Natural Fiber-Polypropylene Composites Made from Caranday Palm

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ABSTRACT: Composites made from polypropylene (PP) and local South American fibers traditionally used in yarn-derived craftsmanships, Caranday Palm, were studied regarding the effect of fiber addition, concentration and characteristics of the coupling agent (molecular weight and percentage of grafted maleic anhydride), as well as type of processing. A laboratory-scale intensive mixing followed by compression, and pilot plant twin extrusion followed by injection, were the two processes investigated. The use of the first one allowed the selection of processable formulations with high fiber concentration and a percentage of coupling agent below the surface fiber saturation. In fact, it was found that there is a concentration of maleic anhydride moieties that saturates the surface of the fiber irrespective of the agent molecular weight. Increasing the concentration of the coupling agent above that value does not produce further improvement of the mechanical properties. The formulations selected from the results of the laboratory process were considered for the pilot plant (extrusion-injection) process. The use of the second process consisting of extrusion-injection molding showed that the high shear developed in this process leads to defibrillation of the fiber bundles. In the case of the Caranday Palm fibers, this defibrillation resulted in elemental fibers (micron size) being the effective reinforcement of the composite instead of the technical fibers (millimeter size) that were present in the composites prepared by compression. Better mechanical properties were achieved by using the latter method.

KEYWORDS: Natural fiber composites, defibrillation, injection molding, compression molding, mechanical properties, coupling agents

1   INTRODUCTION

Markets are increasingly driven by the public demand for products more environmentally friendly [1]. The use of renewable resources in composite materials is becoming more and more common. In the last two decades, the use of natural fibers as reinforcements and/or fillers in the manufacture of fiber-polymer composites has experimented a remarkable growth that has been accompanied by achievements in green technology in the academic and production arenas [1–5].

These fibers have many advantages such as low density, high specific strength and modulus, relative nonabrasiveness, ease of fiber surface modification, and wide availability. Natural fibers are also much cheaper than synthetic fibers and could replace synthetics in many applications where light weight and cost savings outweigh high composite performance requirements. The main disadvantages of natural fibers in composites are the lower allowable processing temperatures, incompatibility between the hydrophilic natural fibers and hydrophobic polymers, and potential moisture absorption of the fibers and as a result, of the manufactured composite. To enhance the compatibility of the two phases in such composites, a compatibilizer or coupling agent is normally added to the mixture. Many researchers have reported improvements in the mechanical properties when a compatibilizer was used or the fibers were chemically modified prior to mixing [6–8].

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Moreover, thermoplastic polymeric matrices are preferred over thermosets due to the fast production cycle, lower cost of processing, better reparability and high possibility of recycling or reuse [9]. Polypropylene (PP) is one of the most extensively used plastics both in developed and developing countries. Fiber-reinforced thermoplastic matrix composites have gained commercial success in semi-structural and structural applications, and various fibers are widely used as reinforcement in thermoplastic polypropylene matrix to prepare composites. However, difficulties have been found in the production of natural fiber-thermoplastic composites because of the much increased viscosity of the filled polyolefins, since fiber contents are usually high. The incorporation of coupling agents, such as maleated polyolefins, with the adequate degree of grafting and molecular weight, alleviate this problem [8,10–13].

Natural fiber thermoplastic composites are fabricated by using traditional manufacturing techniques that are designed for conventional fiber-reinforced polymer composites. These techniques include compounding, compression molding, direct extrusion, pultrusion, and injection molding, among others. Selection of the production process depends on the required properties as well as the desired production rate and the product status (semi or finished). Also, the production technique affects the fiber aspect ratio and fiber orientation, and hence, the mechanical properties are defined. More randomness in the fiber directions is attained in extrusion and injection molding (compared with other techniques, such as pultrusion). Besides these two processes are the most important processes for thermoplastic materials. Single- and twin-screw extruders are used for melting and pumping of polymers and for die extrusion for the production of film, sheet, pipe, tubing, profiles and fibers. Injection molding is the process used for the production of numerous parts, small and large, by injecting a molten polymer into mold cavities [14].

The aim of this study is to evaluate the performance of composites made from polypropylene (PP) reinforced with local South American fibers, which are traditionally used in yarn-derived craftsmanships, Caranday Palm. Thus, the study of its performance as reinforcement/filler in PP composites is of local interest to add commercial value to this fiber that has a large growth in northeastern Argentina. This work covers the laboratory-scale study of the selection of the processable formulation with high fiber concentration, the concentration and characteristics of the coupling agent (molecular weight and percentage of grafted maleic anhydride) that lead to fiber surface saturation. These results allowed the formulation of composites in a pilot plant extrusion step followed by injection using a concentration of coupling agent adequate to observe variations on properties due to the different interfaces. The important effect of the different shear conditions applied in the two processes on the final mechanical properties of the composites is also addressed. Moreover, there are few publications in which the influence of processing was taken into account.

2 EXPERIMENTAL

2.1 Materials

Polypropylene PP R6100 (MFI = 8 g/10 min at 230°C and 2.16 kg, crystallinity 40.32%, density 0.905 g cm³) was supplied by Petroken (Buenos Aires, Argentina).

