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Self-hybridization and Coupling Agent Effect on the Properties of Natural Fiber/HDPE Composites

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Abstract This work investigates the combination of different fiber sizes (self-hybridization) on the mechanical properties of composite materials. High density polyethylene composites based on agave and pine fibers were prepared using different ratios of long and short fibers. Furthermore, the effect of coupling agent (maleated polyethylene) versus self-hybridization was evaluated. Several studies in the past have shown that coupling agents can improve the mechanical properties of natural fiber composites. Nevertheless, this study shows that a combination of two particle sizes is also an interesting option to increase mechanical properties like impact strength, as well as tensile and flexural moduli. On the other hand, the presence of coupling agent enhanced the fiber-matrix interfacial adhesion and its effect was more evident on the tensile strength.

Keywords Self-hybrid composites · Mechanical properties · Coupling agent · Natural fibers

Introduction

In recent years, growing interest in the use of natural fibers as reinforcements for thermoplastics and thermosets was related to their flexibility during processing, high specific stiffness, and low cost (on a volumetric basis) making them attractive to manufacturers [1]. Natural fibers like flax, hemp, jute and sisal have been well recognized as good potential reinforcements for engineering composites. The main advantages of these fibers are lightweight, high specific modulus, non-toxicity and easy processing. These benchmarking properties open a wide range of natural fibers areas in the composite sector and challenge the replacement of synthetic fibers [2]. However, their structural compositions (cellulose, hemicelluloses, lignin, pectin and waxy substances) allow moisture absorption from the environment which leads to poor bonding with hydrophobic matrices. These hydrophilic characteristics subsequently result in poor mechanical properties of the reinforced composites. The fiber-matrix compatibility can be improved by the addition of coupling agents which act as surface modifiers forming a bridge (chemical bonds) between fibers and polymer matrix [3]. Recently, the production and application of thermoplastic polymers reinforced with wood flour increased considerably. Wood flour is obtained from natural resources because it is light, cheap and available in various forms and large quantities. It can also be added to commodity matrices in considerable amounts (up to 70 wt%), thus offering economically advantageous solutions [4]. On the other hand, agave fibers, which are waste from the tequila production, have attracted much attention to produce composite materials due to their low cost with good properties [5–7].

Self-hybrid Composites

Hybrid composites are materials combining two or more different types of reinforcements and offering a range of properties that cannot be obtained with a single type of

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fiber [8]. Hybridization may offset the disadvantages of one component by the addition of another. Typical hybrid composite systems reported in the literature are: bagasse-corn stalk-glass fibers/polypropylene composites [9], pulp fiber-wood flour/polyvinyl chloride composites [10], and pine-agave/polyethylene composites [11]. In all cases, the results showed that the combination of two different natural fibers allowed obtaining composite materials with unique characteristics.

Another kind of hybrid composites can be made with two different sizes of the same reinforcement which are named self-hybrid composites. In this case, it is common to mix particles (flour) with fibers of the same source to have a better distribution into the matrix and consequently an improvement in the mechanical properties. Ashori [12] prepared hybrid composites combining wood flour with newspaper fibers and found that both particles could be effectively used as reinforcing elements in polypropylene. The authors mentioned that with an optimum combination of fibers (especially in terms of aspect ratio) one can succeed in the preparation of good performance composites. Oh and Han [13], studied the effects of short-fiber/particles hybrid reinforcements on fracture toughness and found that the addition of particles to the fibers is effective to reduce void content and improved fracture toughness of the material. Li et al. [14] elaborated composites based on high density polyethylene with carbon black and added small quantities of graphite nanofibers. They found that the thermal properties of these hybrid composites were increased due to hybridization. Isitman et al. [15] prepared composites with two different sizes of glass fibers and found that different length scales alter fiber/matrix interaction. Ramezani-Kakroodi et al. [16] elaborated polypropylene (PP)-hemp self-hybrid composites and found that fiber size has great influence on the mechanical properties of the composites. They reported an increase in tensile strength when hemp powder was blended with hemp fibers, relating this to the combined reinforcing mechanisms in hybrid materials due to smaller reinforcements being able to accommodate between larger ones to produce higher and more efficient specific surface area between the matrix and particles.

In this study, a polyethylene matrix and two different sizes of agave and pine particles were used to produce self-hybrid composites. A complete mechanical characterization of the composites was performed to compare the effect of self-hybridization and coupling agent addition for different total reinforcement content.

Table 1 Chemical composition of the fibers

| Fiber	Extractives (wt%)	Lignins (wt%)	Holocellulose (wt%)	Moisture (wt%)
Agave	6–7	21–24	68–75	7–8
Pine	18–20	29–31	49–54	8–9

Experimental Procedure

Materials

The polymer used was high density polyethylene (HDPE) 60120U supplied by PADMEX (Mexico) with a melt flow index of 18 g/10 min at 190 °C and 2.16 kg (ASTM D1238). The coupling agent was maleic anhydride grafted polyethylene: Fusabond m603 (MAPE). This polymer has an average molecular weight of 124 kg/mol, an acid number of 13.8 mg KOH/g (maleic-acid anhydride grafting level of 12 % [17]), and a melt flow index of 25 g/10 min at 190 °C and 2.16 kg (ASTM D1238). The sample was obtained from DuPont Packaging & Industrial Polymers (USA).

A local tequila company in Jalisco (Mexico) provided fibers of *Agave tequilana* Weber var. Azul. The pine sawdust was obtained from Aserraderos Gómez Farías (Jalisco, Mexico). The chemical composition of the fibers is shown in Table 1 as determined according to TAPPI standards T-204cm-97 (extractives), T-222-om-98 (lignin) and the Jayme-Wise method (holocellulose).

