Research Article

Influence of Ethylene Plasma Treatment of Agave Fiber on the Cellular Morphology and Compressive Properties of Low-Density Polyethylene/Ethylene Vinyl Acetate Copolymer/Agave Fiber Composite Foams

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Received 28 May 2020; Revised 28 January 2021; Accepted 5 March 2021; Published 25 March 2021

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Agave fibers (AF) were incorporated either pristine (AFp) or surface treated by ethylene plasma (AFm) in low-density polyethylene (LDPE)/ethylene vinyl acetate (EVA) blends at a ratio of 1:1 and foamed by chemical means. The role of the AF content (3, 6, 9, 12, and 15 wt.%) and its surface modification on the cellular morphology and mechanical properties of LDPE/EVA/AF foams under compression is investigated herein. Fourier transform-infrared spectroscopy, contact angle, and water suspension of AF suggest that plasma treatment using ethylene successfully modifies the surface nature of AF from hydrophilic to hydrophobic. AF and the surface treatment have an important role on the morphological properties of the foams. Composite foams reinforced with 12 wt.% AFm exhibited the highest mechanical properties improvements. At this fiber content, the composite foams enhanced 30% of the compressive modulus and 23% of the energy absorption under compression with respect to the neat polymer blend foam, as a result to the formation of more uniform cells with smaller size and the enhancement of compatibility and spatial distribution of the AFm in the polymer composite foams due to thin clusters of polyethylene-like polymer deposited on the AF surface.

1. Introduction

The use of natural fiber-reinforced polymers has reached the interest of several sectors such as the automotive, construction, and packaging industries. Natural fibers are attractive for those industries since they are feasible reinforcement alternatives to reduce the use of synthetic fibers [1]. Natural fibers have advantages over synthetic fibers of being extracted from renewable sources and due to their biodegradable nature. One of the most interesting high-strength natural fibers is those obtained from the Agave tequilana Weber Azul. This Agavaceae species plays an important role in Mexico’s economy since it is the only appropriate for tequila production. In 2018, the production of Agave to extract tequila was ~1,138,800 tons, and approximately 60% of the raw material is discarded in form of bagasse [2]. In addition, after juice extraction, disposal of Agave wastes becomes a potential source of infection.

Cellular polymers offer several advantages over the solid counterparts, such as lower weight, good sound, and thermal insulation, as well as excellent impact energy absorption. Polymer foams based on low-density polyethylene (LDPE)/ethylene vinyl acetate (EVA) blends have attracted great attention given their tailorability to fulfill specific
requirements, as they are more suitable for the foaming process. Moreover, LDPE-EVA foams show higher impact resistance, flexibility, thermal conductivity, among others [3] compared to those foams only elaborated with neat LDPE. In particular, the LDPE-EVA foam improves resistance to electrical discharge and solvents, creep behavior, stress cracking resistance, service temperature, and weatherability [4].

Some researchers have studied the incorporation of agave fibers (AF) on the morphological and mechanical properties of several polymeric foams. Moscoso et al. [5] used cellulose of Agave tequilana Weber to reinforce polypropylene foams and observed that the average cellular diameter decreases as the cellulose content increases. They also found that the Young’s modulus and impact resistance of the AF/Polypropylene foams increased by the addition of 30 wt. % of AF. On the other hand, Tissandier et al. [6] studied the incorporation of AF and a chemical blowing agent in high-density polyethylene by injection molding, and they concluded that tensile strength (σ max) and elastic modulus (E) were enhanced according to the fiber content while the elongation at break decreased (ε max); moreover, they found that increasing the foaming agent, the density (ρ), E, σ max, and ε max decreased. In the other study, Vazquez et al. [7] foamed composites based on recycled high-density polyethylene with agave fiber for the removal of heavy metals from polluted water, and their results demonstrated the ability of the composites to immobilize chitosan on the surface and its capacity to adsorb metal ions are a low-cost attractive route for absorbing metal ions from polluted water. Finally, Vazquez-Flletes et al. [8] mixed linear medium-density polyethylene with agave fiber, and the foaming process was done by a rotational process of a three-layer cylindrical liquid container and studied the effect of the composition on the mechanical behavior of rotomolded parts. They found that the impact strength decreases with both Agave fiber content and foaming agent, content due to the poor adhesion between fibers and the matrix.

