composite

All the composites were prepared by mixing in a Haake Rheocord Fision 9000 (Haake, Karlsruhe, Germany) batch mixer with a 60 cm³ chamber capacity with roller rotors. The PLA was preheated and set at 160 °C and 20 rpm for 3 min. Then the cellulose was gradually introduced into the mixer at a constant rate to avoid overflow problems. After achieving the mixing time requirements, approximately 5 min, the mixer was turned off, and the composites were collected immediately in a vessel and allowed to dry at room temperature.

A Carver compression molder (Carver Inc., Wabash, IN, USA) was used to prepare 3-mm-thick, 15 cm × 15 cm plates. The plates were annealed in the molder at 160 °C for 3 min with 100 bar pressure. Subsequently, the pressure was removed for 1 min and resumed at 100 bar for 3 min; this procedure was repeated three times. In the next procedure, the heat continued at 160 °C for 3 min at 200 bar pressure. Subsequently, the pressure was removed for 1 min and resumed at 100 bar for 3 min; this procedure was disconnected, and the plate was allowed to cool at 200 bar pressure at room temperature. The code used to identify the samples was as follows: CEL is cellulose, CEST is cellulose by steam explosion, CETQ is cellulose with PEG treatment, CESTQ is cellulose by steam explosion with PEG treatment, and % is percent by weight. The samples are presented according to the relation of "X" % polylactic acid/ "Y" % treated Cellulose and "Z" % is the amount added of polyethylene glycol into cellulose (wt%). One example is 95% PLA/5% CESTQ_40% PEG. That is, 95% by weight

PLA and 5% by weight of cellulose. The last part is the 40% weight ratio of PEG added to cellulose.

Methods

Scanning electron microscopy (SEM)

The morphologies of the fibers and of the composites were examined using a Hitachi TM-1000 field emission scanning electron microscope (Hitachi, Tokyo, Japan). Specimens, after tensile testing, were fractured in liquid nitrogen and coated with gold prior to imaging (SPi, West Chester, PA, USA).

FTIR-attenuated total reflectance (ATR)

The FTIR analysis of the surface modification of the composites was performed using a Thermo Scientific iS5 Nicolet (Thermo Fisher Scientific, Madison, WI, USA) with ATR. The spectra were obtained at a 4 cm⁻¹ resolution, with 64 scans in the standard wavenumber range from 400 cm⁻¹ to 4000 cm⁻¹. All the samples were oven-dried at 60 °C for 24 h before testing.

Mechanical properties

The test pieces for measuring the mechanical properties were cut by a laser machine at a 5 mm/min speed with a 100% cutting intensity. All of the test specimens were arranged for 7 d at room temperature prior to testing.

The tensile tests were conducted in an Instron 3345 universal testing machine (Instron, Norwood, MA, USA), equipped with a 1-kN electronic load cell and mechanical clamp grips.

The testing was performed following the ASTM D638 (2001) standard at a crosshead speed of 1 mm/min and a distance between mechanical clamp grips of 25.4 mm. The flexural test samples were performed following the procedure of the ASTM D790 (2001) standard for plastic materials with and without reinforcement, using a three-point contact system, in the universal testing machine at 1 kN at a speed of 1 mm/min.

Differential scanning calorimetry (DSC) analysis

The DSC measurements were taken with a Discovery TA (model: Q100, TA Instruments, New Castle, USA). The samples were dried for 24 h in an oven at 60 °C prior to DSC analysis. For the first scan, the samples were heated from 0 °C to 200 °C and kept at 200 °C for 1 min to remove the internal moisture and volatile small molecules. For the second scan, the samples were cooled to 0 °C, kept for 1 min, and subsequently heated to 200 °C, kept for 1 min, before finally cooling to 0 °C. Both the heating and cooling rates were 10 °C/min during the scans.