Composite Preparation

Prior to extrusion, the agave fiber was cleaned as follows: sifting was made to eliminate the solids, later the pithy fibers were soaked in a container with tap water for 24 h to hydrate the fibers and to facilitate pith separation. This separation was made in a Sprout-Waldron refiner (D2A509NH) with two 30 cm diameter discs, one fixed and the other rotating at 1,770 rpm. Using centrifugation, the excess water in the fibers was eliminated. Finally, the fibers were air-dried and milled in a knives mill. The pine fiber was milled using a hammer mill. Both natural fibers were sieved to obtain two different fiber sizes: 44–105 μm (short) and 300–425 μm (long). Both fibers were dried for 24 h at 85 °C before extrusion.

The composites were prepared in a twin-screw extruder Leistritz Micro 27 GL/GG 32D with a temperature profile set to 130/140/150/150/160/160/170/170/160 °C. The
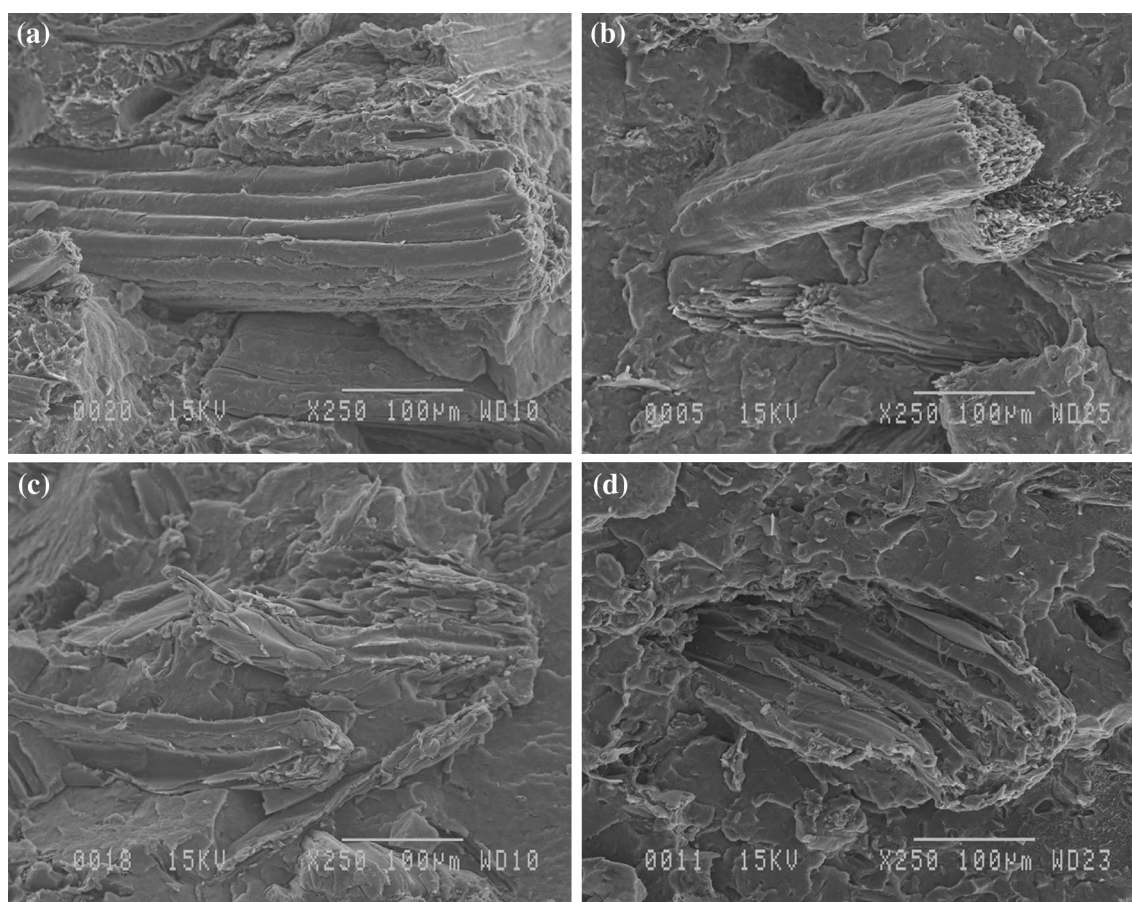
Fig. 1 Micrographs of PE-agave and PE-pine composites with and without MAPE: **a** A20L100, **b** A20L100M, **c** P20L100, and **d** P20L100M

extruder has three circular dies (2 mm in diameter each). The screw rotational speed was set at 120 rpm giving a total flow rate of 4 kg/h. The polymer and fibers were fed at the main inlet of the extruder using two feeders, one for the fibers and the other for polymer pellets. A previous calibration was carried out to set the feeding rate of each material to obtain a constant final composition in the composite. After extrusion, the material was pelletized. Three total fiber contents (10, 20 and 30 %) and five different ratios of long (L)/short (S) fibers (100/0, 70/30, 50/50, 30/70 and 0/100) were used to prepare composites without coupling agent. Additional samples with 3 % (wt/wt) of coupling agent with respect to the total fiber content were prepared using limited ratios (100/0, 50/50 and 0/100). The samples are presented as "$XyLz$" where "X" is fiber type (A: agave or P: pine), "y" is the total amount of fiber in the composite (wt%), and "z" is the amount of long fiber (L) in the long/short fiber ratio. Finally, for samples with coupling agent, the letter "M" is added at the end. The extruded materials were dried for 24 h at 85 °C and afterwards molded in an all-electrical 80 ton injection molding machine (NISSEI ES-1000) to obtain rectangular specimens of $80 \times 40 \times 2.55$ mm^3. The barrel temperature profile

used was 130/170/185/195 °C with a mold temperature of 30 °C. The screw diameter is 36 mm (L/D of 18:1) and the screw speed was set to 80 rpm. The maximum injection pressure used was 65 MPa and the screw position (shot size) was 35 mm. The holding time was 3.5 s and the cooling time 20 s.