Maleic anhydride (MA) grafted PP copolymers (PP-g-MA) were synthesized according to the details given in a previous publication [15]. The main characteristics of these copolymers are reported in Table 1.

Short fibers from Caranday Palm were used as reinforcements for the composites. The fibers were obtained from plant leaves dried, milled (Fritsch knive mill) and sieved (sieve series, Retsch GmbH) [16]. The fraction that passed mesh 30 and was retained in mesh 40 (Figure 1) was used in the composite preparation (length, L = 1–4 mm and diameter, D = 150–350 µm; average aspect ratio, L/D = 10.3). Although the

Table 1 Coupling agents with different MFI and percentages of grafted maleic anhydride.

	MFI (g/10min)	nominal MFI (g/10min)	% grafted MA (g of MA/100 g copolymer)
PP-g-AM 4	19.10	20	0.17
PP-g-AM 3	20.32	20	0.35
PP-g-AM 8	19.52	20	0.46
PP-g-AM 6	103.68	100	0.32
PP-g-AM 10	109.65	100	0.70
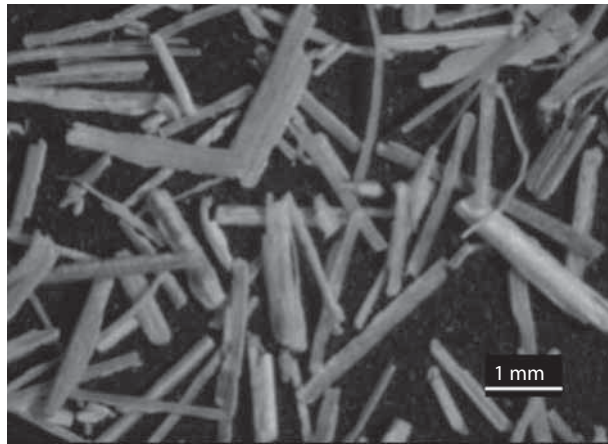
Figure 1 Caranday Palm fibers after being milled and sieved.

concentration of cellulose in the leaves of Caranday Palm can be as low as 32–37 wt%, once the technical fibers are separated and waxes eliminated, cellulose concentration can reach 45–48 wt%. The Young modulus of the fibers (17.85 ± 0.98 GPa) was found to be higher than jute or sisal, but the tensile strength was as low as 200 MPa. Complete chemical and mechanical characterization of the fibers was the focus of a previous publication [16].

2.2 Microscopy and Fiber Dimensions

The dimensions of the fibers used in the composite formulations were measured using a Nikon SMZ-2T magnifying glass at 20X. The values reported are the average of 200 measurements.

The results "after processing" were obtained on fibers extracted from the prepared composite samples. A Soxhlet extraction in toluene was performed during a one day period on composites containing 50 wt% of fibers. The reported fiber dimensions are the average of 65 measurements obtained by micrographs from a Nikon Eclipse E400 optical microscope at a magnification of 330X.

2.3 Composite Samples Preparation

The measured average humidity of the fibers was 8.5 wt% [16], and consequently, fibers were dried at 60°C for 24–48 h before being mixed by using either of the two different methods below.

Batch processing: Composites were prepared mixing the dried components in a Brabender W30 mixer at 180°C and 60 rpm during 8 minutes.

Tensile specimens were molded by compression at 175°C during 12 min in a Mario Smaniotto (AMS 125/22, Argentina) press.

Continuous processing (pilot plant scale processing): The polymer and dried reinforcement, as well as the coupling agent, were mixed in a co-rotating twin-screw extruder from Werner & Pfleiderer (ZSK 25 WLE, Germany) using a temperature profile of 170°C, 170°C, 175°C, 180°C, 180°C, 185°C (head) and rotating speed of 100 rpm. The extruded material was air cooled at room temperature and further pelletized using a Cisca mill (Argentina). Test specimens were molded using an injection machine ENGEL ES 75 ST (Austria) and the following temperature profile: 130°C, 175°C, 190°C, 190°C (nozzle) and 40°C (mold).

2.4 Mechanical Tests

The mechanical test specimens were tested according to standards: tensile tests ASTM D-638 (at 5 mm/min); bending tests, ASTM D-790 (at 2 mm/min), and unnotched Izod impact tests, ASTM D-256. The tensile and flexural tests were carried out using an INSTRON 1125 machine and the impact tests with a Custom Scientific Instruments CS137D-177 pendulum. At least five test specimens were used in all the cases.

Scanning Electron Microscopy: Composite fracture surfaces were observed using a PHILIPS SEM 505 scanning electron microscope. Fracture surfaces were sputtered with a thin gold layer before observation.

3 RESULTS AND DISCUSSION

3.1 Batch Processing Method (Laboratory Scale)

3.1.1 Effect of Concentration of Fibers on the Mechanical Properties of Composites

To analyze this effect, samples containing different concentrations of Caranday Palm fibers were prepared. After processing the composites, the fibers suffered a reduction in their aspect ratio (from the initial L/D = 10.3 to L/D = 4.13), although without losing their original structure.