The degree of crystallinity (X_c) of the PLA and its composites was calculated from the second thermal scan as follows,

$$X_{c} = \frac{\Delta H_{m}}{w \times \Delta H_{mc}} \times 100 \tag{1}$$

where $\Delta H_{\rm m}$ and $\Delta H_{\rm mc}$ are the melting enthalpies for PLA composites and the 100% crystalline PLA, respectively, and *w* is the mass fraction of PLA in the composite. The melting enthalpy of a totally crystalline PLA material ($\Delta H_{\rm mc}$) was considered to be 93 J/g.

RESULTS AND DISCUSSION

Microphotographs of Fibers

The SEM micrographs in Fig. 2 show the effects of the pretreatment on the structure of the fibers. Figure 2A shows the raw, unbroken henequen fibers that are well-defined. Figure 2D shows the raw henequen fibers at $2500 \times$ magnification; the untreated superficial layer was flat and smooth. In Fig. 2B, the henequen cellulose fibers show a changed morphology. This change occurred during the course of pretreatment with sulfuric acid solution and delignification with sodium hydroxide and steam explosion.



Fig. 2. Scanning electron micrographs of the different fibers used 250X: A) raw henequen cellulose fibers, B) henequen cellulose fiber with pretreatment acid/base and steam explosion, C) cellulose fiber with pretreatment acid/base and steam explosion, and chemical treatment with PEG. High magnification scanning electron micrographs to 2500X, D) raw henequen cellulose fibers, E) henequen cellulose fiber with pretreatment acid/base and steam explosion, and F) cellulose fiber with pretreatment acid/base, steam explosion and chemical treatment with PEG.

The removal of the extractives from the superficial layer was able to increase the contact area because the fibrils became more exposed (Sreekumar *et al.* 2009; Pereira *et al.* 2011). As shown in Fig. 2E (high magnification), the fibers pretreated with acid/base and steam explosion exhibited shortening and thinning. Afterwards, typical organic cells, parenchyma, and defibrillated fibers could be observed in the morphology. Figure 2C shows the surface of henequen cellulose pretreated with acid/base, steam explosion, and chemical treatment with PEG. This yielded a superficial texture different than that of the raw fiber and the pretreated fiber, which indicated that the PEG present on the surface somehow interacted between PLA and cellulose (Taib *et al.* 2010). The fibers in the micrographs of Fig. 2C appear small in comparison to Figs. 2A and 2B; this size reduction could have been caused by the mechanical agitation of the water/PEG solution and henequen cellulose fibers during the thermal chemical treatment. Being broken into small pieces enhances contact between the solution and the cellulose fibers (Espitia Sibaja 2010).

The superficial layer of henequen cellulose pretreated with acid/base steam explosion and chemically treated with PEG, at a magnification of $2500 \times$ with the fiber covered with PEG, is shown in Fig. 2F.

FTIR Analysis

The changes in the fiber molecular structures treated by steam explosion were revealed by FTIR analysis. In Fig. 3, the samples prepared under steam pressure gave a very similar spectral pattern to that of henequen cellulose. The only difference observed was the peak intensity, indicating that the treatment of steam pressure did not result in any noticeable changes in the macromolecular structure of the henequen cellulose. The magnitudes of all the spectra were normalized relative to the base line. The reason for of choosing the region at 1024 cm⁻¹ was that all of the samples showed too high absorbance in this area. The normalized in-phase spectra were then used for the peak height calculations, which were required for the cellulose estimation, in accordance with Akerholm *et al.* (2004).