Morphology

A scanning electron microscope (SEM) JEOL model JSM-849 (JEOL, Japan) was used to observe the structures exposed through cryogenic fracture and coated with a thin layer of Au/Pd prior to analysis. A scanning electron microscope SEM HITACHI TM-1000 was also used to analyze the morphology obtained.

Differential Scanning Calorimetry (DSC)

The samples used for DSC were cut from the injected specimens in order to have a weight between 6 and 8 mg. The equipment, Perkin Elmer DSC-7, was programmed to work in the temperature range between 50 and 160 °C under a nitrogen flow of 50 mL/min. The heating and
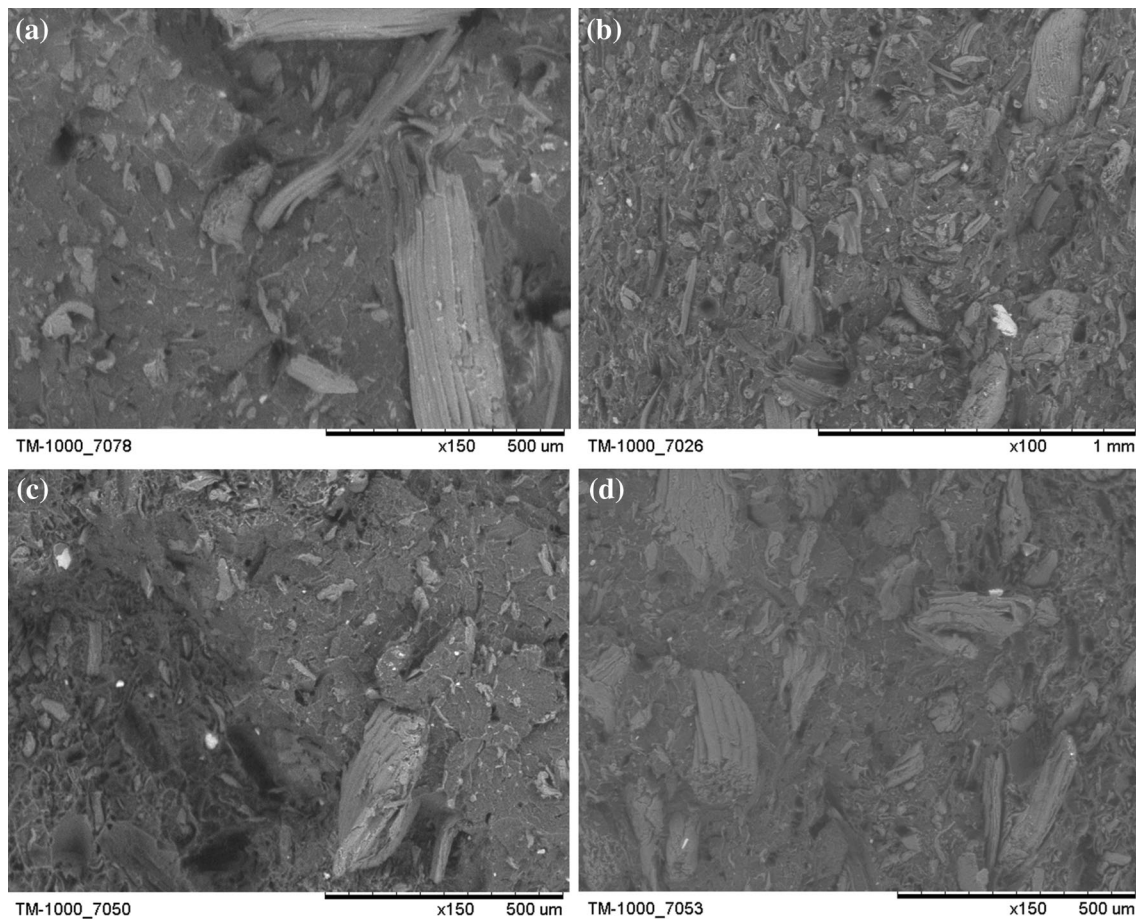
Fig. 2 Micrographs of self-hybrid composites: **a** A20L50, **b** A30L50, **c** P20L30, and **d** P30L70

Table 2 Thermal DSC characterization of HDPE composites

Sample	T_m (°C)	ΔH_m (J/g)	X_c (%)
HDPE	131.2	168.9	57.7
HDPE-M	129.5	167.9	58.5
A20L100	130.7	137.5	58.7
A20L100-M	129.2	131.7	56.2
A30L100	130.7	125.3	61.1
A30L100-M	130.3	115.9	56.6
P20L100	129.3	129.3	55.2
P20L100-M	130.2	124.9	53.3
P30L100	129.3	117.7	57.4
P30L100-M	129.8	115.8	56.5

cooling rates were 10 °C/min. Melting temperature (T_m) and melting enthalpy (ΔH_m) were calculated using MAT-LAB®. Crystallinity level (X_c) was determined as:

$$X_c = \frac{\Delta H_{m,\exp}}{\Delta H_{ref}} \times \frac{1}{x} \times 100 \qquad (1)$$

where $\Delta H_{m,\exp}$ is the experimental heat of fusion determined from DSC, ΔH_{ref} is the theoretical heat of fusion of

fully crystalline HDPE (293 J/g) [18], and x is the weight fraction of HDPE in the composites.