Some of the samples were prepared containing a coupling agent (PP-g-AM 10) in a concentration of 10 wt% with respect to the fibers' weight. This last concentration was selected to be high enough to ensure the saturation of the fibers' surface [17–19] with the grafted PP, as will be discussed in further sections. The use of this agent allowed obtainment of good wetting and dispersion of the fibers in the PP matrix.

Table 2 summarizes the results, showing the expected modulus increase with increasing fiber concentration, and little influence of the presence of the coupling agent, except for concentrations above 40 wt% of the fibers. At these fiber concentrations, the

Table 2 Tensile properties of Caranday Palm-PP composites (batch process) as a function of the fibers content. PP-g-MA 10 was used as coupling agent at a concentration of 10 wt% (with respect to the fibers' weight).

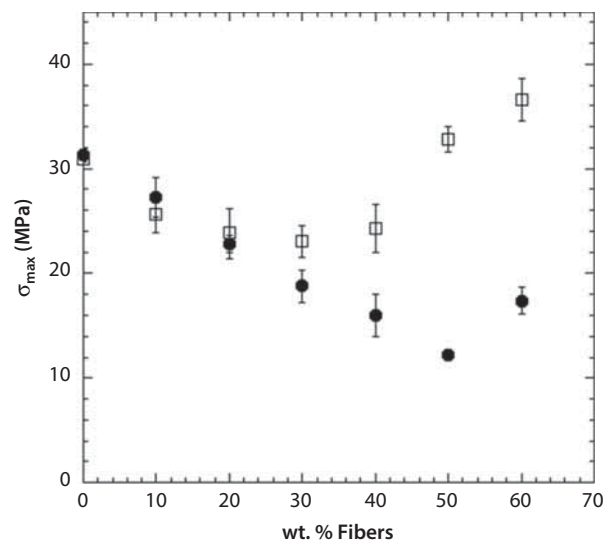| wt% fibers	without coupling agent			with coupling agent		
	Young Modulus (GPa)	Maximum Stress (MPa)	Elongation at break (%)	Young Modulus (GPa)	Maximum Stress (MPa)	Elongation at break (%)
0	1.57 ± 0.20	31.3 ± 0.7	>100*	1.45 ± 0.12	30.9 ± 0.3	>100*
10	1.91 ± 0.19	27.2 ± 1.9	4.0 ± 0.5	1.47 ± 0.07	25.6 ± 1.7	3.6 ± 1.9
20	1.66 ± 0.16	22.8 ± 0.8	3.3 ± 0.3	1.60 ± 0.07	23.8 ± 2.4	3.7 ± 0.1
30	2.05 ± 0.26	18.8 ± 1.6	2.1 ± 0.3	1.92 ± 0.11	23.1 ± 1.5	2.7 ± 0.4
40	2.20 ± 0.26	16.0 ± 2.0	2.0 ± 0.1	2.28 ± 0.13	24.3 ± 2.3	1.9 ± 0.3
50	2.32 ± 0.25	12.2 ± 0.6	1.0 ± 0.3	3.14 ± 0.43	32.8 ± 1.2	1.9 ± 0.5
60	2.60 ± 0.26	17.4 ± 1.3	1.4 ± 0.3	3.67 ± 0.99	36.6 ± 2.0	1.8 ± 0.2

* The large elongation value is related to the formation of stable necking.

improvement of the dispersion obtained by addition of the MA-g-PP affects positively the modulus of the material.

Composites prepared without the coupling agent present high concentration of large agglomerates, thus reducing the efficiency of adding rigid fibers. The elongation at break is relatively low in all the composites, since the presence of the fibers inhibits the formation of necking in the polyolefin. A very mild beneficial effect is observed when coupling agent is added in composites prepared with high fiber concentrations, as has been observed by other authors [20].

The effect of the coupling agent on the maximum tensile stress of the composites is more interesting (Figure 2); it shows a decreasing trend with the fiber concentration up to a critical value, at which point the incorporation of a higher fiber concentration has a reinforcing effect and the maximum stress increases [19,21]. That reinforcement critical concentration corresponds to about 50 wt% of fibers if no coupling agent is added, but it is reduced to about 30 wt% with coupling agent. That is, lower fiber content is needed to achieve the reinforcement of the material. Since above the critical value (30 wt%) the tensile strength of the materials increases, the values for the 50 wt% and 60 wt% composites are higher than that of the unfilled PP.