To improve the chemical interactions between natural fibers and polymeric matrices, in recent years, plasma-based treatments have emerged as a promising strategy for surface modification of fibers [9–12]. Cold plasma is a green technology that includes atoms, free radicals, electrons, and excited molecules, which can break the chemical bonds on the substrate surface inducing several changes, such as chemical groups bonding covalently, deposition of polymer clusters, and ablation of the substrate surface. In contrast with other surface treatments like chemical treatments, physical plasma treatment is a dry process, does not generate residuals during the treatment, and alters only the outermost layer of a substrate [13, 14]. Some authors have reported the advantages of plasma treatments to modify the surface of natural fibers and improve their compatibility with other polymer matrices. For example, Yuan et al. applied argon and air plasma treatments to improve the compatibility of wood fibers (20 wt. %) with polypropylene, which results in an increase of σ max and E in 13% and 150%, respectively. These mechanical improvements were attributed to the formation of oxygen-containing functional groups on the wood fibers upon plasma treatments [15]. In our previous work [16], an increase in E up to 60% in composites based on LDPE/AF was found only when surface modification of agave fibers is carried out by ethylene plasma treatment. The improved E was associated to a good dispersion and compatibility between fibers and LDPE matrix. The surface treatment of natural fibers by the plasma polymerization process also was able to reduce the water absorption of the hydrophilic fibers, and this is an important issue to increase the use of natural fibers for different applications.

In order to extend the study of the role of the surface modification of AF on the mechanical properties of composite foams, the aim of this work is to get insight on the influence of the incorporation of pristine (AF p) and ethylene plasma treated (AF m) agave fibers on the morphological characteristics and mechanical properties of LDPE/EVA/AF foams under compression.

2. Experimental

2.1. Materials. Low-density polyethylene (LDPE) (PX 20020 P) with a 0.92 g/cm 3 density and melt flow index (MFI) of 0.2 g/10 min was supplied by Petróleos Mexicanos (PEMEX). Ethylene-vinyl acetate copolymer (EVA) under the trademark Elvax 460 with an MFI = 2.5 g/10 min was acquired from Dupont. Agave fiber (AF) was provided by Soluyague S. A. de C. V.; it was grinded up and separated in a 325 mesh by Ro-Tap test sieve given, approximately, an average particle size of 44 μm. Azodicarbonamide (ACA) and zinc oxide (ZnO) from Sigma Aldrich, as well as silica (SiO 2) from Nemak S.A. de C.V. on the whole, were used as foaming system. Dicumyl peroxide (DCP) purchased from Suministros y Especiales S.A. de C.V. was used as a crosslinking agent. Ethylene gas monomer supplied by Infra (México) was used for the plasma treatment.

2.2. Surface Modification of Agave Fiber by Ethylene Plasma. The plasma treatment of the AF was carried out in a round bottom flask (500 mL) with a copper wire coiled around the flask acting as an electrode. The electrical energy was supplied to the reactor through the copper wire connected at 13.6 MHz radiofrequency generator (Advanced Energy RF600). According to the capacity of the plasma reactor and to ensure enough surface modification, 7 g of agave fibers was treated by introducing into a flask then vacuum was applied to the system up to reaching 2.9 Pa; ethylene gas valve is open and held at a constant flow rate of 0.6 cm 3/min. The treatment was conducted at 40 W of power for 60 min. More details of this plasma treatment method are available in our previous work [16].

2.3. Characterization of Agave Fiber Surface Modification. To characterize the chemical species formed upon the plasma treatment, agave fibers were analyzed by Fourier transformed infrared spectroscopy using a total attenuated reflection (ATR-FTIR) accessory. The analysis was carried out in both, AF pristine (AF p) and AF treated by ethylene plasma (AF m) samples, using a resolution of 4 cm 1 and 20 scans. As qualitative evidence, the samples (AF p and AF m) were dispersed and suspended in water to observe hydrophilic/hydrophobic
changes in the agave fiber upon the surface treatment. The contact angle technique was also used to corroborate the changes in the hydrophilic nature of AF before and after plasma treatment. The contact angle data was obtained from the interfacial tension measurements using a Ramé-hart goniometer (model 100-00). A microdrop of distilled water was placed on the particle surface of AFp or AFm previously compacted, and the angle observed is registered. All experiments were performed at room temperature.

