



Improving the Compatibility and Mechanical Properties of Natural Fibers/Green Polyethylene Biocomposites Produced by Rotational Molding

Jorge R. Robledo-Ortiz¹ · Martín E. González-López² · Denis Rodrigue³ · Juan F. Gutiérrez-Ruiz² · Fernando Prezas-Lara² · Aida A. Pérez-Fonseca²

Published online: 31 January 2020

© Springer Science+Business Media, LLC, part of Springer Nature 2020

Abstract

In this work, sustainable rotomolded composites based on green polyethylene (Green-PE) and natural fibers (coir and agave) were studied. Fibers' surface was treated with maleated polyethylene to improve the fiber-matrix compatibility. Samples were characterized by morphology, mechanical properties (impact, tension, and flexion) and water absorption. Results showed a more homogeneous morphology with better fiber dispersion and wetting in the treated fibers composites which lead to substantial improvements of tensile modulus from 258 MPa for the neat matrix up to 345 MPa for both, treated agave and coir composites (at 30% wt), and tensile strength from 13.7 MPa for Green-PE to 15.3 MPa for 30% treated coir composites. The positive effect of the surface treatment was also observed in flexural strength with increases up to 100% and 34% in flexural modulus. Also, impact strength was increased up to 46% and water absorption reduced up to 55% for treated fiber composites compared to untreated fiber composites. As an important observation, it was possible to obtain similar or even higher mechanical properties with the Green-PE natural fiber composites than for a petroleum-based rotomolded polyethylene, which is interesting in terms of sustainability and performances for specific applications like automotive and packaging.

Keywords Green polyethylene · Composite · Coir · Agave · Fiber modification · Mechanical properties

Introduction

Over the years, the use of biopolymers increased as a promising alternative to petroleum-based polymers to reduce environmental pollution and greenhouse gas emissions [1].

In this sense, green polyethylene (Green-PE or Bio-PE), produced from sugarcane ethanol, it has been introduced to the polymer market. Besides its renewability, another advantage of this process is that sugarcane plants absorb CO₂ as they grow, helping to fight against the greenhouse effect [2].

It is known that Green PE's carbon footprint is less than petroleum-based PE, which is 2.1 t CO₂/t polymer. In fact, Green PE has a negative value (− 2.5 t CO₂/t polymer) indicating that it contributes to lower CO₂ emissions by carbon fixation [3]. Unfortunately, Green-PE is still more expensive than conventional (petroleum-based) polyethylene and is still non-degradable. Nevertheless, the costs are expected to go down in the near future as it was the case for polylactic acid (PLA) in recent years.

On the other hand, improving the mechanical properties of polymers with natural fibers has received great interest due to the rising concern about the environmental, processing and economic issues associated with synthetic reinforcements such as glass, carbon and aramid fibers [4]. The advantages of natural fibers are their availability, good strength and eco-friendly (biosourced) nature, as well as their lower density and cost compared with inorganic reinforcements [5]. In this sense, the reinforcement of Green-PE with natural fibers is an ideal option to produce more sustainable materials than petroleum-based polymer composites while decreasing the costs because less polymer is used to

✉ Aida A. Pérez-Fonseca
aida.perez@academicos.udg.mx

¹ Departamento de Madera, Celulosa y Papel, CUCEI, Universidad de Guadalajara, Zapopan, Jalisco, Mexico

² Departamento de Ingeniería Química, CUCEI, Universidad de Guadalajara, Blvd. Gral. Marcelino García Barragán # 1451, 44430 Guadalajara, Jalisco, Mexico

³ Department of Chemical Engineering and CERMA, Université Laval, Quebec, QC, Canada

produce a final part. Moreover, each component of these composites would become biodegradable and return to the cycle, from a circular economy point-of-view, in the form of CO₂ source for the generation of biomass from which bio-based Green PE and natural fibers can be obtained again as described in Fig. 1.

It is well known that the mechanical properties of the composites are strongly affected by the interfacial bonding/adhesion between the hydrophilic fibers and the hydrophobic matrices [6]. Several methods are available to improve the fiber/matrix interaction, but the most popular and effective one is the addition of a coupling agent. In general, these coupling agents are incorporated during the composite blending, allowing some reaction (chemical) or interaction (physical) between the fibers and the matrix. The final composites can be obtained by extrusion to produce profiles or by compression or injection molding to produce finished parts [7–9]. For example, Boronat et al. [10] used Bio-PE to produce composites using eggshell as a filler. The compounds were prepared via extrusion followed by injection molding and titanate was used as a coupling agent to improve the interfacial bonding. But the tensile strength was reduced with the eggshell addition due to its low interaction with the matrix even though the tensile modulus increased.

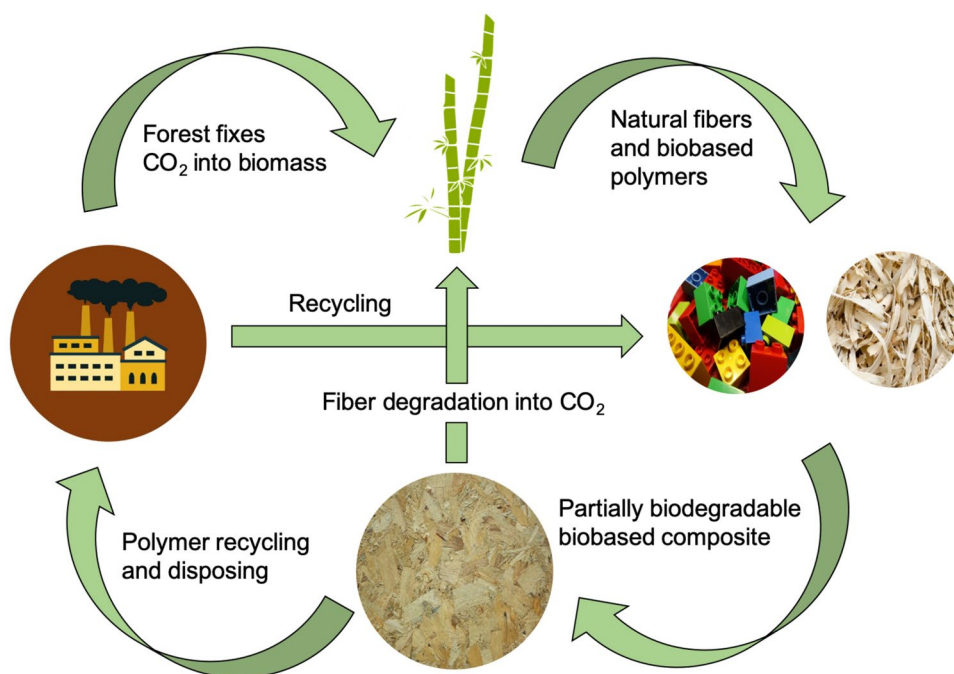
Maleic anhydride grafted polyethylene (MAPE) has provided excellent results in terms of enhancing compatibility. De Oliveira et al. [1] prepared injected blends of Bio-HDPE, polylactic acid and nanosized calcium carbonate using MAPE as a compatibilizer. There was a significant decrease in the melt flow index (MFI) values (from 7.7 to 4.4 g/10 min) when the compatibilizer was added to the material