Fig. 3. FTIR ATR spectra of raw henequen cellulose, PEG, and henequen cellulose treated at 150 °C

The hydrophilic tendency of the untreated and treated henequen cellulose was reflected in the broad absorption band in the 3321 cm⁻¹ to 3329 cm⁻¹ range, which was related to the -OH groups in the main component. Additionally, the C-H stretching vibration of CH₂ and CH₃ (2874 cm⁻¹ and 2893 cm⁻¹) in CEST was greater than that of CEL, which might have been due to an increase in C–C condensed structures resulting from condensation reactions of lignin during steam explosion treatment (Zhang et al. 2016). The peaks at 1440 cm⁻¹ and 1428 cm⁻¹, corresponding to the aromatic peak C-C stretch from the aromatic rind of lignin, C–O stretching at 1290 cm⁻¹, and unconjugated C=O stretching at 1647 cm⁻¹ were larger for the CEST than for the CEL (Table 1) (Nelson and O'Connor 1964; Tobimatsu et al. 2013). This result was attributed to the steam explosion treatment breaking the β -O-4 linkages of lignin, leaving more exposed hydroxyl groups (Feng et al. 2017). The intensity of the peak at 2874 cm⁻¹ in the spectrum of the CESTQ_40PEG was greater than those in the spectra of the CEL and CEST. This result indicated that the proportions of the CH₂ and CH₃ were higher in the treated with steam explosion cellulose and PEG than in the raw cellulose, as the PEG contained a greater proportion of these groups. Furthermore, the enlarged view of the regions at 889 cm⁻¹ and 1372 cm⁻¹ showed peaks with an increase in the spectrum of the CESTQ_40%PEG versus CEL. These were assigned to the outer surface C–OH asymmetric scissoring vibration and to the inner-surface C–H shear vibration of the PEG, respectively. Moreover, the peak representing the ether groups in CESTQ_40%PEG also underwent noticeable changes; it became wider at 1256 cm⁻¹ compared against the peak at 1290 cm⁻¹ in the CEL spectrum. This procedure confirmed that the CEST molecules were able to interact with the hydroxyl at the end of PEG.

Table 1 shows the bands of FTIR of cellulose and composites. The intensity area index of the peak at 2874 cm⁻¹ in the spectrum of the CESTQ_40%PEG was greater than the corresponding one in the CEST spectrum. This indicated that the proportions of CH_2 and CH_3 were higher in the PEG-treated cellulose than in the raw cellulose with steam explosion, as the PEG contained a greater quantity of these groups. These observations indicate that CESTQ treated with PEG and temperature to 150 °C increased the probability of interaction between the PEG and the cellulose (Hammiche *et al.* 2016).

| Functional | Henequen | | Cellulose, Steam | | PEG | | Cellulose 40% | |
|-------------------------------------|-------------------------------------|---------------------|------------------------------------|---------------------|-------------------------------------|---------------------|------------------------------------|---------------------|
| Group | Cellulose | | (CEST) | | | | PEG | |
| | (CEL) | | | | | | (CESTQ_40PEG) | |
| | λ ⁻¹ (cm ⁻¹) | A/A ₁₀₂₄ | λ^{-1} (cm ⁻¹) | A/A ₁₀₂₀ | λ ⁻¹ (cm ⁻¹) | A/A ₁₀₈₇ | λ^{-1} (cm ⁻¹) | A/A ₁₀₂₇ |
| O-H | 3321 | 2.37 | 3329 | 2.97 | 3369 | 3.63 | 3334 | 3.71 |
| CH ₂ and CH ₃ | 2874 | 0.84 | 2893 | 1.10 | 2890 | 1.47 | 2874 | 1.26 |
| C=O | 1647 | 0.53 | 1640 | 0.65 | 1652 | 1.23 | 1643 | 0.80 |
| C-O | 1290 | 0.11 | 1226 | 0.13 | 1247 | 0.38 | 1256 | 0.16 |
| C-O-C | 1024 | 1 | 1020 | 1 | 1087 | 1 | 1027 | 1 |

Table 1. Wavenumbers Related to Fibers of Henequen Cellulose, Henequen

 Cellulose Treated by Steam Explosion, PEG, and Cellulose/PEG Composite

Thermogravimetric Analysis (TA) of Fibers

The TGA curves for henequen fibers with and without treatment are shown in Fig. 4. Three distinct decomposition peaks can be seen in the TGA curves of CEL and CEST. The first decomposition peak at approximately 100 °C was attributed to the removal of moisture from the samples. The second peak at approximately 200 °C was ascribed to the decomposition of hemicelluloses, while the final peak at approximately 350 °C was attributed to the decomposition of cellulose and lignin (George *et al.* 2014).