The observed behavior, a minimum in tensile strength (at 50 wt% for the uncoupled fiber composites and at 30 wt% for the composites with added coupling agent), is related to defects or points of stress concentration introduced in the matrix by the fiber inclusion, and the large effect of the formation of a physical network of fibers at high concentrations, which results in improved tensile strength. Discontinuity at the

Figure 2 Maximum tensile stress vs. weight concentration of Caranday Palm fibers in PP composites (batch process). Filled circles: composites without coupling agent, open squares: composites with coupling agent.

interface (low interfacial strength) results in the particle not carrying the load in the composite and, thus, the material strength decreases with increasing particle concentration. The effect is overcome at a critical concentration at which a network of fibers percolates the sample. Not only fiber/matrix interactions should be considered, but also fiber/fiber interactions. This last type of interactions results in aggregation, which is more probable to occur in composites prepared without addition of a coupling agent. The low surface energy between technical fibers (micron size) in the

aggregates is not strong enough to produce load transfer from fiber to fiber; the aggregates have low strength and are easily separated, resulting in the reduction of the materials' strength [22].

Obviously, in well dispersed fiber composites with high interfacial adhesion, the initial decreasing effect is ameliorated and the increasing trend appears at lower concentrations.

Minimum values of tensile strength as a function of filler concentration are not uncommon in the literature, but are not a general rule, and different behaviors have been reported [23,24]. The difference in the concentration of fibers corresponding to the minimum is a clear result of their improved dispersion in the presence of the coupling agent, in which case the percolation threshold (critical fiber concentration) is reached at a lower fiber content.

Taking into account that commercial applications usually require the use of high volume fraction of fibers and considering the improvement of mechanical properties at high fiber concentration (for composites prepared with addition of the coupling agents), a concentration of 50 wt% of fibers was selected to carry out the rest of the studies.

3.1.2 Effect of Molecular Weight and Grafting Level of the Coupling Agent on Mechanical Properties of Composites

Three different PP-g-MA were selected of approximately equal MFI (PP-g-MA 3, PP-g-MA 4, PP-g-MA 8), but different grafting level from 0.17% to 0.46% (molar MA concentration in the copolymer). Figure 3 summarizes the tensile strength of the 50 wt% Caranday Palm fibers vs. the content of copolymer added (referred to as the fibers' weight). The results obtained for the composites without additive (filled circle in the figure) is also included for the sake of comparison. Clearly, the use of small amounts of copolymer produced an improvement of the composite behavior and the curves suggest that in all cases a constant value of strength is achieved at high concentrations (not so clear in the PP-g-MA 4 curve), and that this plateau value is independent on the grafting level of the copolymer. Moreover, it seems that the plateau is achieved at lower copolymer concentrations as the level of grafting increases (from about 50 wt%, referred to as the fibers' weight, to about 10 wt% for the composites containing PP-g-MA 4 and PP-g-MA 8, respectively). This would suggest that the surface of the fibers reached the saturation point for the copolymer attached to the surface, a concentration that appears to be a function of the concentration of MA in the copolymer.

To further analyze the effect of the copolymer characteristics on the mechanical properties of the
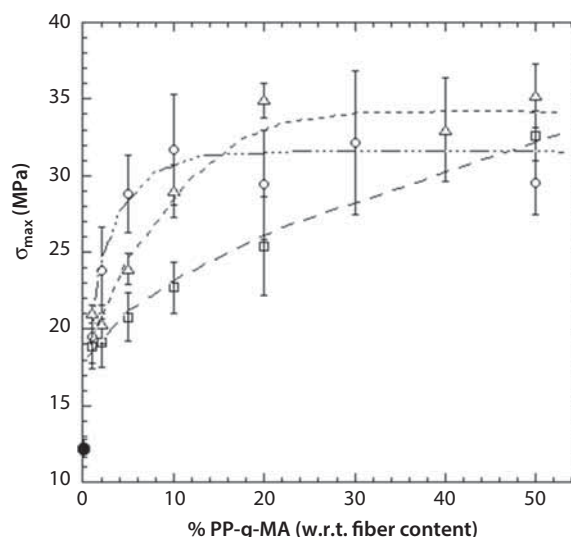
Figure 3 Maximum tensile stress as a function of the concentration of coupling agents of similar MFI (nominal value = 20 g/10 min) and different grafting level (batch process). Lines are just a visual help. Squares: PP-g-MA4 (0.17% grafted MA), triangles: PP-g-MA3 (0.35% grafted MA), circles: PP-g-MA8 (0.46% grafted MA).
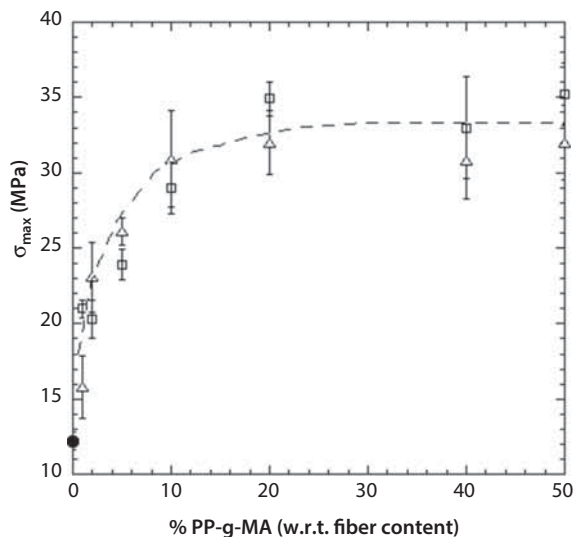
Figure 4 Maximum tensile stress as a function of the concentration of coupling agents of similar grafting level and different MFI (batch process). Line is just a visual help. Squares: PP-g-MA3 (nominal MFI: 20), triangles: PP-g-MA6 (nominal MFI: 100).