2.4. Composite Formulation and Foaming. The composites were manufactured with 3, 6, 9, 12, and 15 wt. % of AF a C.W. Brabender Plasticorder mixing chamber CFF6 model with a 350 ml volume capacity equipped with a medium shear stress blades (CAM type) were used to blend the polymers LDPE/EVA at a wt-% ratio of 1 : 1, because at this ratio the polymer blend presents a cocontinuous phase morphology, not dispersed phase is presented, that will act as a cell nucleant agent, affecting the nucleant effect of the AF [17, 18]. Once the polymers were melted, the AF was added, followed by the incorporation of the foaming system (ACA/ZnO/SiO2) and crosslinking agent (DCP) at 110°C and 60 rpm. First, EVA and LDPE were sequentially added into the chamber and mixed for 3 min (for the composites AFp or AFm were incorporated and mixed here during 2 min); then, ZnO and SiO2 were incorporated into the chamber and continued mixing for another 10 min. Finally, the ACA/DCP was added up to the blending process reached 15 min. A squared preform of 15 cm width and length and 0.6 cm in thickness was obtained by molding the bulk blend at 100°C using a Carver hot press model 1128. To foam the preforms, they were placed in between two hot plates and pressed at 25 ton of load and 170°C for 10 min. Finally, the samples are ejected and expanded out the mold and cooled at room temperature.

2.5. Composite Foamed Characterization. The morphology of the composites was observed using a Topcon SM510 scanning electron microscope (SEM). The samples were cryogenically fractured and Au/Pd-coated to provide the electrical conductivity and reduce charge effects. From the micrographs, a statistical cell size (d) distribution was conducted by measuring at least 200 cells diameter per sample. Cell density (Nc), defined as the number of cells per cubic centimeter of foam, was obtained according to the following equation.

\[
N_c = \frac{1 - \rho / \rho_p}{10^{-4} d^3},
\]

where \(d\) is the average cell size in \(\mu m\), \(\rho\) is the apparent density of the foam, and \(\rho_p\) is the apparent density of the solid material [19].

Gel fraction (GF) was determined by solid-extraction with xylene, following the procedure recommended by the ASTM D2765 standard. According to this procedure, 1 g of the foamed sample was placed in a preweighed stainless-steel mesh for 24 h. After extraction, the solid residue is dried in an oven at 70°C and then weighted again. GF of polymer foams is obtained as the weight ratio between the sample weight after extraction and the initial one.

The mechanical characterization of the composites under compression loadings was conducted on squared specimens with 50 mm sides and 25 mm thick, following the procedure recommended by the ASTM D3575. The samples were placed between two parallel plates and loaded at a 12.5 mm/min crosshead displacement rate using an MTS Criterion Model 43 equipped with a 5 kN load cell. The recorded data was used to obtain the compressive modulus (\(E_s\)) and the toughness at \(\varepsilon = 50\% (K_{50})\).