which was attributed to better interfacial adhesion between the Bio-HDPE matrix and the dispersed nanoparticles. Tarres et al. [11] used two Bio-PE (low and high melt flow index) and thermomechanical pulp (TMP) fibers to produce composites via extrusion followed by injection molding. The fiber content was 20% wt with different amounts of MAPE. The results showed increases in the tensile strength from 20 to 30 MPa for both Bio-PE with 4% wt of MAPE.

A great deal of information is available on extrusion, compression and injection molding, but very few works have been done on rotomolding. Rotational molding is a processing method to produce stress-free hollow plastic parts. It represents a relatively small part of the plastics industry: about 2500 companies around the world consume approximately 0.7% of the world's plastic production [12]. Although rotomolding has been available for over 50 years, it had a substantial development only in the last decade or so to put the process on a competitive ground with injection, thermoforming and blow molding [13]. One important limitation of rotomolding is that the raw materials should be in the form of a plastisol or powder with specific particle size distributions. Today, about 95% of all the rotomolded products are made with different grades of polyethylene (LDPE, LLDPE, HDPE, XLPE, mLLDPE, EVA) followed by PVC (3%) and other resins such as nylons, polypropylene and polycarbonate [13]. To our knowledge, there are no studies reporting on the production of rotomolded Green-PE composites.

In the rotomolding process, the low-shear conditions make difficult the direct use of coupling agents since there is no melt blending/dispersion as can be done in high-shear processes such as extrusion or injection molding. One option

Fig. 1 Circular economy scheme of the production of Green-PE natural fibers composites



is the direct modification of the fibers allowing to modify their surface chemistry to promote compatibility/adhesion with the polymer matrix [14, 15]. For example, Cisneros-López et al. [15] evaluated the effect of different agave fiber surface treatments on the mechanical properties of PE-agave (15% wt) composites produced by rotational molding. Their results showed that the surface treatments improved the homogeneity of the composite. The best results were obtained for modified fibers in a MAPE solution leading to higher mechanical properties (tensile and flexural strength and modulus, hardness and impact strength) than the composites with untreated fiber and even than the neat matrix. Also, Cisneros-López et al. [16] showed that at low fiber contents (10 and 20% wt), the mechanical properties of rotomolded PE/coir and PE/pine composites can be improved using the MAPE solution treatment of the surface of the fibers and produced rotomolded parts with up to 40% wt of fiber content with acceptable properties.

Based on our previous studies [15–17], the objective of this work was to evaluate the effect of MAPE surface treatment of agave and coir fibers in the production of rotomolded natural fiber reinforced biocomposites using Green-PE as a sustainable matrix.

Experimental

Materials

ICO GREEN linear low-density polyethylene (LLDPE) (called Green-PE here) for rotomolding (A. Shulman, México) with a melt flow index of 4.3 g/10 min (190 °C/2.16 kg) and a density of 0.94 g/cm³ was used as the matrix. As a coupling agent, maleated polyethylene (MAPE) Fusabond M603 (Dupont Packaging and Industrial Polymers, USA) was selected. As reinforcement, agave fibers (*Agave tequilana* Weber var. Azul) with tensile strength of 126 MPa and tensile modulus of 4446 MPa were supplied by a local tequila company in Jalisco (Mexico) and coir fibers with tensile strength of 106 MPa and tensile modulus of 2093 MPa were provided by Agrocoir S.A. de C.V. (Colima, Mexico).

Fibers Surface Modification

The agave (A) and coir (C) fibers were washed with water to remove surface impurities. Both fibers were then dried, milled and sieved to keep only particles between 50 and 70 mesh, obtaining average values of fiber length and aspect ratio (L/D) of 2.43 mm and 10.4 for agave and 1.58 mm and 8.5 for coir, respectively. The fiber surface treatment was carried out by dissolving 3% wt of MAPE in xylene at 100 °C. Then, the previously washed and dried fibers were added to the solution at 10% wt with high intensity mixing

at 90 °C for 30 min. Afterward, the fibers were separated from the solution and oven-dried (65 °C) for solvent removal to allow a layer of the polymer to cast onto the fibers. The treated fibers are identified as TA or TC for agave and coir, respectively.

FTIR-ATR

Surface changes due to fiber treatment were evaluated using Fourier transform infrared (FTIR) spectroscopy. The spectra were collected using a Spectrum 100 Fourier transform spectrometer (Thermo Scientific Nicolet iS5, USA) with an attenuated total reflectance (ATR) device. All spectra were obtained after 50 scans within a frequency range from 4000 to 600 cm⁻¹ and a resolution of 4 cm⁻¹.