composites, two PP of similar MA grafting level but different MFI (PP-g- MA 3 and PP-g-MA 6) were added in different concentrations to the 50 wt% fiber composites. The results shown in Figure 4 indicate that in this case a plateau value is also reached for the tensile strength and in the same range observed

in the previous figure. In this case, however, there are no important differences between the two set of data, indicating that the effect of the molecular weight of the copolymer is not so important in determining the saturation of the fiber surface, at least in the range of molecular weights and grafting levels investigated.

Considering the apparent importance of the grafting level of the copolymer on the strength of the composites, all the results were replotted as strength vs. the concentration of MA, as mol of MA per 100 g of fibers (Figure 5). The plot shows that all the points fall closely in a single curve independently of the level of grafting or the MFI of the copolymer, which stresses that the MA concentration is the most important variable in the saturation of the fiber surface with the copolymer, especially regarding the constant value of strength reached, as well as the critical value of the MA concentration needed to reach this plateau value. The critical value of concentration at which the plateau value is reached corresponds approximately to 8.0×10^{-4} mol MA/100 g of fibers.

Summarizing, the most important result from this study of the composites prepared by a discontinuous process in an intensive mixer was that a critical concentration value of maleic anhydride (grafted moieties) is needed to saturate the surface of the fibers. Above this critical concentration a maximum value of tensile strength is reached, and further addition of coupling agent is of no significance. Consequently, this value is important at the moment of selecting the optimum concentration of a given coupling agent to be incorporated into a composite formulation.

3.2 Composites Prepared by a Continuous Process: Extrusion-Injection

The results analyzed in the previous sections supported the viability of preparing composites at 50 wt% fiber concentration. It was also evident that using 10 wt% of PP-g-MA (with respect to fiber content) resulted in the fiber saturation; consequently little or no variations were to be expected from the use of different coupling agents. For these reasons, in the continuous compunding of Caranday Palm fibers with PP (extrusion-injection), a fiber concentration of 50 wt% and a coupling agent content of 5 wt% (with respected to fiber mass) were selected. At this PP-g-MA concentration variations in the final properties of the composites due to differences in the efficiency of the coupling agents should be detected. It is also important that the selected concentration of coupling agent was in the range of commercial formulations. According to the results of the previous section, at this concentration the coupling agents with high MA grafting level allow reaching the maximum strength of the composites, while the copolymers with low MA content lead to composites that perform poorly.

As anticipated in the experimental section, the dimensions of the fibers were monitored in this process because of the variations observed. The type of mixing utilized strongly affected the morphology of the fibers, which consisted mainly on elemental fibers instead of technical ones at the end of the extrusion process. Table 3 shows the values of diameter and
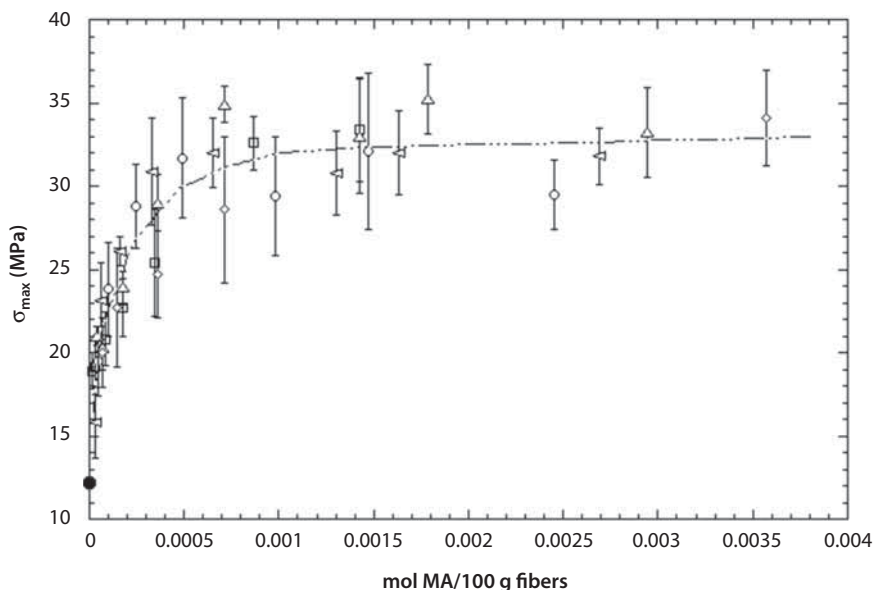
Figure 5 Maximum tensile stress as a function of the MA concentration in the various composites (batch process). Line is just a visual help. Triangles: PP-g-MA3, squares: PP-g-MA4, turned triangles: PP-g-MA6, circles: PP-g-MA8, diamonds: PP-g-MA10.