3. Results and Discussion

3.1. Agave Fiber Surface Modification. The FTIR spectra of the AFp and AFm with ethylene plasma are shown in Figure 1(a). The broadband located at 3600-3100 cm⁻¹ of AFp spectrum comes from cellulose \(I_g\) and corresponds to O-H stretching vibration and hydrogen bond of hydroxyl groups [20]. The band at 2920 cm⁻¹ is related to C-H stretching from CH and CH₂ groups in cellulose and hemicellulose [20]. The peak at 1730 cm⁻¹ is attributed to C=O stretching of esterified hemicellulose [20]. The band located at 1640 cm⁻¹ is associated to C=O stretching vibration of the \(\alpha\)-keto carboxylic acid in the lignin or ester group in hemicellulose [21]. Aromatic structure vibration from lignin and lignocellulose present a band between 1510 and 1520 cm⁻¹ [22]. Peaks at 1250 and 1000 cm⁻¹ are related to C-O-C and C-O stretching vibrations on the cellulose chain bone [23]. Finally, the peak at 1080 cm⁻¹ is associated with the C-O groups of polysaccharides and hemicelluloses [24, 25]. On the other hand, the strongest signals of ethylenic functional groups are located at ~2950 cm⁻¹ and ~1460 cm⁻¹, which are associated to asymmetric stretching of C-H bonds and bending deformation of -CH2⁻, respectively. In the spectra shown in Figure 1(a), plasma-treated agave fibers exhibit a slight intensity increment of peak located at 2950 cm⁻¹; this change is associated to the polyethylene nanometric clusters deposited on the fibers upon the ethylene plasma treatment. This result is in accordance with the findings obtained by Neira-Velasquez et al. in the surface modification of nanoclays by plasma polymerization of ethylene [26]. Although the plasma state is generally identified by the ionization of gases, the reactions involved during plasma treatment are generally complex, and the elucidation of the mechanisms of plasma polymerization is controversial. Friedrich studied several reaction mechanisms from the formation of plasma polymers from a chemical point of view and concluded that there are two main mechanisms involved. The plasma-induced radical chain-growth polymerization mechanism is like radical polymerization involving initiation, chain-growth, and termination processes. Radicals or radical fragments are produced in the plasma and initiate the reaction. The polymer chain grows by the addition of monomer molecules, and chain growth is terminated by radical recombination, thus, forming a polymer. In the atomic fragmentation-recombination mechanism, the monomer molecules are fragmented into single atoms or atomic fragments in high-power plasma. Finally, the atoms and fragments bombard the substrate.
surface, forming plasma polymers with a high degree of irregularity by random recombination [27]. The surface modification was also evidenced by comparing the dispersion stability in water of the $AF_p$ and $AF_m$. The hydrophilic nature of $AF_p$ allows good dispersion in water (Figure 1(b), left); however, upon surface treatment by ethylene plasma, the fibers turn from hydrophilic to hydrophobic, due to thin clusters of polyethylene-like polymer are deposited on AF particles surface which promotes a repulsion with the water. Nonpolar character of these clusters is evidenced by the fibers suspended in water in Figure 1(b) (right) [28]. Contact angle measurement on the fibers was also conducted to corroborate the surface modification by plasma treatment. Contact angle measurements on pristine agave fibers were not possible, since water drops are rapidly absorbed by the hydrophilic fibers, because the AF has a lot of hydroxyl groups. On the other hand, the water contact angle of plasma-treated agave fibers was $\sim 75^\circ$ (Figure 1(c)). This finding was due to the
polyethylenic nonpolar clusters were randomly deposited on the surface of the fiber, thus, reduces the polarity of the plasma-treated fibers decreasing the wettability.

3.2. Density and Gel Fraction of the Foams. Results of density ($\rho$) and GF of foams reinforced by AF$_{p}$ and AF$_{m}$ are showed in Figure 2. In general, it is reported that foaming agents can reduce the apparent density ($\rho$) of polymer foams [29]; however, other authors report an increase of $\rho$ with the incorporation of fillers [8, 30]. In this work, the $\rho$ of foams containing agave fibers at 3 and 6 wt. % are lower than that of the neat polymer foam, regardless of the fiber surface modification (Figure 2(a)). The low density of the foams at low agave fiber contents (3 and 6 wt.%) is related to an increment in cell nucleation due to external agent and to the low polymer melt elasticity that allows free cell growth [29]. Polymers with low melt elastic properties (low content of AF and GF) produce larger cells with brittle walls which is associated with the collapse (diffusion of foaming gas from small to adjacent larger cells) and coalescence phenomena (adjacent cells merge each other to form a bigger one). Zhang et al. [31] mentioned in his work that at a given volume, the foam system with fewer larger cells is more stable than that with several smaller cells. This energy minimization gives place cell coalescence during the foaming process, yielding foams with bigger cell size and low $\rho$. The density of the foams increases at higher AF$_{p}$ and AF$_{m}$ contents (12 and 15 wt.%); it is due to three factors: (i) the higher loading of the fibers with a density of 1.486 g/cm$^3$, it is higher than the blend polymers [6]; (ii) the increment of the number of cells (nucleant effect); and (iii) because the viscosity and GF are higher at higher AF contents such as is observed in Figure 2(b), it last restricts the cell expansion and the density is increased [6, 32, 33].