Composites Preparation

The composites were prepared with different fiber contents (20 and 30% wt). The compounds were prepared by dry-blending using a kitchen blender with dull blades operating at 3,750 rpm during 3 intervals of 1 min. Then, the dry-blends were rotomolded in a laboratory-scale rotational molding machine with a rectangular-shaped stainless-steel mold with dimensions of 15 cm × 15 cm × 16 cm and a wall thickness of 2 mm. After some preliminary trials to optimize the processing conditions, the samples were produced as follows: (1) preheating the oven at 280 °C, (2) loading 300 g of the dry-blended mixture in the mold and heating inside the oven for 20 min with a rotational speed ratio of 4:1, (3) cooling with air convection for 20 min and (4) demolding. The Green-PE based composites are identified as “*xF*” where *x* is the fiber content (20 or 30% wt) and *F* is the type of fiber (A, TA, C or TC).

Density and Porosity

The real—or skeletal density—(ρ_s) of the fibers, PE and composites was determined using a gas pycnometer ULTRAPYC 1200e (Quantachrome Instruments, USA) using nitrogen. Also, the bulk density (ρ_b) was determined according to ASTM D2395. From these values, it was possible to calculate the sample porosity as:

$$\text{Porosity (\%)} = \left(1 - \frac{\rho_b}{\rho_s} \right) \times 100 \quad (1)$$

Morphology

Fractured samples (from Charpy impact tests) were coated for 120 s with gold under vacuum using an SPI Module Sputter Coater. Then, micrographs at different magnifications

were taken on a scanning electron microscope (SEM) TESCAN MIRA3 LMU to characterize the state of fiber adhesion/dispersion in the matrix.

Mechanical Properties

Tensile and flexural properties were measured on an Instron model 3345 universal testing machine with a 1 kN load cell. Tensile tests were carried out according to ASTM D638 with type IV samples at a crosshead speed of 5 mm/min. The reported values for modulus and strength are based on the average of at least five samples. Flexural tests were performed according to ASTM D790 using a crosshead speed of 2 mm/min and a span to depth ratio of 16 times the average thickness of the samples on at least five samples to report the average and standard deviation for modulus and strength. Charpy impact test was performed according to ASTM D6110 using an Instron CEAST model 9050 impact tester. The values reported represent the average of eight samples notched by a manual sample notcher Instron CEAST 6897 at least 24 h before testing.

Water Absorption

Water absorption was determined via ASTM D570. Five samples per composition with dimensions of $2 \times 5 \times \varepsilon$ (varying thickness) cm^3 were dried and weighed. Then, the samples were submerged in distilled water at 50 °C for 42 days (1008 h). The samples were removed after specific periods of time to follow the absorption kinetics. Each time, the surface water was wiped off with a dry cloth and the sample was immediately weighed before being returned in the water bath. The amount of water absorption (M_t) was calculated as:

$$M_t = \frac{w_i - w_0}{w_0} \times 100 \quad (2)$$

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

Results and Discussion

FTIR-ATR

Figure 2 presents the FTIR-ATR spectra of the untreated and treated coir and agave fibers and Fig. 3 the reaction mechanism between MAPE and cellulosic fibers. In all spectra, the characteristics bands of natural fibers are observed: the C-H stretching bands of methyl and methylene groups from cellulose at 2900 cm^{-1} , while between 3200 and 3600 cm^{-1} a wide band appears corresponding to the hydroxyl groups. The C=O stretching band of the carboxyl group in

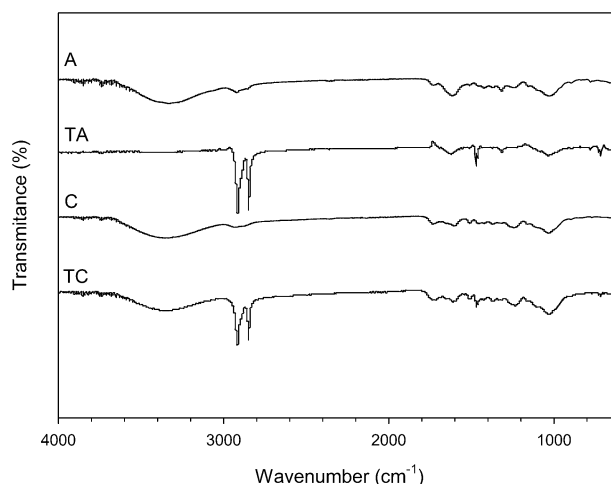


Fig. 2 FTIR-ATR spectra of the untreated (A and C) and treated (TA and TC) natural fibers

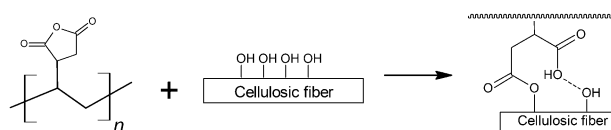


Fig. 3 Reaction mechanism between MAPE and cellulosic fibers

hemicellulose is located at 1750 cm^{-1} and a band attributed to the aromatic rings of lignin is observed at 1510 cm^{-1} [18]. C–O–C and C–O bonds of cellulose and lignin are seen at 1030 cm^{-1} . But treated agave and coir fibers showed two important peaks at 2916 and 2849 cm^{-1} which are characteristic of the alkane groups associated with the polyethylene chains. These bands indicate that surface treatment was successful as the coupling agent is covering the surface of both agave and coir fibers. The successful treatment can also be confirmed by the reduced intensity of the bands between 3200 and 3600 cm^{-1} as lower hydroxyl groups intensity is the result of a reaction with MAPE [16].