Table 3 Dimensions of the Caranday Palm fibers after the pilot plant processing (continuous process).

	Length (mm)	Diameter (microns)	Aspect ratio (L/D)
After extrusion	> 0.30	12.5 ± 2.2	> 24
After injection	> 0.31	12.1 ± 1.9	> 26

0.5 mm
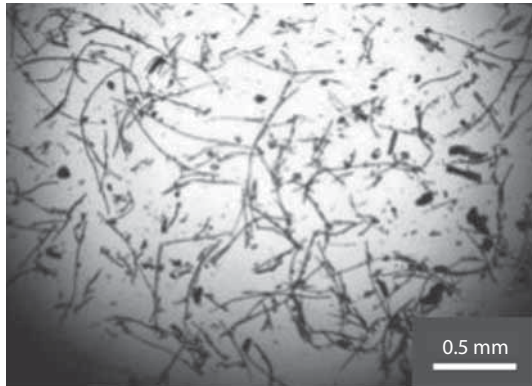
Figure 6 Dimensions of the Caranday Palm fibers after extrusion and injection.

length of the fibers after processing and Figure 6 displays the appearance of the fibers. The diameter of the fibers after compounding was comparable to the size of elementary fibers that presented a diameter of 9.06 ± 1.34 microns [16]. Although the length and diameter of the fibers are reduced, the aspect ratio increased, more than doubling the original value. The majority of this transformation takes place during the extrusion step (mixing) and there is essentially no further change during injection. This result is quite different from what was observed during the mixing in the laboratory chamber in the intensive mixer. In that case only a moderate reduction of length and diameter was observed, which did not improve the aspect ratio of the fibers.

Although there are not many articles dealing specifically with the fibrillation of the natural fibers due to processing, our observation agrees with a previous study on carbonate filled PP [25] in which the high shear of injection molding broke carbonate aggregates, while they remained almost unchanged in compression molded samples.

Other authors have reported their results on the effects of the extrusion processing on mechanical properties of a fully biodegradable composite made from sisal fibers and an industrial biodegradable polymer (Mater-Bi) [26]. They found that the fibers

suffered damage during the extrusion process and showed a rougher surface. Fibrillation, breaking down of the fiber bundle into smaller fibers, was produced during the processing. This effect increased the effective surface area available and reduced the fiber diameter. However, the aspect ratio increased only very slightly (from 13 to 16), because fibers were shortened during processing. On the other hand, Silva Spinace et al. [27] prepared composites from recycled polypropylene and curaua fibers by extrusion. They reported partial fibrillation of the curaua fibers, leading to increased aspect ratio of the fibers in the composite that improved the reinforcing effect. No comparison with the fibrillation effect that could be induced by other types of processes was included in any of the previous works.

A more closely related publication by Hietala et al. [28] studied the extrusion of thermoplastic starch with cellulose fibrillation, focusing on the shear-induced fibrillation of cellulosic microfibers aimed at obtaining improved mechanical properties on the composites. Since the intial fibers were microsized, the authors did not find much change in the fibers before and after the processing step, and only improved disperison was reported.

Tensile, flexural and impact properties of the extruded-injected samples were determined and are reported in Table 4.

The first important observation is the overall better performance of these composites as compared with those prepared at laboratory scale. The differences are due to the lower defect concentration of the samples prepared at pilot plant scale. The extrusion-injection method produced samples with less holes and better fiber dispersion. Additionally, the extrusion process reduced the diameter of the fibers and increased their aspect ratio, a fact that is well known to lead to composites of improved mechanical properties [29]. Fibrillation has been traditionally produced by alkaline treatments of the technical fibers, leading to the loss of lignin and hemicellulose, and resulting in the individualization/separation of the cellulose fibrils from the technical bundle. This chemical pretreatment is utilized to increase the aspect ratio of the fibers (by much reducing the fiber diameter) as well as increasing the interfacial area for interaction between fibers and polymer, with the final aim of improving the final properties of the composites.

Furthermore, an important increase of the Young modulus occurs by the incorporation of the high modulus fibers irrespectively of the coupling agent selected. This was expected, since the Young modulus of a composite is mainly dependent on the modulus of the matrix and filler. There is, however, a small improvement with the addition of coupling agents.

Table 4 Mechanical properties of composites prepared from PP-Caranday fibers with different coupling agents. Composites were prepared with 50 wt% of fibers and 5 wt% of coupling agent (wt% of coupling agent is calculated with respect to the weight of the fibers).