Fig. 4. Weight (%) and DTGA of CEL, CEST, and CESTQ_40% PEG composite

The TGA curves plotted by percentage weight loss against temperature indicated that the CEL and the CEST were stable up to 230 °C. The percentage weight losses for the CEL and the CEST at 230 °C were 6% and 4%, while that for the CESTQ_40%PEG was 10%. In the CEL and the CEST, 50% weight losses were observed at 348 °C, while that of the CESTQ_40%PEG was 335 °C. The thermal degradation temperature was affected by structural parameters such as molecular weight, crystallinity, and orientation (Cai and Kim 2010). The thermal degradation temperature of the CESTQ_40%PEG was lower than that of the raw cellulose and steam explosion cellulose. This result could have been because the CESTQ_40%PEG had a lower crystallinity than cellulose. The ash that remained at the end of the TGA analysis for the samples of CEL and CEST was approximately 11% of the total sample weight.

FTIR spectroscopy was performed to compare the structure of cellulose before and after chemical modification with PEG. The composition 85PLA/15CESTQ was 20 and 40 wt% of PEG into cellulose. This was chosen because it was the most concentrated in PEG and this was useful for quantifying the relative intensity of the functional groups in cellulose. Figure 5 shows the PLA spectrum peaks; the stretching and bending peaks of C=O appeared at 1751 cm⁻¹ and 1290 cm⁻¹, respectively. The characteristic absorption peaks of the 85PLA/15CESTQ 40%PEG composites were nearly the same as those of the CESTQ_40%PEG composites. Only a few functional groups underwent changes in the intensity, and these changes were small shifts in wavenumber. This observation is consistent with an assumption that henequen cellulose was only combined with the PLA and PEG through physical interactions without forming new functional groups. With the addition of the henequen cellulose/PEG, the C=O peak of the PLA at 1751 cm⁻¹ increased in the composite when the PEG content increased (Table 2). This can indicate molecular interaction between the C=O of PLA and the -OH of henequen cellulose. This could mean that there was an intermolecular interaction in the PLA/henequen cellulose composites, and the PEG could improve the intermolecular interaction and then enhance the interfacial interaction between the PLA and the henequen cellulose (Qu et al. 2010).



Fig. 5. FTIR of composites and PLA

Table 2 summarizes the FTIR spectroscopic data of the PLA and composites. As shown in Table 2, the intensities of the peaks representing the carbonyl groups (near 1751 cm⁻¹) and methyl groups (near 2928 cm⁻¹) in composite materials increased. The increase of the relative area index indicates that the thermal compression increased the probability of intermolecular interactions in the PLA and the cellulose of henequen and the PEG, when the composite materials were produced. This improved the interfacial interaction between the PLA and the cellulose of henequen treated with PEG.

| | - | | | | | | | |
|--------------------|-------------------------------------|---------------------|-------------------------------------|---------------------|-------------------------------------|---------------------|-------------------------------------|---------------------|
| Functional | | | 85PLA/15CESTQ_ | | 85PLA/15CESQ_ | | 85PLA/15CESTQ_ | |
| Group | PLA | | 0 PEG | | 20 PEG | | 40 PEG | |
| | λ ⁻¹ (cm ⁻¹) | A/A ₁₀₈₂ | λ ⁻¹ (cm ⁻¹) | A/A ₁₀₂₄ | λ ⁻¹ (cm ⁻¹) | A/A ₁₀₂₆ | λ ⁻¹ (cm ⁻¹) | A/A ₁₀₂₇ |
| O-H | | | 3003 | 3.02 | 3351 | 4.50 | 3337 | 4.31 |
| CH₂ and CH₃ | 2853 | 2.33 | 2899 | 1.21 | 2881 | 1.69 | 2895 | 3.17 |
| C=O | 1751 | 2.26 | 1719 | 0.54 | 1719 | 0.81 | 1725 | 0.82 |
| CH₃ | 1455 | 0.73 | 1454 | 0.51 | 1454 | 0.62 | 1455 | 0.68 |
| CH-CH ₃ | 1359 | 0.75 | 1364 | 0.24 | 1364 | 0.38 | 1363 | 0.37 |
| C-O-C | 1082 | 1 | 1024 | 1 | 1026 | 1 | 1027 | 1 |