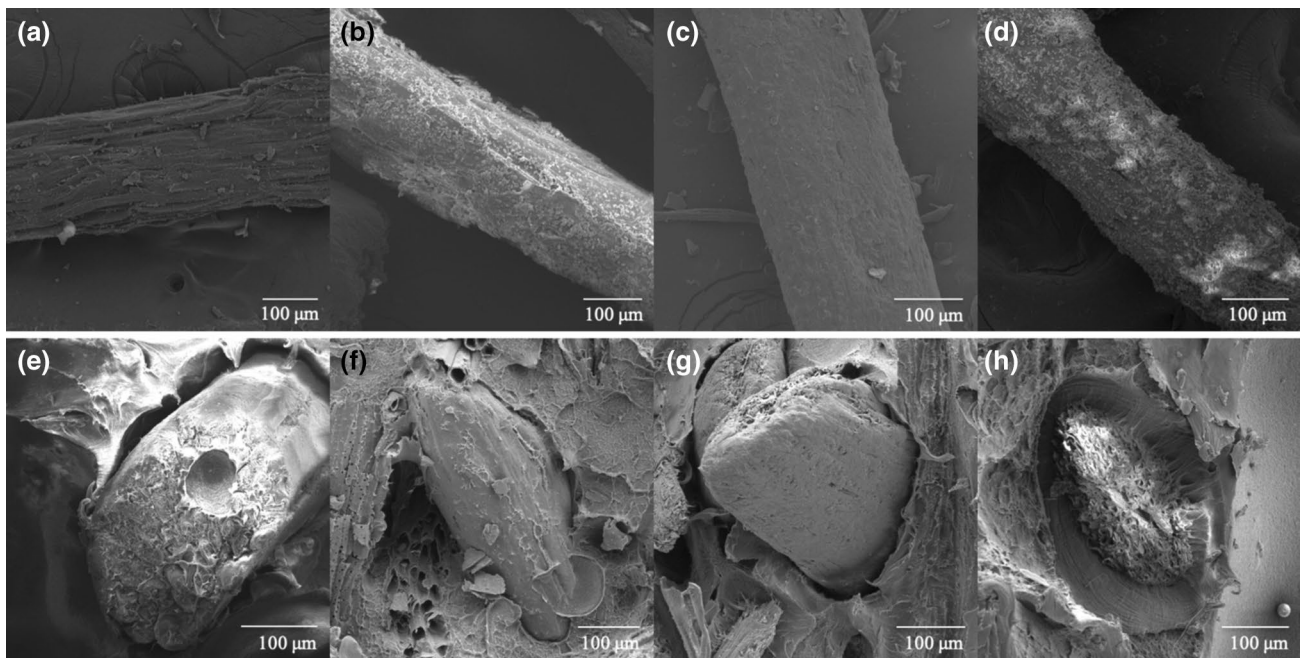
Porosity and Morphology

The porosity of the rotomolded materials is shown in Table 1. It is observed that the porosity of the composites is higher than that of the neat Green-PE, which is due to the voids and gaps between the matrix and the fibers. Nevertheless, the porosity decreased in all the composites with treated fibers, which indicates that the MAPE surface treatment successfully improved the interfacial compatibility, lowering the number of voids and gaps as reported in the morphological analysis as described next.

Figure 4 presents typical images of the surface of the treated and untreated fibers, as well as their interfaces with

Table 1 Porosity of the rotomolded Green-PE and its composites

Sample	Green-PE	20A	20TA	30A	30TA	20C	20TC	30C	30TC
Porosity (%)	0.8	25.3	16.0	31.1	21.4	22.4	15.7	27.9	20.2

**Fig. 4** Micrographs of the fibers: **a** agave, **b** treated agave, **c** coir, **d** treated coir as well as the fiber-matrix interfaces in the composites: **e** Green-PE/agave, **f** Green-PE/treated agave, **g** Green-PE/coir, **h** Green-PE/treated coir

the Green-PE within the composites. Figure 4a shows the rough surface of the agave fiber and it is clear that after the chemical treatment (Fig. 4b) the fiber surface was coated by MAPE resulting in a brightness change with small MAPE particles deposited all over the fiber surface. In the case of untreated coir fibers (Fig. 4c), their surface seems more uniform and softer than agave fibers. This is due to chemical differences in their composition. Coir fibers have a higher lignin content than agave [19] acting as a structural support (glue) material in plants; i.e. lignin fills the spaces between the polysaccharide fibers, cementing them together [20]. After the coir surface treatment (Fig. 4d), the appearance is similar to the agave fiber showing that MAPE coated the fiber surface. The state of adhesion between coir and agave fibers in the composites is shown in Fig. 4e–h. It is possible to see fiber pull-out and important gaps between the untreated fibers and the matrix due to interfacial incompatibility and debonding due to rapid deformation resulting from impact testing [21]. These gaps practically disappeared when treated fibers are used and a more uniform fracture of the material occurs indicating better adhesion between both phases.

Figure 5 shows the composites' structure. As mentioned before, the rotomolding process does not impose pressure

or shear stresses that are known to improve adhesion and dispersion between the components. This is why it is difficult to incorporate fibers (especially at high content) inside polymers and achieve uniform/defect free materials. This is observed in the micrographs of the untreated fibers composites (Fig. 5a–d) where the fibers are free or pulled-out on the fractured surface of the composites as several voids can be observed. On the other hand, in the treated fibers composites images (Fig. 5e–h), a more uniform structure is observed because of a strong interfacial fiber-matrix adhesion leading to less pull-out and the fibers being better embedded into the polymer matrix [9, 18].

Tensile Properties

Figure 6a presents the tensile strength of Green-PE-agave and Green-PE-coir composites. This property is reduced with natural fibers addition. The neat Green-PE has a tensile strength of 13.7 MPa. However, by adding 20% wt of untreated agave and coir fiber, the values decreased to 7.7 and 9.7 MPa, respectively. Further addition (30% wt) of both agave or coir fibers reduced the tensile strength down to 7.4 MPa. Natural fibers promote voids formation, fiber agglomeration and poor interfacial adhesion between the polymer