	MFI (g/10min)	% grafted MA	Young Modulus (GPa)	Tensile Strength (MPa)	Elongation at break (%)	Flexural Modulus (GPa)	Flexural Strength (MPa)	Impact Strength (J/m)
unfilled			1.24 ± 0.09	31.6 ± 0.1	>100%	1.46 ± 0.05	42.2 ± 0.6	---
filled without coupling agent			3.46 ± 0.24	30.3 ± 0.3	2.8 ± 0.3	4.79 ± 0.08	50.7 ± 0.5	42 ± 3
filled with coupling agent								
PP-g-MA 4	20	0.17	3.45 ± 0.20	34.9 ± 0.1	2.6 ± 1.9	4.67 ± 0.08	57.4 ± 0.4	43 ± 4
PP-g-MA 3	20	0.35	3.61 ± 0.36	41.4 ± 0.8	2.7 ± 0.2	4.68 ± 0.06	65.8 ± 0.5	47 ± 4
PP-g-MA 8	20	0.46	3.86 ± 0.42	50.5 ± 0.5	2.7 ± 0.2	4.63 ± 0.03	74.9 ± 0.9	58 ± 4
PP-g-MA 6	100	0.32	3.88 ± 0.32	42.9 ± 0.8	2.3 ± 0.2	4.85 ± 0.10	67.4 ± 1.1	53 ± 4
PP-g-MA 10	100	0.70	3.83 ± 0.49	51.0 ± 1.0	2.8 ± 0.3	4.75 ± 0.05	77.0 ± 1.4	62 ± 4

A progressive improvement is detected for the composites prepared with the PP-g-MAs with MFI=20 as the concentration of maleic anhydride in the polymer increases. The maximum value reached is similar to that value reached using the PP-g-MAs with MFI=100, which indicates that the surface of the fibers is already saturated by the adsorbed coupling agent.

On the other hand, the tensile strength of the material is more sensitive to the good dispersion of the filler and the strength of the interfacial adhesion. Consequently, an important increase of the tensile strength was observed as the concentration of maleic anhydride in the coupling agent increases. This was true for all the coupling agents, reaching a maximum increase of the tensile strength of about 67% at the maximum MA concentration for the agents. As above, the maximum values reached are similar for the agents prepared with two different MFI, indicating that the fiber surfaces are already saturated by the compatibilizer in both cases, an observation that is in agreement with the results obtained from the laboratory scale results.

Regarding the elongation at break, the main difference is caused by the incorporation of the fibers, regardless of the used coupling agent, which has no major effect at the high concentration of filler incorporated.

Flexural properties of these samples show essentially the same characteristics. The modulus is rather unaffected by the type of coupling agent used and the only important change observed is just due to the incorporation of the fibers. Instead, the strength shows a progressive increase as the concentration of MA increases in the coupling agent, with no differences due to the molecular weight for the same percentage of grafted MA.

The addition of a coupling agent to the composite improves the fracture resistance of the material. In unnotched tests (as in the present case), the fracture initiation is reduced by the presence of the agent that increases the interfacial adhesion and reduces the negative effect of the end of the short fibers [30]. According to this, Table 4 shows that the impact strength increases with the addition of coupling agent as compared to the composite formulated without compatibilizer. It also shows that at a fixed concentration of the coupling agent, the impact strength increases with the % of grafted MA, indicating a better coverage of the surface. This is in agreement with the results discussed for the laboratory-scale processing shown in Figure 3 that shows that maximum strength is reached at lower concentration of the compatibilizer when the percentage of grafting is higher. Additionally, in this case, a slightly better impact performance is observed for the low molecular weight (high MFI) PP-g-MA.

A further comparison is valid: the smaller size and higher aspect ratio of the fibers in the extruded-injected composites result in higher values of strength because of the larger interfacial area fiber/polymer. Thus, 12.2 ± 0.6 MPa is the value of the tensile strength of the sample prepared under laboratory conditions and 50.5 ± 0.5 MPa is the value found for the pilot plant extruded-injected composite. Size and aspect ratio are well known to have a large impact on the composite strength [29,31].

3.2.1 Morphology of Tensile Fracture Surfaces

The surfaces of samples tested under tensile loads until breakage were observed using scanning electron microscopy. Figures 7(a) and (b) correspond to the composite prepared with 50 wt% of fibers and no coupling agent, and illustrate the lack of adhesion at the interface. The images show clean surfaces on the fibers that remained in that face of the fractured sample, while the high magnification also shows some holes left by the pulled-out fibers. Debonding of the fibers occurs easily because of the interfacial incompatibility of the vegetable fibers and the PP matrix. This leads to low strength of the composites, in agreement with the already presented laboratory-scale results, which showed reduced strength. The plastic deformation of the polymer matrix around the fibers is clearly observed. These features are in agreement with the reported strength of the material, since the values are close to those reported for the unfilled PP, indicating that the load is mainly supported by the polymer.

On the other hand, in the fracture surfaces of the compatibilized composites, Figures 7(c) and (d), less plastic deformation of the matrix is observed, with well-adhered fibers and low concentration of holes. Strong adhesion occurs when compatibilizers are added, resulting in higher values of debonding stress, and for this reason this mechanism is inhibited in the tensile fracture of the compatibilized composites. The improved adhesion favors the load transfer from the matrix to the fibers and results in a clear increase of the mechanical strength of the composite, as was discussed for the results presented in Table 4.