| Table 2 Bonds' | Wayopumbore | Polatod to | Pogione | of DLA | and Com | nocitoc |
|------------------|-------------|------------|---------|--------|---------|---------|
| I able Z. DUIIUS | wavenumbers | Related to | Regions | ULLA | and Com | posites |

Figure 6 shows that the weight loss of the PLA and composite materials occurred in a one-step degradation process from 300 °C to less than 400 °C. This result was confirmed by the presence of peaks in the DTG curves, at temperatures from 340 °C for the composites and 354 °C for the PLA. The mass loss of the PLA and composite materials started at 300 °C and continued rapidly to 350 °C. It continued slowly above about 400 °C. For the PLA and 85PLA/15CESTQ, 50% weight losses were observed at 343 °C, while the same for 85PLA/15CESQ_ 20%PEG and 85PLA/15CESQ_ 40%PEG were at 338 °C and 328 °C. In this stage, the degradation process of the sample of 85% PLA and 15% cellulose was slightly affected by the PEG present in the blend of the composite materials.



Fig. 6. Weight (%) and DTGA of composites

Generally, the addition of PEG to the henequen cellulose in the PLA matrix increased the decomposition temperature of the composites. This finding seems to be in accordance with Hammiche *et al.* (2016), who found that the addition of cellulose nanowhiskers (CNW) extracted from alfa fiber enhanced the thermal stability of PVC especially for CNW dispersed in PEG. This result probably can be ascribed to a protection role of adsorbed PEG chains in the surface of CNW. This improved thermal stability and lower thermal degradation of nanocomposites processed from CNW dispersed in PEG.

DSC Analysis

Figure 7 shows the thermal transitions occurring in the composite materials by thermal compression molding, such as glass transition (T_g), cold crystallization (T_c), and melting (T_m). The samples were cooled at room temperature until the process ended, and the data of the thermograms were determined during the second heating cycle. Table 3 shows the DSC data and the degree of crystallinity (X_c). The incorporation of henequen cellulose steam explosion in the composites 95% PLA/5% CESTQ, 90% PLA/10% CESTQ and 85% PLA/15% CESTQ increased by circa 1 °C the T_g of composites with respect to PLA. This increase confirmed adhesion between the fiber and the matrix upon blending with henequen cellulose steam explosion without PEG in accordance to Jandas *et al.* (2013), when the concentration increased only henequen cellulose to 5%, 10%, and 15% in the PLA matrix.



Fig. 7. DSC thermograms of composites

The increase from 10% to 40% PEG in the henequen cellulose blended to the PLA matrix in the composites and yielded decreases in the T_g of approximately 2 °C to 4 °C, indicating that a plasticization effect occurred. According to Mohapatra *et al.* (2014), this is primarily due to the plasticizing effect of PEG. Smaller molecules such as PEG can enter in between the PLA macromolecules during the melt mixing process and can establish physical interactions like hydrogen bonding or dipole–dipole interaction in between atoms. As a result, some of the rigid homogeneous PLA/PLA interaction will be replaced by heterogeneous PLA/PEG interactions. This phenomenon may provide better macromolecular movement and thereby lead to a decreased energy consumption during glass transition or decreasing the T_g . The T_m of the composites decreased compared to that of neat PLA. The degree of crystallinity, when only henequen fiber was incorporated, increased compared to the PLA. Such an increase of crystallinity confirmed that a cellulose

fiber induced the nucleating. Similar observations were made by Frone *et al.* (2013) and Jandas *et al.* (2013). When the henequen fiber was incorporated with PEG, the degree of crystallinity of composites decreased with increasing henequen fiber and PEG content. This result may be attributed to the increase in amorphous nature of the henequen fiber (Sun *et al.* 2017).