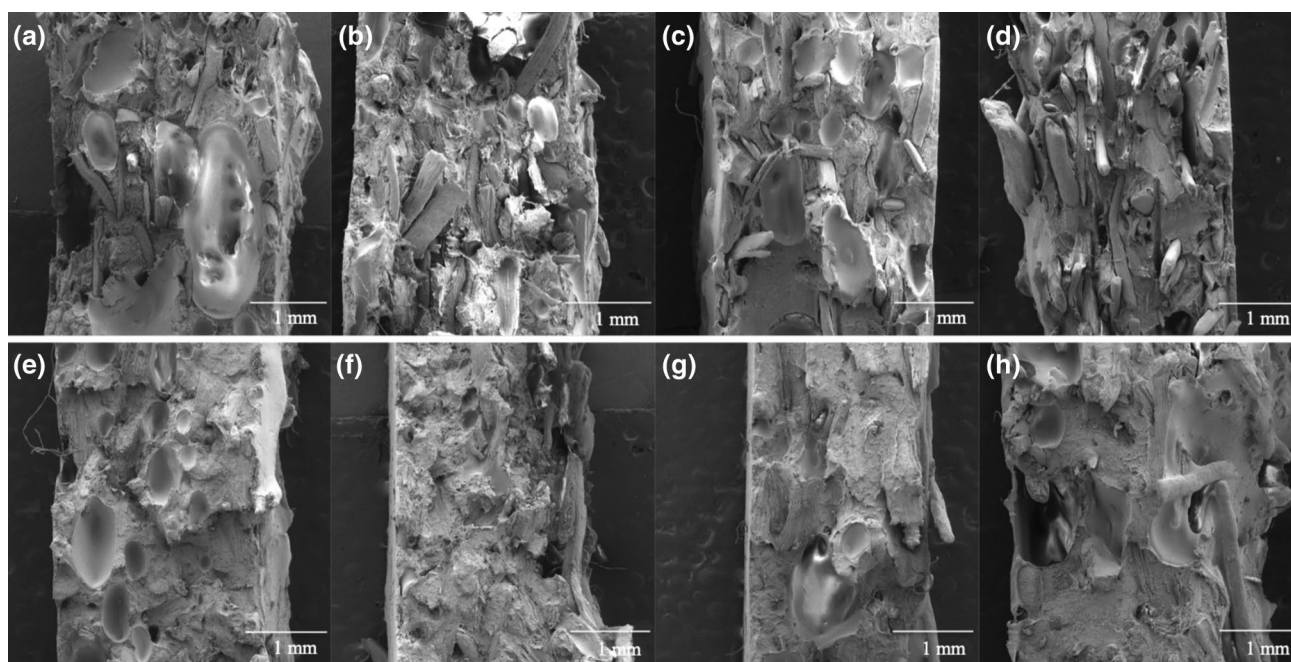


Fig. 5 Micrographs of the untreated fibers composites: **a** 20A, **b** 30A, **c** 20C, **d** 30C and the treated fiber composites: **e** 20TA, **f** 30TA, **g** 20TC, **h** 30TC

matrix and the fibers (Figs. 4, 5) resulting in poor interfacial stress transfer [6]. For this reason, it is important to use coupling agents to improve the fiber-matrix compatibility and the interfacial stress transfer during deformation. But the tensile strength of the treated fibers composites showed significant increases in this property. The 20TA and 30TA composites have a tensile strength of 11.5 and 11.0 MPa, respectively. This represents 50% increases (1.5-fold) compared with the untreated agave fiber composites. For treated coir composites, interesting results were observed with increases not only compared to untreated fibers, displaying properties above those of neat Green-PE (14.1 and 15.3 MPa for 20CT and 30CT respectively). For the tensile modulus (Fig. 6b), it was found that incorporating untreated agave fiber decreased this property compared to neat Green-PE dropping from 258 to 218 MPa and 240 MPa for 20A and 30A, respectively. Conversely, for untreated coir fiber at 20% wt, the tensile modulus slightly increased to 307 MPa while for 30% wt the value decreased to 256 MPa. This behavior can be explained by the presence of a larger number of voids and fibers pull-outs. The fiber surface treatment was positive for all the treated composites showing that at 30% wt of TA and TC, the tensile modulus reached a value of 345 MPa which is 33% higher than neat Green-PE. Arrakhiz et al. [22] used different chemical treatments for coir fibers to enhance the tensile properties of HDPE composites. The best results were obtained with a silane coupling agent with increased tensile strength by up to 16% compared to the untreated fiber composites. However, this treatment caused a reduction in

the tensile modulus. In a previous study, Cisneros-López et al. [15] reported that LMDPE/agave composites also showed better tensile strength using a chemical treatment of agave with MAPE (38% increase compared to the untreated fiber composites).

Flexural Properties

Flexural results of the Green-PE and its composites are presented in Fig. 7. The highest value for flexural strength was observed for the neat Green-PE (21.4 MPa). It was observed that incorporating untreated fiber to the matrix decreased this property to 10.4 MPa at 20% wt with both agave and coir addition, and to 8 MPa with 30% wt fiber (also for both fibers). A slight improvement in the composites' flexural strength with treated agave was observed: 12 MPa and 8.6 MPa for 20TA and 30TA, respectively. Otherwise, for the treated coir fibers, the results were much more interesting with values of 20 MPa and 13 MPa for 20CT and 30CT, respectively. This indicates that adding 20% of treated coir fiber allows to keep the same properties as the neat Green-PE. This improvement could be related to the chemical composition of coir which has a higher amount of lignin. In previous studies, it has been mentioned that lignin influences the structure, properties and morphology of the fibers [20]. Nevertheless, at 30% of fiber content, even with treated fibers, the porosity increases due to the low-shear conditions and consequently the flexural strength decreased.