Mechanical Testing

Flexural tests were performed according to ASTM D790 using an Instron testing machine Model 4411. The specimens were cut into rectangular bars with dimensions of $80 \times 13 \times 2.5$ mm³. At least six samples for each composition were tested at a crosshead speed of 10 mm/min over a span of 41 mm. The tensile properties were evaluated according to ASTM D638 using the same testing machine as for flexural tests. The samples were prepared according to type V specimens of ASTM D638. Seven samples were analyzed for each composition. A load cell of 1 kN was used and the strain rate was 5 mm/min. Impact tests were performed in accordance to ASTM D5420 using a Gardner impact tester (falling weight). In this case, 20 samples were tested to get a representative average and standard deviation. All the tests were performed at room temperature 23 °C (±2 °C).

Fig. 3 Flexural modulus of **a** PE-agave and **b** PE-pine composites
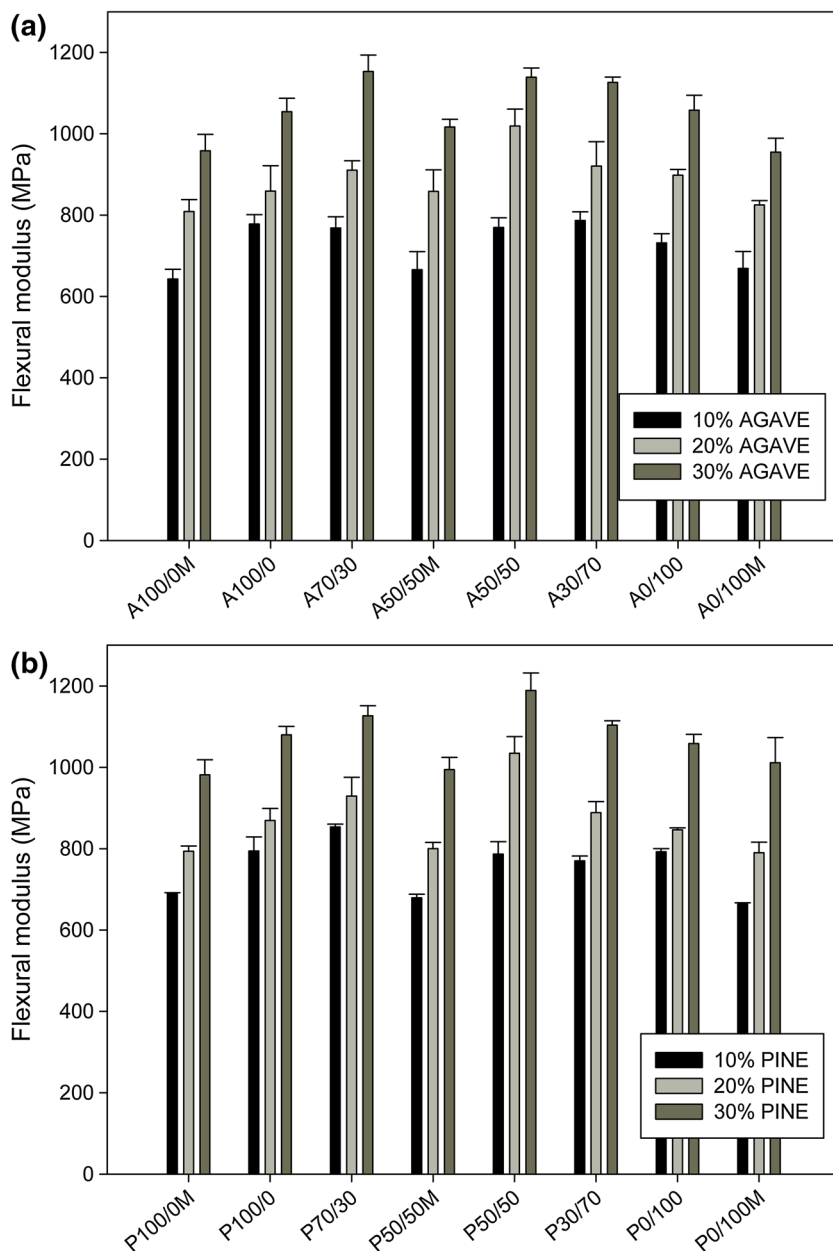

Results and Discussion

Morphology

SEM micrographs of the composites are presented in Fig. 1. It can be seen in micrographs Fig. 1a, b for agave composites that better adhesion with the matrix is obtained with coupling agent, which implies a decrease in the thickness of the interface between the fibers and the polymer matrix [19]. In micrographs Fig. 1c, d, pine-based composites with and without MAPE are shown. It can be observed that the interface is similar in both micrographs probably due to the fact that the coupling agent used did

not have good interaction with pine because of higher extractives content as reported in Table 1. In several studies, to enhance the effect of chemical coupling agents, an additional fiber treatment with NaOH (mercerization) was found necessary to reduce the amount of lignin and extractives, and consequently increase the number of available OH groups [20], but this aspect would need further study.