Figure 2(b) shows the GF (the insoluble fraction of the polymer foam) of foam composites containing different weight contents of AF$_{p}$ and AF$_{m}$. At low AF$_{p}$ and AF$_{m}$ contents (3 and 6 wt. %), the GF slightly decreases from 0.87 (reference foam) to 0.69. This behavior could be associated with a reduction of free radical concentration available to crosslink the polymer blend, such as was reported by Janigova et al. [34], who assume that oxy radicals formed by thermal decomposition of peroxides also attack the organic filler surface (wood flour), besides the polyethylene. Those radicals formed on the organic filler surface can in turn recombine with polyethylene macroradicals, creating grafts on the fibers. For their part, Mokoena et al. [35] studied the blend of linear low-density polyethylene/sisal fiber in the presence of dicumyl peroxide (DCP); they found that using a 1 wt% of DCP in the blend, the strength was improved until 70% respect to the blend without DCP, and they conclude that is the consequence of the organic peroxide-induced grafting between hydrophobic LLDPE matrix and hydrophilic sisal fibers [36]. In agreement with Janigova and Mokoena, free radicals available in the system react not only to crosslink the polymer blend but also are consumed by reacting with the surface of the cellulosic reinforcement; it suggests that the foam composites at low fiber contents the crosslinking reaction are favored on the polymers blend (intramolecular crosslinking); however, a slight grafting is occurred on the fibers surface, and it decreases the GF of that foam composites. While, at higher content of agave fibers the grafting and crosslinking reaction is favored on the surface of the AF (treated or not treated), it forms linkages polymer-fiber and fiber-polymer-fiber, increasing the GF at higher contents of agave fiber, such as is reported by Ahmad and Luyt who found the grafting reaction of sial fiber in presence of DCP, and that the GF is increased with the content of sial fiber, such as is showed in Figure 2(b) once the AF$_{p}$ and Af$_{m}$ contents are increased from 6 to 15 wt%.

3.3. Morphological Characterization. Morphological characterization of the foams involves SEM analysis and statistical distribution of cell size. Results of this morphological characterization for composite foams with AF$_{p}$ are shown in Figure 3. In this figure, above each SEM micrograph, the statistical distribution is presented. As seen in Figure 3(a),

![Figure 2: Apparent density (ρ) and GF of composite foams containing AF$_{p}$ and AF$_{m}$. (a) ρ and (b) GF.](image-url)
Figure 3: Continued.
the reference foams (without agave fibers) exhibited two cell size \((d)\) population (60-120 \(\mu m\) and 180-220 \(\mu m\)) as consequence of a combination of homogeneous and heterogeneous nucleation, which occurs into each polymer phase and at the interface between LDPE and EVA blends [4]. Large cells are generated from the homogeneous nucleation in the EVA phase; as polymer has lower viscosity than the LDPE phase, it allows the cell growth without great restriction. While the higher viscosity of the LDPE phase avoids the growth of cells. Since during foaming small cells have thicker walls than larger ones, they are more capable to retain higher gas pressure, thus, the entrapped gas diffuses to larger cells until the small ones collapse or eventually disappear [37]. However, at low AF contents (3 and 6 wt. %), cell coalescence phenomenon dominates the foaming process, producing a more homogeneous cell size. The coalescence phenomenon consists in the formation of cells through wall rupture among adjacent cells during growth (cells combination). At 12 wt.% of agave fibers, the cell size of composite foams tends to decrease as seen in Figure 3(e). Smaller cell size in these foams is attributed to greater restriction to cell expanding imparted by an increment in the blend polymers viscosity at higher GF and contents of agave fiber. Its behavior is reported by other authors who concluded the high viscosity of the polymer blend by the incorporation of microreinforcements; the cell size growth is restricted [4, 17, 38]. Higher contents of AF (≥15 wt.%) may tend to form fiber clusters yielding again two cell size population.