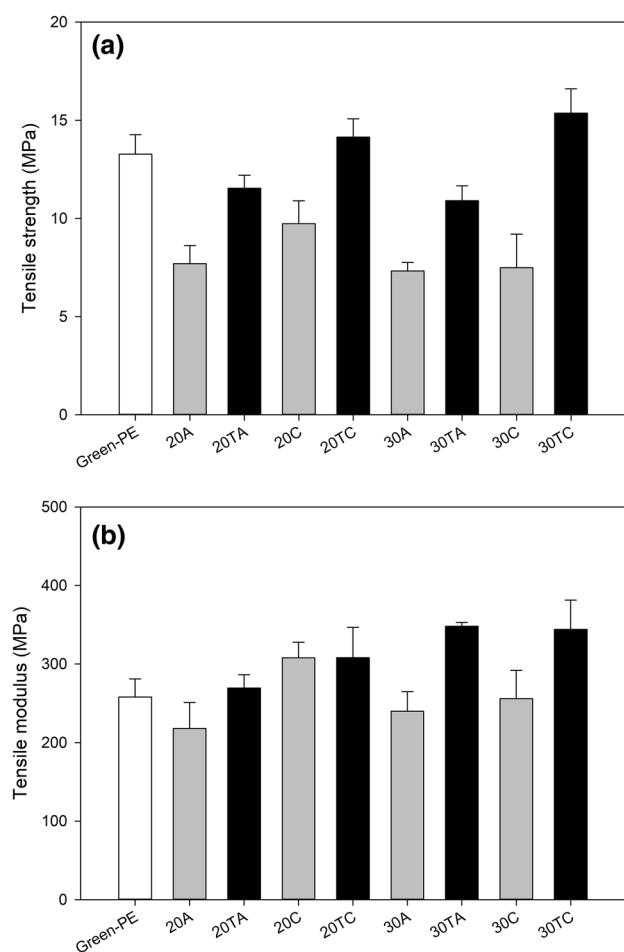


Fig. 6 Tensile properties of the Green-PE and its composites: **a** tensile strength and **b** tensile modulus

The flexural modulus of neat Green-PE was 514 MPa. Similar to the tensile properties and flexural strength, the addition of untreated fiber decreased the flexural modulus to 465, 400, 490 and 451 MPa for 20A, 30A, 20C and 30C, respectively. Once again, this behavior is a consequence of the poor compatibility of the materials and the high porosity observed in the morphology of the composites. Curiously, the chemical treatment did not improve this property with the exception of the 20% wt content of treated coir fiber showing a 27% increase (657 MPa).

Impact Strength

The impact results are shown in Fig. 8. Impact strength of neat Green-PE was 200 J/m and this property is reduced with fiber addition. At 20 and 30% wt of agave fiber, the impact strength decreased from 65 to 60 J/m. In the case of coir fiber, the decreases were lower than with agave fibers: from 80 J/m for 20% wt to 109 J/m for 30% wt. It was observed that the surface treatment with the coupling agent increased

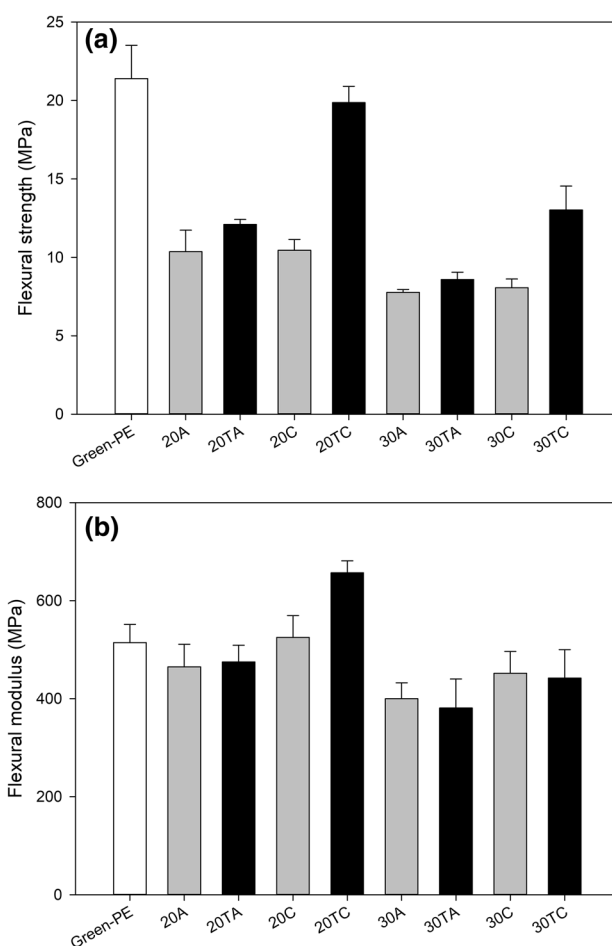


Fig. 7 Flexural properties of the Green-PE and its composites: **a** flexural strength and **b** flexural modulus

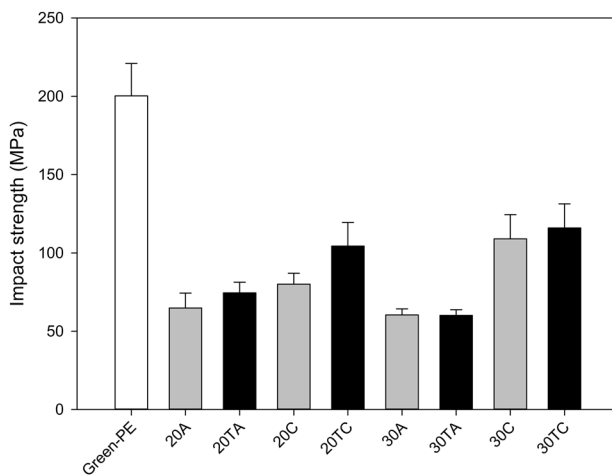


Fig. 8 Impact strength of the Green-PE and its composite

the impact strength only in the composites with 20% wt of fiber, which was 15% for the treated agave fiber composite and 30% for the treated coir fiber composite. In the treated fiber composites with 30% wt, no effect was observed with the chemical surface treatment which could be related to the high porosity (as it can be observed in Table 1) and the fiber agglomeration affecting the stress transfer and fracture propagation mechanism [23].

Also, Table 2 summarizes the mechanical properties of the composites prepared in this study and compares them with petroleum-based LMDPE (one of the most used polyethylene in rotomolding) and Green-PE. It can be seen that some properties are improved in comparison with conventional rotomolded PE, which is interesting in terms of substituting this polymer for more sustainable applications like packaging. For instance, only the tensile and flexural strength were higher for the petroleum-based PE. However, in both cases, similar properties were obtained with Green-PE or its composites.