The fractured surfaces of the self-hybrid composites are shown in Fig. 2. These micrographs show that better fiber distribution is possible when two different sizes are used. Figure 2a, b correspond to agave self-hybrid composites with 20 and 30 % and show that even when the amount of

**Fig. 4** Flexural strength of **a** PE-agave and **b** PE-pine composites
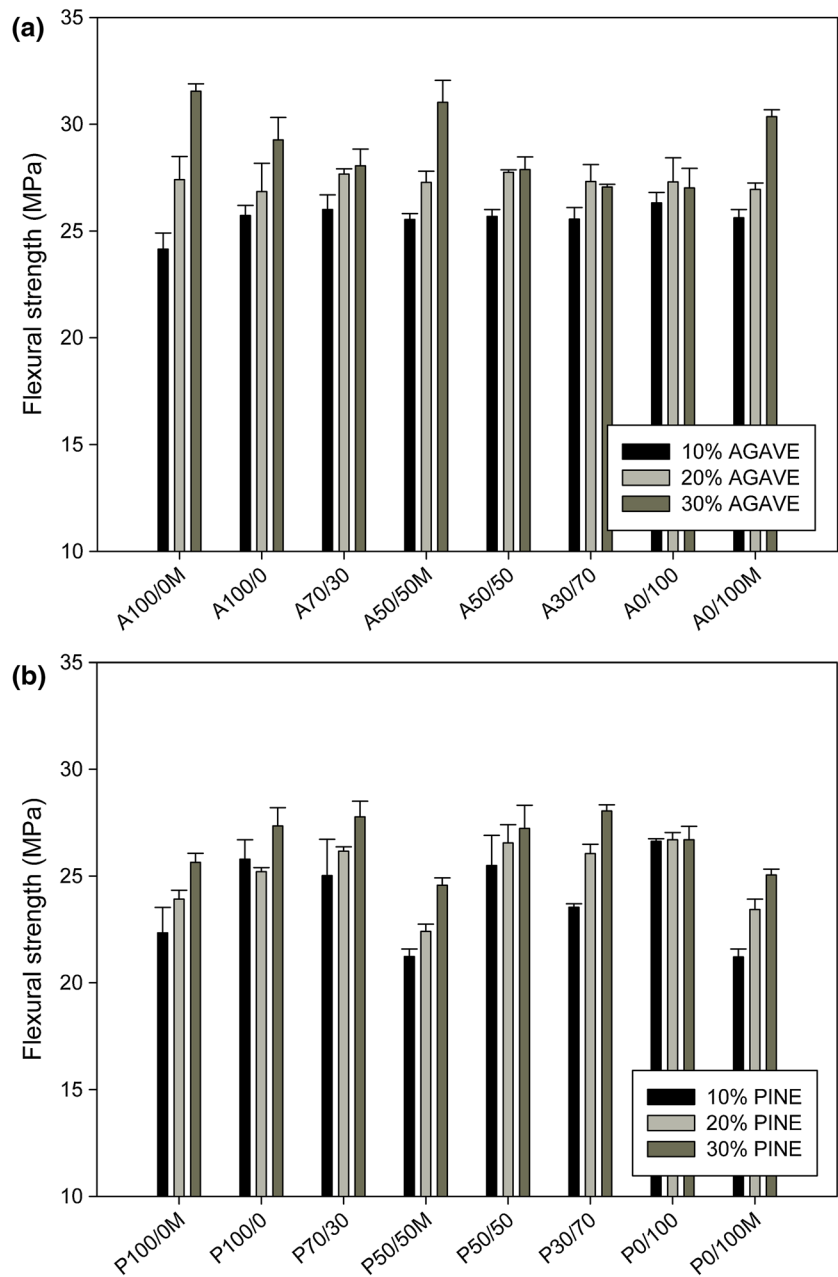
fiber increased the distribution of short and long fibers was good. Nevertheless, it can be observed that due to higher fiber content, there is still fiber agglomeration. In the case of pine composites, fibers arrangement is very similar to agave composites (Fig. 2c, d).

DSC

The thermal properties of HDPE self-hybrid composites were determined by DSC and the results are presented in Table 2. The thermograms (not shown) obtained for the neat matrix, as well as for all fibers composites were very similar among them. The melting temperature does not present significant change when adding fibers to the matrix, remaining roughly constant around 129–131 °C. The values of X_c for agave composites without MAPE where higher than the value obtained for neat HDPE due to fibers acting as nucleating agents providing increased crystallinity [18]. In all the samples, the crystallization level was reduced when MAPE was added. Lei et al. [18] suggested that MAPE reduces the degree of perfection of HDPE crystals. Araujo et al. [21] explained that this phenomenon occurs due to the higher surface area of the fibers, while composites with coupling agents have some part of the