| PEG (%) | T _g (°C) | $\Delta H_{\rm c} ({\rm J/g})$ | T _c (°C) | $\Delta H_{\rm m}$ (J/g) | T _m (°C) | X _c (%) | | | |
|-------------------------|---------------------|--------------------------------|---------------------|--------------------------|---------------------|--------------------|--|--|--|
| 0 | 58.15±0.21 | 21.10±0.14 | 97.85±0.21 | 41.97±0.04 | 169.13±0.18 | 45.12±0.05 | | | |
| 95%PLA/5%CESTQ_X%PEG | | | | | | | | | |
| 0 | 59.92±0.03 | 34.15±0.06 | 101.45±0.17 | 47.53±0.16 | 167.01±0.12 | 53.66±0.18 | | | |
| 10 | 58.18±0.07 | 35.25±0.19 | 101.59±0.06 | 45.14±0.14 | 166.21±0.15 | 51.10±0.01 | | | |
| 20 | 58.15±0.01 | 35.90±0.06 | 100.90±0.12 | 45.93±0.05 | 165.96±0.21 | 52.03±0.05 | | | |
| 30 | 57.06±0.23 | 35.66±0.16 | 98.07±0.21 | 41.84±0.20 | 166.70±0.05 | 47.36±0.23 | | | |
| 40 | 57.13±0.16 | 34.06±0.04 | 98.73±0.11 | 41.89±0.03 | 166.96±0.26 | 47.42±0.03 | | | |
| | | 90% P | LA/10% CEST | Q_X%PEG | | | | | |
| 0 | 59.86±0.10 | 33.63±0.15 | 101.23±0.15 | 45.75±0.07 | 167.68±0.13 | 55.86±0.09 | | | |
| 10 | 58.47±0.19 | 33.79±0.13 | 101.98±0.07 | 45.21±0.18 | 167.35±0.21 | 54.01±0.20 | | | |
| 20 | 56.72±0.16 | 33.29±0.18 | 98.53±0.01 | 45.21±0.16 | 166.47±0.03 | 54.76±0.20 | | | |
| 30 | 54.12±0.20 | 33.68±0.10 | 96.97±0.16 | 45.24±0.19 | 166.88±0.11 | 54.05±0.22 | | | |
| 40 | 55.82±0.15 | 31.28±0.07 | 96.86±0.14 | 44.88±0.09 | 166.02±0.01 | 53.62±0.10 | | | |
| 85% PLA/15% CESTQ_X%PEG | | | | | | | | | |
| 0 | 60.07±0.15 | 30.87±0.05 | 102.90±0.11 | 45.48±0.02 | 169.04±0.13 | 57.53±0.02 | | | |
| 10 | 58.50±0.12 | 31.90±0.16 | 101.25±0.07 | 44.27±0.10 | 167.15±0.20 | 56.08±0.13 | | | |
| 20 | 55.78±0.05 | 28.29±0.24 | 97.56±0.16 | 44.65±0.07 | 166.29±0.20 | 56.48±0.08 | | | |
| 30 | 54.00±0.10 | 28.84±0.19 | 94.79±0.20 | 44.24±0.07 | 166.04±0.16 | 55.96±0.09 | | | |
| 40 | 52.88±0.03 | 30.76±0.09 | 93.92±0.04 | 43.74±0.14 | 164.98±0.16 | 57.28±0.17 | | | |

| Table 3 | DSC Data | Correspond | lina to the | Second | Heating/C | Colina | Scan |
|----------|----------|------------|-------------|--------|---------------|--------|------|
| Table J. | | Concapone | | | i icalii iy/O | | ocan |