Water Absorption

Water absorption is an important property for composites reinforced with natural fibers as their introduction causes deterioration in surface quality and ultimately in mechanical behavior [24]. It is reported that above 25% of weight gain (water absorption), the mechanical properties start to decrease and bacterial growth starts to occur. It is thus important to determine whether the material could be used for outdoor applications where dimensional stability is necessary [25]. Table 3 presents the water absorption uptake at equilibrium after an immersion of 1008 h (M_{∞}). As expected, the neat Green-PE exhibits a low water uptake (less than 1%) due to its hydrophobic nature. However, the incorporation of agave and coir fibers at 20 and

Table 3 Parameters of the hindered diffusion model (Eq. 3)

Sample	M_{∞} (%)	M_{1008} (%)	D (10^{10} m ² /s)	α (-)	β (-)
Green-PE	0.2	0.3	0.240	0.0113	0.7775
20A	19.2	19.5	213	0.0035	0.0179
20TA	12.1	11.7	183	0.0050	0.0276
30A	20.0	21.1	218	0.0057	0.0153
30TA	18.1	18.5	197	0.0436	0.0079
20C	16.9	17.1	220	0.0031	0.0169
20TC	7.5	7.6	149	0.0029	0.0077
30C	16.9	17.4	272.3	0.0073	0.0092
30TC	13.2	13.7	185	0.0041	0.0071

30% wt increases water absorption up to 17.4% and 21.1%, respectively.

Nonetheless, MAPE surface treatment decreased the water affinity of the composites, leading to water absorption values of less than 20% in all cases. A classic theory suggests that water affinity depends on the weight fraction of the hydrophobic polymer, the weight fraction of the hydrophilic reinforcement and the interactions between these components [26]. For this reason, improving the interfacial compatibility by surface treatment of the fibers leads to lower water diffusion through the composite and through the fibers themselves. Moreover, as compatibility increases in treated fiber composites, the number of voids in which water can diffuse becomes lower in comparison to untreated fiber composites. In this sense, the hindered diffusion or Langmuir diffusion model proposed by Carter and Kibler [27], was used to calculate the diffusion coefficients of the composites from the water absorption kinetics curves (Fig. 9). This model introduces the parameters α and β as the probabilities of water molecules to become diffused or bound respectively, as well as the moisture

Table 2 Mechanical properties of LMDPE, Green-PE and its composites

Material	Tensile		Flexural		Impact strength (J/m)
	Strength (MPa)	Modulus (MPa)	Strength (MPa)	Modulus (MPa)	
LMDPE ^a	20.7	172	23.1	533	121
Green-PE	13.7	258	21.4	514	200
20A	7.7	218	10.4	465	65
20TA	11.5	269	12.0	475	74
20C	9.7	307	10.4	490	80
20TC	14.1	308	20.0	657	104
30A	7.4	240	8.0	400	60
30TA	11.0	345	8.6	381	60
30C	7.4	256	8.0	451	109
30TC	15.3	345	13.0	436	117

Bold numbers indicate the maximum value of each property

^aLMDPE values were taken from Cisneros-López et al. [16] for LMDPE rotomolded under similar processing conditions

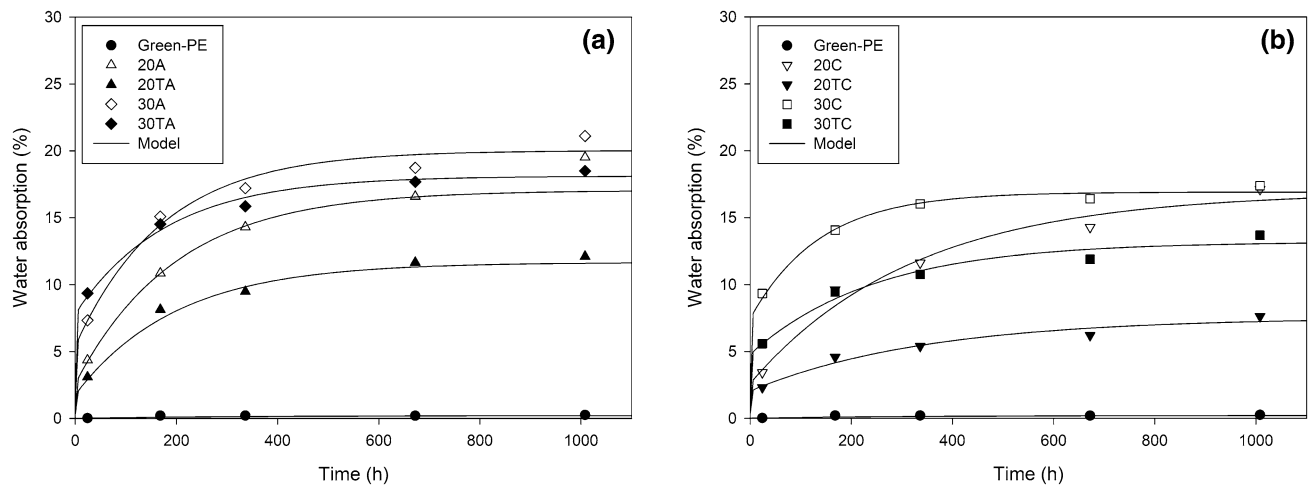


Fig. 9 Water absorption kinetics for the Green-PE and its composites: **a** agave and **b** coir. The curves represent fittings to Eq. (3) with the parameters of Table 3

uptake at equilibrium (M_{∞}) and the diffusion coefficient (D):

$$\frac{M_t}{M_{\infty}} = 1 - \frac{\beta}{\beta + \alpha} e^{-\alpha t} - \frac{\alpha}{\beta + \alpha} \cdot \frac{8}{\pi^2} e^{-\frac{D\pi^2}{l^2} t} \quad (3)$$

Table 3 summarizes the parameters for the diffusion model, from which it could be observed that the water diffusivity decreased with the surface treatment in all cases. The proposed mechanism between MAPE and natural fibers consists in the esterification of the hydroxyl groups and the deposition of a polymer layer onto its surface. Through this modification, the composites' hydrophilicity decreased due to the PE high hydrophobicity; i.e. the polymer coating restricts water diffusion along the fibers and consequently through the composite.