Fig. 5 Tensile modulus of
**a** PE-agave and **b** PE-pine
composites
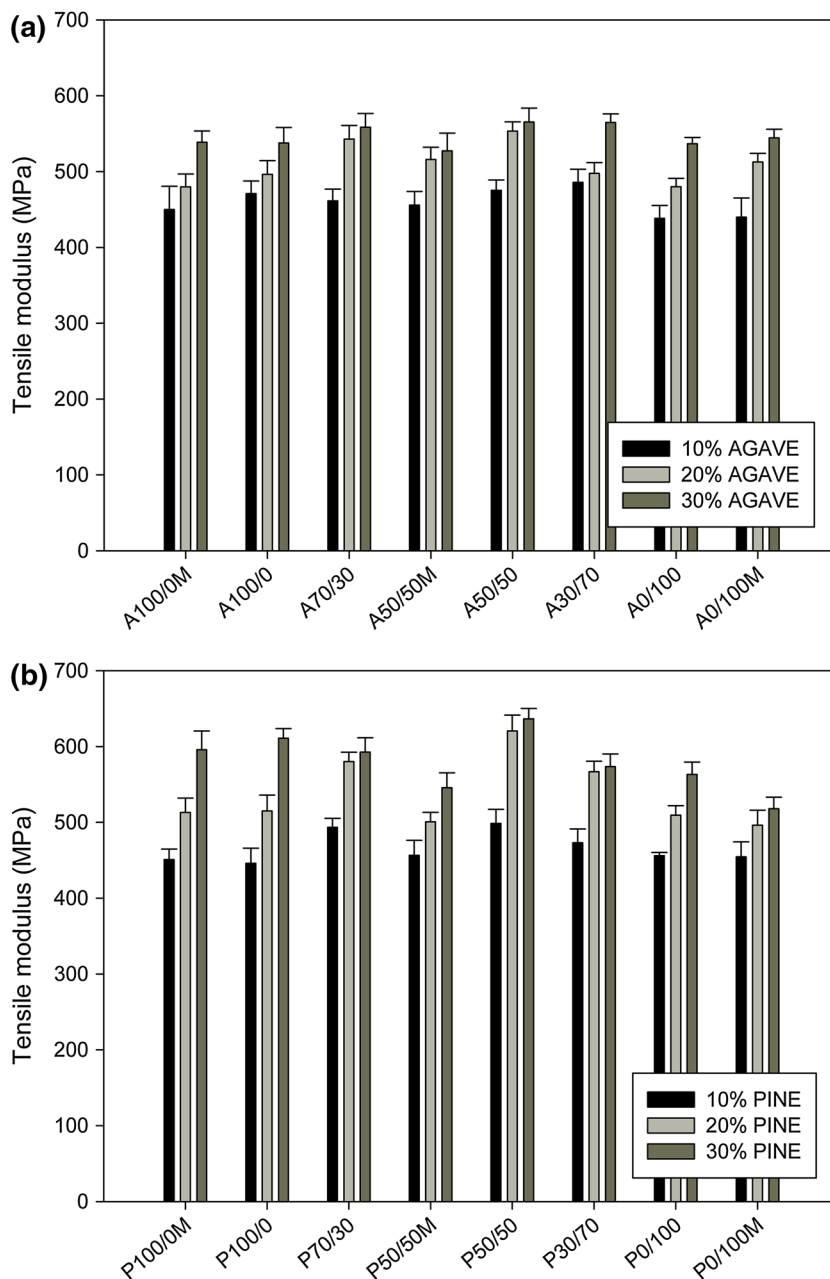
fiber surface area occupied by the coupling agents, decreasing the transcrystallinity effect.

Flexural Properties

The flexural moduli of the self-hybrid composites are presented in Fig. 3. Agave and pine composites made with two fiber sizes showed increases of 19 % in flexural moduli compared to single fiber size. This increase was maximum when a hybrid ratio of 50/50 was used at a total fiber content of 20 %. The flexural modulus achieved for HDPE-agave composites with 20 % of fiber was 1,019 MPa which

was higher than the value obtained with MAPE (858 MPa). For HDPE-pine with 20 % of fiber the flexural modulus was 1,035 MPa, once again higher than the value with MAPE (800 MPa). ANOVA analysis was performed (using Statgraphics software) and these data were founding statistically different ($p < 0.05$). As expected, increasing fiber content helps improving flexural modulus compared to neat HDPE (566 MPa). From these results, it was found that a good combination of different fiber sizes is a great option to improve flexural modulus. The composites made with coupling agent presented lower flexural moduli than without coupling agent. Incorporation of coupling agents

Fig. 6 Tensile strength of **a** PE-agave and **b** PE-pine composites
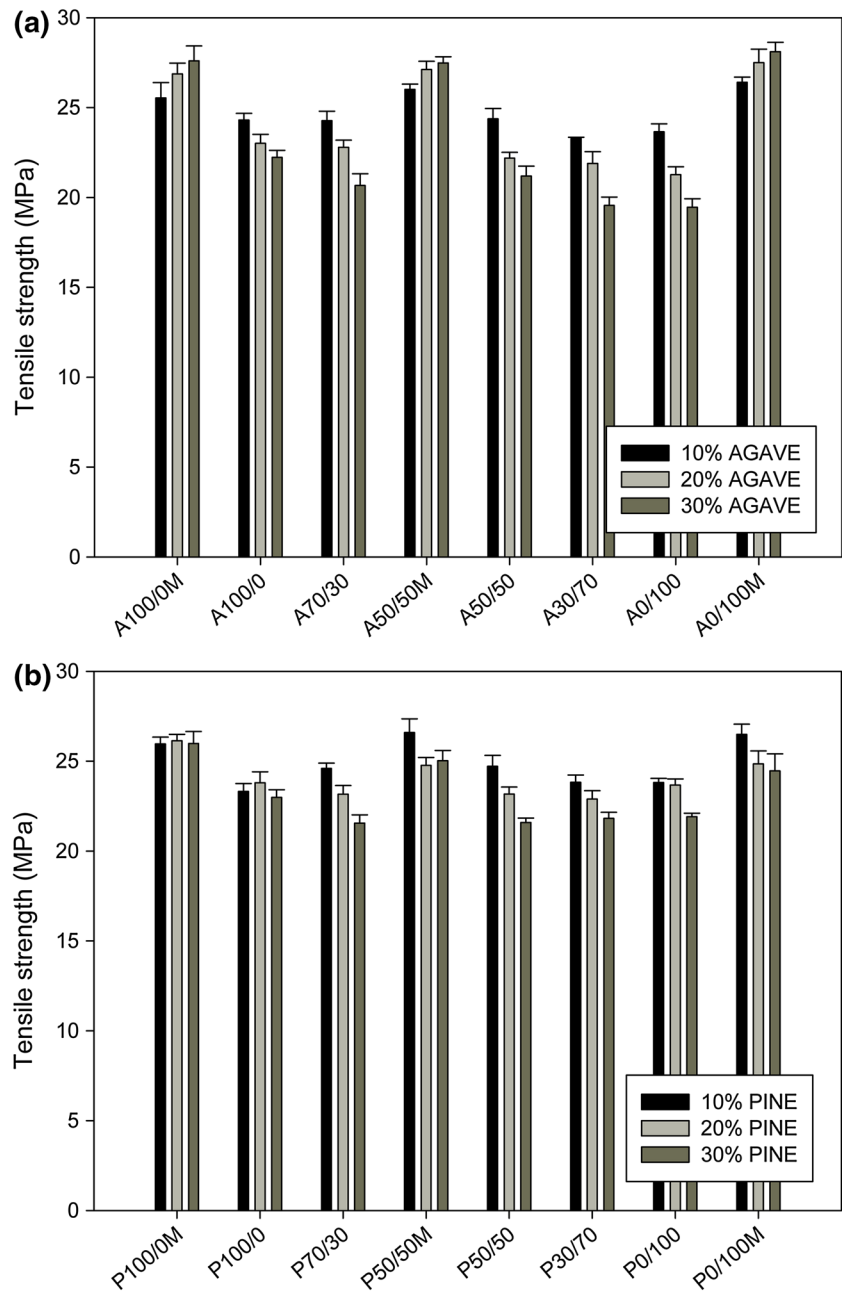
sometimes does not produce significant improvement in flexural modulus of polymer-lignocellulose composites [22]. Lower modulus may possibly be due to the plasticizing effect of low molecular weight MAPE which caused a reduction of the composite stiffness [23, 24].