Micrographs and cell size distribution of foams containing agave fibers treated by ethylene plasma (AF\(_m\)) are shown in Figure 4. At 3 wt. % (Figure 4(a)) and 6 wt. % (Figure 4(b)) of agave fiber, cells have sized ranging between 25 and 500 \(\mu m\) with two cell size population, 25-150 \(\mu m\) and 150-500 \(\mu m\). At 9 wt. % of agave fibers, the composite foams also exhibit two cell size populations; however, the distributions shifted to small cell size, ranging from 25-300 \(\mu m\). By increasing the agave fiber content up to 12 wt. %, the population of small size cells dominates the distribution. However, the presence of larger cells of 200 \(\mu m\) suggests that at higher AF\(_m\) or AF\(_p\) contents, the heterogeneous nucleation diminish because the fibers form clusters and the surface area in the interface diminish, it provokes minor sites to nuclei cells, however, the cell size distribution is shifted to low cell sizes [18, 39]. Finally, at 15 wt. % of fibers, the foams exhibit a monomodal cell distribution with a binomial line shape.

By comparing the cells of foams with plasma-treated fibers (Figure 4) and those with the pristine ones (Figure 3), no significant differences regarding the morphology and size distributions are observed. In general, at higher agave contents (≥9 wt. %), composite foams with AF\(_m\) have smaller cell sizes than those with the pristine ones, in agreement with McClurg, it is due to a homogeneous spatial distribution that make efficient the nucleation phenomenon [38].

As has been reported in the literature [40, 41], the ethylene plasma surface treatment enhances the matrix/fiber interactions, such as is observed in Figure 5. The polymer blend has a partial interfacial adhesion on the fiber surface as is evidenced by the fibril polymer deformation (white circles) from the composite foam with 15 wt. % of AF\(_m\). In agreement with the literature [28], plasma treatment, in presence of a polymerizable monomer, creates clusters not a homogeneous polymer thin layer on the substrate surface; those polymer clusters interact partially with the polymer matrix, once the composite foam cryogenically fractured the polymer fibril deformation presented, such as is reported by Janigova et al. [34] who used DCP to treat the surface of organic fillers. In the same sense, the interaction behavior yields foams with smaller cell size and a narrower statistical distribution. Regarding the foams with 15 wt. % of AF\(_m\) (Figure 4(e)), they exhibit smaller cell size and narrower size
Figure 4: Continued.
distribution, contrary to those with AFₚ ones. In the composites with AFₘ, the fiber plasma treatment improves the fibers spatial distribution in the polymers blend, generating higher surface area, at the interface polymer/fiber, and more cell nucleus was generated. This behavior is explained by McClurg [39] who reported that a uniform spatial distribution of nucleants, such as the agave fibers, minimizes the impact of early activating nucleants on the activation of other nucleants and concludes that a random nucleant distribution is not quite as effective as the uniform distribution. In general, at higher agave fiber contents (12-15 wt.%), by introduction the AFₘ cell morphology was more uniform, cell size was smaller and cell size distribution was narrowed as we can see previously compared with reference foam material. These parameters have an important impact on the cell density and mechanical properties.

Results of cell density (Nₑ) characterization are shown in Figure 6. In this figure, it seems that Nₑ of the foams does not have a linear trend as a function of the agave fiber content, regardless of the surface treatment. Foams containing 3 wt. % of AFₚ have similar Nₑ value ($1.9 \times 10^5$ cells/cm³) as the neat polymer foam ($2.3 \times 10^5$ cells/cm³). However, by increasing the fiber content (6, 9, and 12 wt. %), Nₑ also increases randomly, being the foam containing 12 wt. % of AFₚ, the one with the highest Nₑ. At 15 wt. % of AFₚ, Nₑ decreases probably due to the presence of the cluster fibers. For the composite foams containing 3 and 6 wt. % of AFₘ show a similar Nₑ ($1.7$ and $2.4 \times 10^5$ cells/cm³) as the
reference foam (2.3 × 10^5 cells/cm^3). Then, at 9 wt. %, the N_C begins to increase due to good dispersion and distribution of the fiber in the polymer matrix promoting more nucleation sites, because of high melt viscosity (that restrict the cell growth) and therefore a decrease in the cell size and increases N_C, such as is reported by McClurg [39], because a homogeneous spatial fiber distribution allows an efficient nucleation, minimizing the effect of early nucleant sites. While at 12 and 15 wt. %, the cell density increases one order of magnitude with respect of the composite foams at low loading of fibers; this behavior is due to both the AF_m and AF_p act as a nucleant agent, however, the well dispersed and distributed AF_m because the plasma treatment promotes greater control over the number of sites to form cell nucleus as is shown in Figure 6. Where the N_C for the AF_m composite foams increases gradually with the AF_m content, while, for the foamed composites with AF_p, N_C values fluctuate randomly within the interval of the fiber content studied. It last because the fiber is randomly dispersed and distributed on the polymer blend, such as is shown in Figure 6. It is assumed that in the case of the composite foam with 12 wt. % of AF_p, the spatial distribution is inhomogeneous; however, at the interface polymer-fiber is lack strong interaction with the polymer matrix [39], it is the other factor that improves the nucleation efficiency; in this case, it increases the N_C values at 12 wt. % of AF_p to respect the N_C value for the composite foam with 12 wt. % of AF_m.