4 CONCLUSIONS

The preparation and characterization of polypropylene matrix composites reinforced with local fibers, Caranday Palm, were presented. The composition (content of fibers and coupling agent) that optimized the mechanical behavior of these materials was determined by means of a batch processing (laboratory scale). Then a continuous process (extrusion-injection)
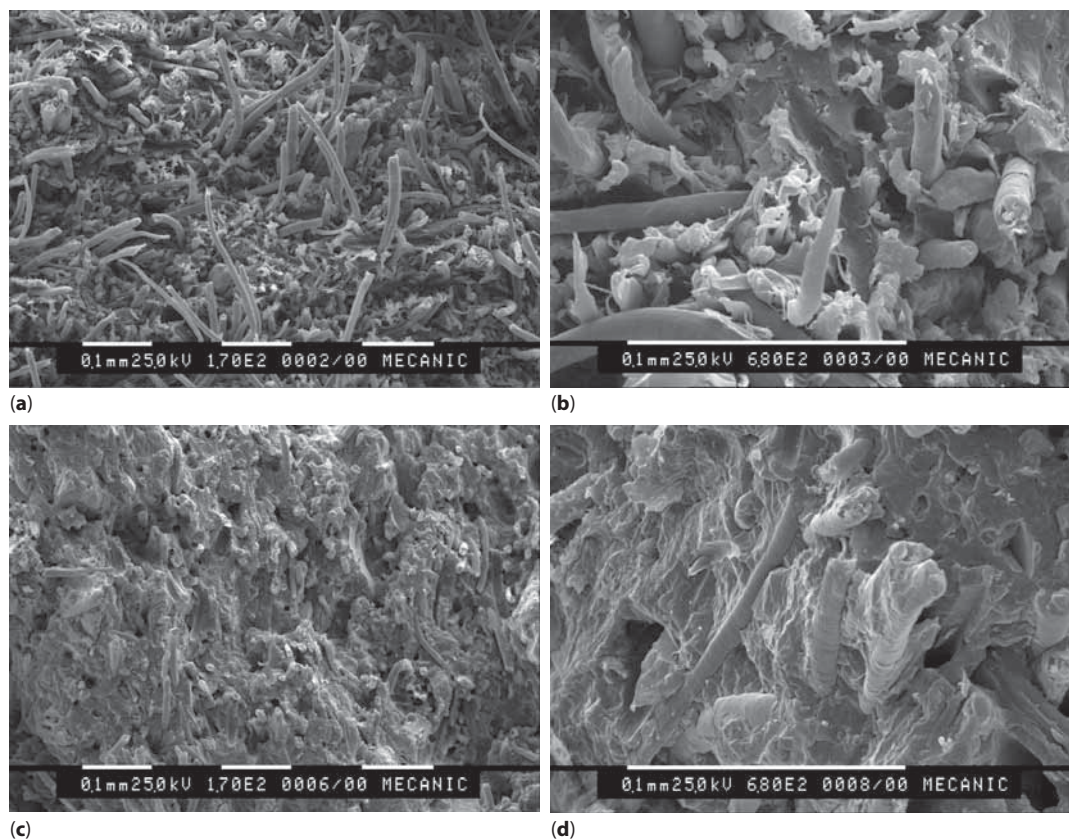
Figure 7 Tensile fracture surfaces of the composites prepared by extrusion-injection (continuous process): (**a**) and (**b**) composite without coupling agent, (**c**) and (**d**) with 5 wt % of PP-g-MA8 (with respect to the fibers' weight).

was used, allowing evaluation of the mechanical properties of the materials.

Although stiffness is not too sensitive to the use of interfacial agents, the incorporation of PP-g-MA allowed obtainment of a better dispersion of the fibers with less aggregation and, thus, achievement of higher values of modulus at high concentrations of fibers. Tensile strength as a function of the fiber content showed an initial decreasing trend, which reverts at concentrations of 50 wt% in the uncompatibilized samples and at 30 wt% when interfacial agents are used. This critical concentration for reinforcement is lowered in the presence of PP-g-MA due to reduced aggregation (lower percolation threshold) and stronger interfacial adhesion.

It was also concluded that as the percentage of grafted MA in the coupling agent increased, lower concentration was necessary to optimize the final properties of the composites. A concentration of MA (8.0 x 10-4 mol/100 g of fibers) saturates the surface of the fiber, and when this concentration is used, the strength reached a maximum value and it was not modified by further addition of greater amounts of

PP-g-MA regardless of its molecular weight or percentage of grafting.

Extrusion-injection processing led to composites with better dispersion of the fibers and had an additional beneficial effect. The process broke the original structure of fibers releasing elementary fibers, having greater reinforcement capacity due to their smaller size and higher aspect ratio. This fibrillation effect was shown to result in better final properties of the composites, even those without compatibilization. The addition of the coupling agent improved even further the mechanical properties of the composites at a fixed fiber content, particularly the strength of the material (tensile, flexural and impact testing). The tensile fracture surfaces of the composites also illustrate that while extensive debonding occurs in the uncomatibilized samples, it is much reduced in the composites prepared with coupling agents.

The results obtained in the laboratory-scale study cannot be directly extrapolated to the study at the pilot plant; however they were very useful at the time of determining the best combination of raw materials to be used.

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