In Fig. 8, the composite with PEG content in the henequen cellulose of the matrix of PLA demonstrated a different trend in tensile strength properties. As shown in Fig. 8A, the tensile strength of the 85 PLA/15 CEST presented an increase in respect to the matrix of PLA. However, by increasing the weight percentage of PEG in the cellulose of composites 85%PLA/15% CESTQ 10%PEG to 85%PLA/15%CESTQ 40%PEG, the tensile strength decreased up to a certain limit. The composites prepared at 90PLA/10% CESTQ_0%PEG to 90PLA/10%CESTQ_40%PEG and 95%PLA/5%CESTQ_0%PEG to 95% PLA/ 5% CESTO 40% PEG exhibited a decrease in tensile strength when the content of cellulose into PEG treatment in the composite was reduced. This could be attributed to the plasticization of PLA by PEG and the presence of PEG that somehow interfered with the interaction between PLA and cellulose in the composites. This is supported by Taib et al. (2010), who found the presence of PEG might have disturbed the fiber-matrix interaction in the PLA/ kenaf fiber composites. Another factor in the reduction of tensile strength is related to the decreased cellulose /PEG loading, whereas the applied stress is not uniformly distributed and the matrix bears most of the load. Thus, the composite strength of the matrix dominated and cellulose/PEG may act as flaws or weakening points; this would reduce the composite strength (Hu and Lim 2007; Baillif and Oksman 2009; Taib et al. 2010). For composites 90 PLA/ 10 CEST and 85 PLA/ 15 CEST, the cellulose loading was 10 and 15 wt%; this was considered an improvement in the properties of tensile, which indicated a better interfacial interaction between henequen cellulose and PLA, in accordance with Abu Ghalia and Dahman (2017). When the content of PEG in these composites increased, the tensile strength property decreased.



Fig. 8. Mechanical properties of composites: A)Tensile strength, B) Tensile modulus, C) Flexural strength, and D) Flexural modulus

The Young's modulus of the PLA henequen cellulose/PEG increased slightly with an addition of PEG into cellulose content (Fig. 8B). This was attributed to the stiffening that occurred from the cellulose grafted with PEG in the PLA. Another additional situation was that henequen cellulose had a high crystallinity degree, which was the result of an increase in the Young's modulus (Abu Ghalia and Dahman 2017).

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Fig. 9. Scanning electron micrograph showing the fracture surfaces of biocomposite made from PLA and henequen cellulose (85/15CESTQ) treated with different content in percent in weight of PEG to 250X: A) PLA , B) 0%PEG, C) 20%PEG, D) 40%PEG. High magnification scanning electron micrograph to 1000X: E) PLA, F) 0% PEG, G) 20%PEG, and H) 40%PEG.

Figures 8C and 8D demonstrate the flexural strength and flexural modulus for the composites of PLA/henequen cellulose with PEG, which presented slight differences

compared to the neat PLA. This led to less flexural strength and a slightly different behavior in the flexural modulus with respect to PLA. This could have been caused by agglomeration of henequen cellulose/PEG in the matrix of the PLA and the irregularities in the composite's composition, resulting in a reduction of flexural behavior (Tse *et al.* 2018). Cisneros-Lopez *et al.* (2018) used the process of rotomolding and compression molding and obtained similar values of flexural modulus in composites of polylactic acid and agave fiber.