3.4. Mechanical Characterization. Figure 7 shows the results of the mechanical characterization of the foams subjected to compression loadings, σ vs. ε curves of foams reinforced with AF_p and AF_m are shown in Figures 7(a) and 7(b),
respectively. As seen in these figures, all cellular materials show a linear elastic behavior at low levels of deformation, then, the materials experience yielding in which cells start collapsing. Followed, the curve shows a in which the stress slightly increases as a function of $\varepsilon$ (plateau), which is attributed to plastic deformation and wall microbuckling. Finally, the stress again starts increasing prominently due to the densification of the foam. The mechanical properties of flexible foams not only depend on the mechanical properties of the raw material but also on the morphological properties of the cells (type, shape, size, size distribution, wall thickness, and cellular density). The incorporation of the fibers can reinforce flexible polymer foams, due to their higher mechanical properties and through tailoring the morphological properties of the cells. For composite foams containing pristine fibers, only the composites with 12 wt. % of reinforcement (AF$_p$12) exhibit higher load-bearing capacity than the reference material (foams without AF). Lower AF$_p$ and AF$_m$ contents (3 and 6 wt.%) produce fewer sites to cell nucleation, however, this results in cells with similar size, form big cells with thin walls, and edges as is observed in Table 1, yielding low modulus (see Figure 7(c)). On the other hand, increasing the AF$_p$ and AF$_m$ contents considerably reduces the cell size, and the distribution of cell sizes is narrower, which increases the cell density and the thickness of the wall and edges, which consequently increases the elastic modulus, as is observed in Table 1 and Figure 7(c). This increase in the elastic modulus was greater for those foams with contents of 9-12 wt. % of fibers treated by ethylene plasma, which is due to a better interaction between the treated fibers and the LDPE/EVA foam compounds. A better interaction between AF$_m$ and LDPE/EVA compound suggests, on one hand, a better dispersion of the fibers creating more nucleation sites, and on the other hand, a greater increase in the viscosity during the foaming process, both factors affect the morphological parameters before mentioned and therefore provide higher modulus in these foam compounds. It is well known that higher density of the foams increases their mechanical properties, and that big cells have weaker walls than the small ones, in the same polymer blend, because at higher cell size in the AF composites, the wall and edges are thinnest than at small cell sizes, as is observed in Table 1. While AF with plasma treatment, at higher AF$_m$ contents, produced thicker walls and edges and therefore better mechanical properties due to the induced compatibility, as observed in Figure 5.

Highlighting, again, the effect of the surface treatment, Figure 7(c) and Table 1 indicate that the foams containing AF$_m$ (>9 wt. %) exhibited more significant improvements in their compressive modulus. Reinforcing the foams with 12 wt. % of AF$_p$ improves their compressive modulus only ~7%; with the same reinforcement content (12 wt. %) but with AF$_m$, the composite foams improve their compressive modulus up to ~30% with respect to those with the pristine ones. This suggests that ethylene plasma treatment of agave fibers is an effective method to improve, cell size distribution, cell size, walls and edges thickness, and mechanical properties of the composite foams. Results of the energy absorption of the foams subjected to compressive loadings up to $\varepsilon = 50\%$ ($K_{50}$) are shown in Figure 6(d). Foams without fibers are capable to absorb $K_{50} = 107.7$ kJ/m$^2$. Incorporation of low fiber contents (3 and 6 wt.%) significantly reduces the energy absorption capabilities of the composite foams; being the most critical reduction at 3 wt.%, its behavior is mainly associated with a lower wall thickness at these fiber contents with respect to the reference material at a similar cell size as is shown in Table 1. However, at 12 wt. % of agave fibers, energy absorption can be enhanced up to 14% and 23% for composites foams reinforced with pristine and plasma-treated agave fibers, respectively. In general, the incorporation of 12 wt. % of agave fibers treated by ethylene plasma produces higher improvements in the mechanical properties of the composite foams under compression than the pristine ones. While, at 15 wt.% of AF$_p$ and AF$_m$ composite foams shows a slightly reduction in $K_{50}$, probably because at this fiber contents, the cell size produced is not homogeneous such as is showed in Figures 3(f) and 4(e).