The results of flexural strength of agave and pine composites are shown in Fig. 4. It can be observed that for 30 % agave fiber composites, the addition of coupling agent increases the flexural strength by approximately 10 %. The improvement in flexural strength was attributed to the increased adhesion of the fiber with the matrix,

which leads to more uniform distribution of applied stress which requires more energy for fiber deboning [25]. In pine composites, the addition of coupling agent reduced flexural strength, which again could be due to higher extractives content as reported in Table 1 since waxes and non-cellulosic substances could interfere with the coupling agent [26], lowering its efficiency.

An important result is that flexural strength of PE-pine self-hybrid composites was higher than those with coupling agent, the flexural strength of neat HDPE was 22 MPa and for composites with 30 % of total fiber content and a 30/70

Fig. 7 Impact strength of **a** PE-agave and **b** PE-pine composites
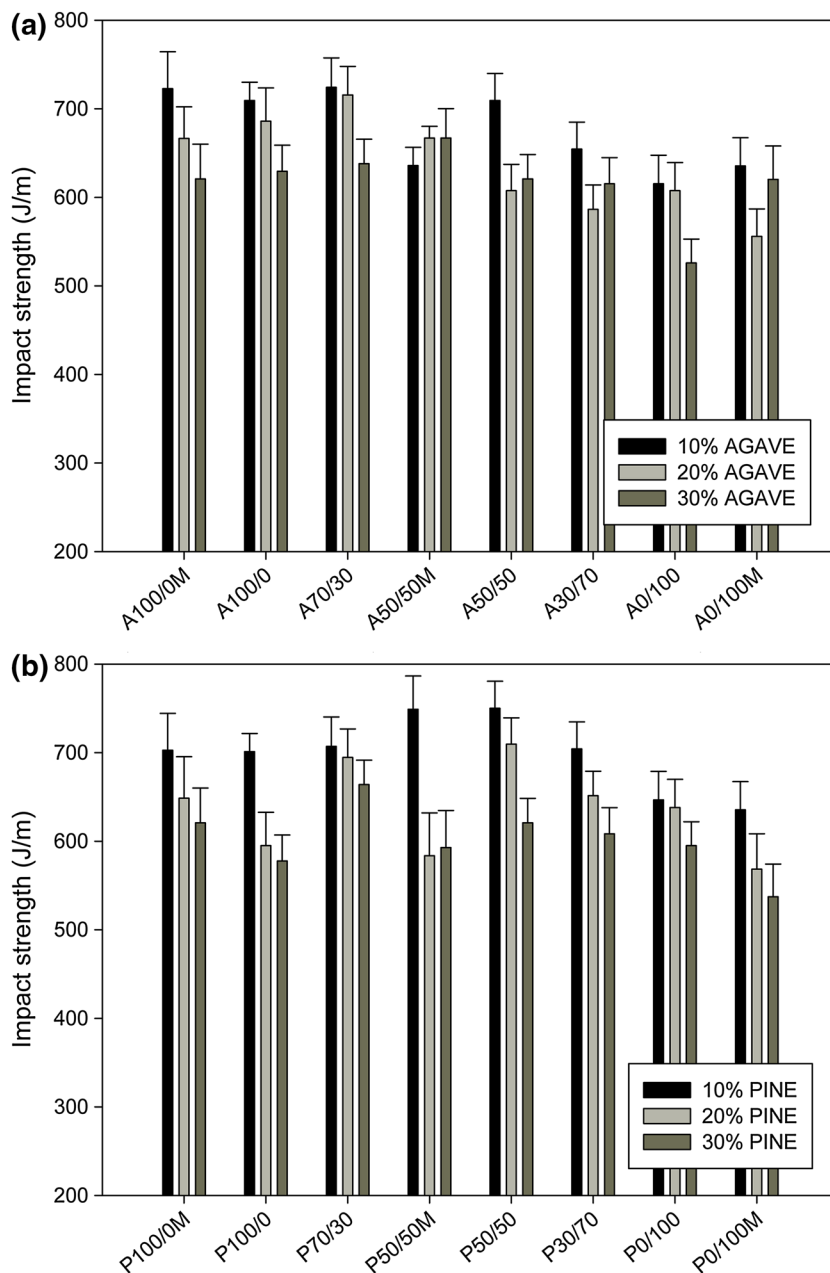
ratio a maximum value of 28 MPa was achieved, while for composites with coupling agent the maximum flexural strength was only 25 MPa.