Conclusions

In this work, rotomolded biocomposites based on Green linear low-density polyethylene (Green-PE) and natural fibers (agave and coir) were successfully produced. These materials are combining the advantages of using a biobased polymer and a biosourced agro-industrial wastes such as agave and coir fibers. To improve adhesion and dispersion, fiber surface treatment was successfully performed using maleated polyethylene (MAPE) in solution.

It was found that both fibers decreased the tensile strength of the Green-PE composites due to poor fiber-matrix compatibility from 13.7 MPa to 7.4 MPa at 30% of coir or agave fibers content. However, these properties were recovered using treated fibers leading to values higher than the neat

matrix up to 11.0 MPa and 15.3 MPa for treated agave and treated coir composites respectively. Composites based on treated fibers showed good flexural properties, for 20% of treated coir it was obtained a flexural strength of 20.0 MPa that is very similar to Green-PE (21.4 MPa). For impact strength, the best results were obtained with treated coir fibers, achieving up to 117 J/m which is a similar value than that of a commercial petroleum-based polyethylene (121 J/m). Also, the maximum water absorption of the composites decreased by using treated fibers compared to untreated ones. These results showed that the replacement of a petroleum-based polyethylene by its biobased alternative in rotomolding is a viable option and the positive effect of treated natural fibers addition may not be limited to mechanical properties, but also form an economic and sustainable point of view.

Acknowledgements One of the authors (M.E. González-López) acknowledges a scholarship from the Mexican National Council for Science and Technology (CONACyT #481448). Also, the technical help of Dr. Martín Flores and Dr. Sergio Oliva of the Materials Science Graduate Programs (University of Guadalajara, CUCEI) was highly appreciated for their assistance in SEM analysis.

References

1. De Oliveira AG, Nazareth da Silva AL, Furtado de Sousa AM, Moreira-Leite MCA, Jandorno JC, Escocio VA (2016) Mater Chem Phys 181:344
2. De Vargas Mores G, Spanhol-Finocchio CP, Barichello R, Avila-Pedrozo E (2018) J Clean Prod 177:12
3. Samper-Madriral MD, Fenollar O, Dominici F, Balart R, Kenny JM (2015) J Mater Sci 50:863
4. Varghese AM, Mittal V (2018). In: Gopal-Shimpi N (ed) Biodegradable and biocompatible polymer composites. Woodhead Publishing, Cambridge, p 157 Chap. 6

5. Bujjibabu G, Chittaranjan DV, Ramakrishna M, Nagarjun K (2018) *Mater Today Proc* 5:12249
6. Zhao X, Li RKY, Bai SL (2014) *Composite A* 65:169
7. Hemmati F, Yousefzade O, Garmabi H (2018) *Adv Polym Technol* 37:1345
8. Pérez-Fonseca AA, Robledo-Ortíz JR, Moscoso-Sánchez FJ, Fuentes-Talavera FJ, Rodrigue D, González-Núñez R (2015) *J Polym Environ* 23:136
9. Savas LA, Tayfun U, Dogan M (2016) *Composites B* 99:188
10. Boronat T, Fombuena V, Garcia-Sanoguera D, Sanchez-Nacher L, Balart R (2015) *Mater Des* 68:177
11. Tarres Q, Melbo JK, Delgado-Aguilar M, Espinach FX, Mutjé P, Chinga-Carrasco G (2018) *Composite B* 153:70
12. Nugent P (2017). In: Kuts M (ed) *Applied Plastics Engineering Handbook*. Elsevier, Delmar, p 321 Chap. 15
13. Ramkumar PL, Ramesh A, Alvenkar PP, Patel N (2015) *Mater Today Proc* 2:3212
14. López-Bañuelos RH, Moscoso-Sánchez FJ, Ortega-Gudiño P, Mendizabal E, Rodrigue D, González-Núñez R (2012) *Polym Eng Sci* 52:2489
15. Cisneros-López EO, Pérez-Fonseca AA, Fuentes-Talavera FJ, Anzaldo J, Gonzalez-Nuñez R, Rodrigue D, Robledo-Ortíz JR (2016a) *Polym Eng Sci* 38:96
16. Cisneros-López EO, González-López ME, Pérez-Fonseca AA, Gonzalez-Nuñez R, Rodrigue D, Robledo-Ortíz JR (2016) *Compos Interface* 24:35
17. González-López ME, Pérez-Fonseca AA, Cisneros-López EO, Manríquez-González R, Ramírez-Arreola DE, Rodrigue D, Robledo-Ortíz JR (2019) *J Polym Environ* 27:61
18. Hossen F, Hamdan S, Rahman R, Islam S, Liew FK, Hui-Lai JL, Rahman M (2017) *Polym Compos* 38:1266
19. Pérez-Fonseca AA, Arellano M, Rodrigue D, González-Núñez R, Robledo-Ortiz JR (2016) *Polym Compos* 37:3015
20. Mohanty AK, Misra M, Hinrichsen G (2000) *Macromol Mater Eng* 276/277:1
21. Sari PS, Sabu T, Petr S, Zoya G, Zdenka J (2019) *Composite B* 177:1
22. Arrakhiz FZ, ElAchaby M, Kakou AC, Vaudreuil S, Benmoussa K, Bouhfid R, Fassi-Fehri O, Qaiss A (2012) *Mater Des* 37:379
23. Barbosa V, Ramires EC, Tanaka-Razera IA, Frollini E (2010) *Ind Crop Prod* 32:305
24. Kuciel S, Jakubowska P, Kuzniar P (2014) *Composite B* 64:72
25. Ferrero B, Fombuena V, Fenollar O, Boronat T, Balart R (2015) *Polym Compos* 36:1378
26. Pervaiz M, Oakley P, Sain M (2014) *Mater Sci Appl* 5:845
27. Carter HG, Kibler KG (1978) *J Compos Mater* 12:118

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.