4. Conclusions

The behavior of composite foams made from Agave fibers modified by plasma was investigated. Composite foams containing low contents of agave fibers (plasma-treated or pristine) exhibit bigger cell sizes, wider cell size distribution, and thin walls and edges compared to the reference foam (without agave fibers). While polymeric foams with plasma-treated fibers (AF$_m$) above 9 wt. % showed smaller cells with a narrow cell size distribution and thicker walls and edges. The highest mechanical improvements were achieved by the incorporation of 12 wt. % of agave fibers. At this fiber content, the compressive modulus improved 7% with the addition of pristine fibers and 30% by using the plasma-treated fibers. The highest energy absorption improvement (23%) with respect to the neat polymer foam was also achieved by the addition of 12 wt. % of plasma-treated fibers (AF$_m$). These findings suggested that the introduction of the AF$_m$ ethylene plasma treated fibers, promoting a cell size distribution narrowed; the cell size was smaller, wall and edges were thicker, and the cell morphology was more

| Foam composite    | Average cell size (μm) | 1AWT (μm) | 2AWT-SD | Elastic modulus (MPa) |
|-------------------|------------------------|-----------|---------|-----------------------|
| Reference         | 193                    | 7.7       | 1.4     | 2.7                   |
| AF$_p$3           | 219                    | 2.8       | 0.5     | 0.7                   |
| AF$_p$6           | 159                    | 3.1       | 0.6     | 1.2                   |
| AF$_p$9           | 138                    | 8.4       | 1.4     | 2.3                   |
| AF$_p$12          | 86                     | 8.6       | 1.8     | 2.9                   |
| AF$_p$15          | 111                    | 8.4       | 1.0     | 2.7                   |
| AF$_p$3 12        | 218                    | 6.1       | 0.6     | 0.8                   |
| AF$_m$6           | 194                    | 5.7       | 1.5     | 1.0                   |
| AF$_m$9           | 127                    | 7.1       | 1.2     | 2.4                   |
| AF$_m$12          | 101                    | 5.9       | 0.8     | 3.5                   |
| AF$_m$15          | 110                    | 8.9       | 1.3     | 3.0                   |

1AWT: average wall thickness; 2AWT-SD: standard deviation of AWT.
uniform, because of the clusters of polymer like-polyethylene deposited on the AF surface increases the interactions with the polymer blend and allow a better spatial distribution of the AF, it increased the cell nucleation sites and the viscosity and affected the morphological parameters before mentioned. Using AFm, in the foam composites shows a better control of the Nc values with respect to Nc values with AFp. This behavior is attributed to the randomly spatial distribution of AF in the polymer blend matrix that affects the heterogeneous nucleation during foams obtention. Polymer foams developed in this work have potential applications in sandwich structures, as well as impact-resistant applications such as body protection.

Data Availability

The methodology and physicochemical, morphological, and compressive characterization data to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflict of interest.

Acknowledgments

The authors want to thank Myriam Lozano, M. G. Méndez-Padilla, J. F. Zendejo-Rodriguez, J. L. Saucedo-Morales, Josue Campos, Efrain Alvidrez, Mario Palacios, and Concepcion Gonzalez for their technical support in the preparation and characterization of the composite foams. This research was financially supported by the Mexican National Council of Science and Technology (CONACYT), specifically through the Laboratorio Nacional de Materiales Grafénicos (LNMG) and the Laboratorio Nacional en Innovación y Desarrollo de Materiales Ligeros para la Industria Automotriz (LANIAUTO) (grant numbers 232753 and 294030, respectively).

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