Tensile Properties

Tensile modulus of the self-hybrid composites is presented in Fig. 5. These results show that for both fibers, tensile modulus increases with fiber content. The tensile modulus of neat HDPE was 421 MPa and adding 30 % of agave or pine fibers increased the value to 565 and 591 MPa, respectively. Again, it can be observed that the use of two fiber sizes is better than using only one size. For composites with 20 % of

fiber and a 50/50 ratio, an increase in tensile modulus of 15 and 20 % for agave and pine composites over the use of one fiber size was achieved; the values obtained were 553 and 620 MPa, while for the composites with MAPE and 20 % of fiber it was 516 and 513 MPa. The use of coupling agent in pine composites help increasing tensile modulus, but only for total fiber contents of 10 and 20 %. Once again, self-hybridization helped more increasing tensile moduli than coupling agent for all total fiber contents. This self-hybrid effect was also observed in a previous study on polypropylene [27]. The tensile strength results can be seen in Fig. 6. It was found that tensile strength decreases when the amount of fiber increased. Fiber surfaces have waxes and

other non-cellulosic substances such as hemi-cellulose, lignin and pectin, which create poor adhesion between matrix and fibers [3]. Faruk et al. [1] reported that when PP is reinforced with natural fibers, tensile modulus is improved, but tensile strength decreases. They suggested that in order to improve and develop natural fiber reinforced polymer composites with better tensile properties, it is necessary to increase fibers hydrophobicity by chemical treatments or use coupling agents. Here, it is observed that the use of coupling agent improved polymer-fiber adhesion. For agave composites with 30 % of fiber and coupling agent, tensile strength increased 24 % over composites with the same amount of fiber, while for pine composites the increase was only 13 %. These results showed again that coupling agent has better effect on agave fiber composites. Kim et al. [28] elaborated PP-wood composites with coupling agent and explained that generally tensile strength is controlled by the weakest part of the composites which is interfacial interaction between PP and wood fiber. Therefore, tensile strength of PP-wood fiber composites decreases with increasing wood fiber content.

Impact Properties

The results of impact strength are presented in Fig. 7. All the values are lower than neat HDPE (7,670 J/m) with a maximum value of 750 J/m for HDPE-pine composites at 10 % fiber content. Impact strength frequently decreases when fiber content increases [25, 29]. In Fig. 7 this behavior occurred when pine fiber was used. In the case of composites with 20 % agave and a 70/30 ratio, a maximum value of 715 J/m was obtained, while for composites with 20 % of agave and MAPE the maximum value obtained was 666 J/m. This result indicates that self-hybridization plays a very important role over impact strength properties. In case of HDPE-pine composites, the combination of 70/30 and 50/50 showed significant improvements in impact strength compared to the use of one fiber size. For pine composites with 20 % of long fibers the impact strength obtained was 594 J/m and for a self-hybrid composite with the same total content of pine fibers and a 50/50 ratio a value of 710 J/m was achieved, on the other hand the value obtained using MAPE was 648 J/m. Nourbaksh and Ashori [25] observed that higher impact strength was obtained when more long fibers than short fibers are used. Nevertheless, it has been reported that the main reason for fracture in reinforced systems is the formation and coalescence of voids when long fibers are present in the matrix, but when the fibers are smaller greater strain localization will be needed to fracture the material [13]. In this sense a combination of small and long fibers could increase impact strength due to the combined effect of each fiber size. For example, a combination of 70/30 (long/short fibers) and 20 % of total fiber content

produced an impact strength of 715 J/m, while the maximum achieved was 722 J/m for HDPE-agave composites with 10 % of fiber. These results suggest that self-hybridization could maintain impact strength values regardless of total fiber content. Nevertheless, no significant effect of coupling agent was observed on impact strength results.

Conclusions

In this work, it was shown that the mechanical properties of HDPE composites based on agave or pine fibers can be improved by self-hybridization (combination of two fiber sizes) instead of using a single fiber size. SEM micrographs showed the two effects of interest in this study, the self-hybrid effect to improve the distribution of fibers and the addition of a coupling agent helping to improve fiber-matrix adhesion (agave only). With an adequate combination of short and long fibers, it is possible to succeed in the preparation of good composite materials performance containing waste and renewable natural resources. The effect of coupling agents in the composites was found to be important to improve tensile strength with 24 and 13 % increase for agave and pine composites respectively; as well as flexural strength of agave composites with an improvement of 27 %. On the other hand, the use of different fiber sizes has great influence over impact strength, as well as flexural and tensile moduli, especially for 20 % fiber contents. For HDPE-pine composites with 20 % of total fiber, these properties increased by 19, 19 and 20 % respectively due to self-hybridization; while in the case of HDPE-agave composites with the same total fiber content the improvements were 9, 19 and 15 %. From the results obtained, hybridization seems more important than coupling agent addition, at least for the system studied here.

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