The morphologies of the fracture surfaces of biocomposites made from the PLA and henequen cellulose modified with PEG are shown in Fig. 9A to 9D at 250× magnification and Fig. 9E to 9H at 1000x magnification. Figure 9A shows the fracture of PLA. The increased amount of PEG in the henequen cellulose at 20 wt% and 40 wt% (Figs. 9C and 9D) led to a rougher fracture surface than in the case of 0 wt% PEG in the biocomposites (Fig. 9B). Consequently, the increase of cellulose content is associated with rougher fracture of the surfaces (Boontima et al. 2015). There were voids in all of the biocomposites. There were smaller and fewer voids on the surface of 85% PLA/15% CESTQ 20% PEG and 85% PLA/15% CESTQ 40% PEG, which in turn indicated better interfacial strength (Sheltami et al. 2015). Figures 9E to 9H (high magnification scanning electron micrographs) display the contact between henequen cellulose treated with PEG and the PLA. This closeness between fiber and matrix provided a good adhesion, which was also observed from the near absence of holes around the fillers and from the breaking of fillers during fracture in compositions of 85% PLA/15% CESTQ at 85% PLA/15% CESTQ_20%PEG, and 85% PLA/15% CESTQ_40%PEG. In each case, the major component surrounding the treated fibers seemed to be the continuous phase. The henequen cellulose was smooth and had a rough surface and a large reactive area due to the pretreatment, which is an important factor to enhance adhesion (Canché-Escamilla et al. 1997). When the concentration of henequen cellulose increased in the matrix of the PLA, the surfaces of the pull-out cellulose fibers had a rough appearance due to their containing adhered traces of polymer matrix. This result demonstrated a better adhesion between the PEG-grafted fiber and the matrix.

CONCLUSIONS

In this research henequen cellulose fiber was treated on the surface by steam explosion technology combined with the addition of polyethylene glycol (PEG). The treated polylactic acid (PLA)/fiber blend produced composites by thermocompression. The following results were obtained:

- 1. The FTIR-ATR spectra showed some changes in the intensity. These alterations affected the interactions of the functional groups in the composites.
- 2. The SEM micrographs of high magnification showed that the fibers were changed. The raw fiber was smooth, yet the fibers that were steam-explosion pretreated had a rough surface and more reactive area due to the pretreatment. The fiber pretreated with steam-explosion and PEG showed a rough surface covered with PEG. In the composites, the fiber exhibited good wetting, which was apparent from the near absence of holes around the fibers. In each case, the major component surrounding the treated fibers seemed to be the continuous phase.

- 3. It was considered that tensile strength and Young's modulus showed improvement for 90 PLA/10 CEST and 85 PLA/15 CEST with all contents of PEG. This was ascribed to the appropriate dispersion, with a better interfacial interaction between henequen cellulose/PEG and PLA. Henequen cellulose exhibited a high crystallinity degree, which gave rise to an increase in the Young's modulus upon its addition to the matrix. A lower flexural strength was present and there was a very slightly different flexural modulus compared to the PLA. This was ascribed to agglomeration of henequen cellulose/PEG in the matrix of PLA.
- 4. The composites showed notable thermal stability for all the composites, due to the surface modification of cellulose with PEG. With the incorporation of henequen cellulose subjected to steam explosion without PEG to the PLA matrix, the T_g of composites increased 1 °C with respect to PLA. This increase confirmed efficient adhesion between the fiber and matrix upon blending with henequen cellulose steam explosion without PEG. The T_g of PLA was treated from 59 °C to 52 °C in the reinforced composite with the incorporation of PEG from 10% to 40% in the henequen cellulose blended to the PLA matrix. Such results indicated that change in the degree of plasticization occurred.
- 5. The degree of crystallinity, determined by DSC, was higher for the PLA composites than for the neat PLA. This increase of crystallinity confirmed that cellulose fibers induced the nucleating.
- 6. The thermal degradation temperature of the fiber with the PEG was lower than the raw cellulose and steam explosion cellulose. From the TGA of the composites, the increased decomposition temperature of the composites was attributed to adhesion between the cellulose/PEG and PLA matrix.

There are many potential applications of these composites, such as rotational molding, to obtain hollow pieces of medium size, manufacture cylinders, pots, *etc.* In injection molding, it could be used in the manufacture of disposable covers, packaging, plates, and cutlery or for low-end packaging. In spite of the promising properties of composites, there still remains much research required to understand the fundamentals of these materials and to find suitable industrial applications.

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