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PIASSAVA FIBER REINFORCED POLYPROPYLENE COMPOSITES.

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Abstract

The mechanical and morphological properties of composites of PP containing different proportions (20, 40 and 60 wt%) of short piassava fiber were prepared and compared with PP composites with $CaCO_3$. Samples were prepared using a K-mixer and the composites were characterized by density, tensile test and the scanning electron microscopy (SEM). The theoretical modeling for Young´s modulus was observed with micromechanical models. The composite with piassava fiber was less dense than composites with filler and in the Young's modulus values showed that the inclusion of fibres reinforced the PP and increased the stiffness. The results showed that the inverse rule of mixtures equation to be an adequate mechanism for predicting the Young`s modulus and micrographs of the composites showed the interaction of the fiber in the matrix even the highest content (60 wt%).

Keywords: Composites, Short fiber, Theoretical modelling, Piassava, Polypropylene.

1 INTRODUCTION

We last few years there has been an increase in products manufactured with plastics in Brazil and in the World. Most of these materials are produced from commodity polymers, especially polyolefins have been used in the preparation of composites with natural and synthetic fiber as filler, aiming at the improvement of their unique properties without adding cost to the materials, for applications in aerospace, marine and automotive industries, as well as in construction [1, 2].

Some studies have compared methods for obtaining composites with satisfactory properties and in other have evaluated the effect of coupling additives (coupling agents) to improve the interaction at the fiber (hydrophilic character) and matrix (hydrophobic character) interface [1, 3]. To investigate the effect of fiber content in the composites and the need to pretreat the fibers, Elzubair *et al.* [3] compare the thermal and mechanical properties in composites with PEAD with piassava fiber with NaOH and silane and without treatment and proved that treatments of piassava fibers by NaOH and a silane coupling agent lead to an overall improvement of the mechanical properties of the composites. This was probably, due to an increase in the fiber–matrix adhesion and as such a higher strength, but the piassava fiber composites were found to be suitable for application as a reinforcement phase in thermoplastic matrix composites and presented good potential even without any surface treatment.

Bledzki *et al.* [4] compared the properties of PP composites containing 40% (wt%) coconut fibers, grain and wood in the absence and presence of 5 wt% with PP-g-MA. Analysis of the mechanical, chemical, thermal and morphological properties of these composites showed the importance of PP-g-Ma with compatibilizer and that the tensile strength of a composite containing wheat fiber was 10% higher than a composite containing wood fiber. For elongation at break, the inclusion of coconut fiber resulted in values 80% higher than for wood, whereas for wheat the increase was only 40% compared to wood fiber. The differences in the properties of these composites, including tensile strength, were largely attributed to variations in the morphological form and the surface properties, size and shapes of the fibres.

Despite the various studies [4, 5] mentioned above, there are few studies with piassava fiber, at a content > 40 wt% of fiber with PP. In this study, we examined the properties of PP composites containing short piassava fiber at high contents (60 wt%) with not pre treatment of the fibers (fibers in nature).

2 MATERIALS AND METHODS

2.1 Materials

Polypropylene (PP) (CP 202XP; MFI 26 g.10 min-^{1} by ASTM D1238) with density of 0.9 g.cm^{-3} and modulus of 498 MPa was supplied in pellet form by Braskem S.A. (RS, Brazil).
The piassava fibers from Bahia-Brazil (*Attalea Funifera*) were freshly ground in a model TE-625 mobile and stationary slicer (Tecnal, SP, Brazil) and subsequently passed through a sieve with set range of 8 mesh. Some of their physical and chemical properties are shown in Table 1 [6].

Table 1 – Physical and chemical properties of the piassava fibers

	Cellulose	Hemicellulose	Lignin	Others	Density	Module
Fiber piassava	%	%	%	%	g.cm^3	MPa
	39.3	18.3	32.4	60.7	1.06	5600

Calcium carbonate ($CaCO_3$) with density of 2.65 g.cm^{-3} with reference OB1260 (Minérios Ouro Branco, SP, Brazil) and the coupling agent PP with maleic anhydride (PP-g-MA) that reference Licocene PP MA 7452 TP (Clariant S/A, SP, Brazil) were used. Licolub H12 (Clariant S/A, SP, Brazil) and calcium stearate (Chemson, SP, Brazil) were used as external and internal process lubricants, respectively, and Hostanox (Clariant S/A, SP, Brazil) was used as an thermal antioxidant.

2.2.Processing of composites

The composites of PP with piassava fibers (in nature) either composites with $CaCO_3$, as show in Table 2, were processed using a K-mixer (model MH-1000 CT by MH Equipamentos, SP, Brazil) fitted with a probe temperature control processing parameters and a system for removing moisture from the materials during processing.

Table 2 – Fractional weight of components used to prepare the PP composites

Components	Proportion of components used in sample preparation		
	Fiber content (wt%)	PP (wt%)	Additives* (wt %)
PPadded	0.0	94.68	0,2% Calcium stearate 0,12% Antioxidant Hostanox 2% Licoclub H12 3% Licocene PP MA 7452
Fiber Piassava or $CaCO_3$	20.0	74.68	
	40.0	54.68	
	60.0	34.68	

* All composites contained the same percentage of additives.

After preparation, the composites, in the form of solid mass, were ground in a mill (model P2005G, Primotécnica, SP, Brazil). Subsequently, the specimens were injected to prepare the using an injector (model PIC-BOY 22, Petersen, SP, Brazil).

2.3. Characterization

The density of the PP and the composites (samples form) was determined according to ASTM-D-792 with ethyl alcohol (density 0.7951 g.cm^{-3}) at 25 °C with five determinations.

The tensile strength was determined in a universal mechanical testing machine (model 5569, Instron, PR, Brazil), according to ASTM D638-10-IV and with ten determinations.
The surface of the composites were investigated by microscopic observation JEOL model JSM 6010 LA, in inject samples freeze-fractured after 10 minutes in N_2, in the uncoated sample, SEI mode, at 5 mm away and 1kV.

2.4. Micromechanical models

The elastic properties of materials can be experimentally determined or derived from a variety of mathematical models. The advantage of a comprehensive mathematical model is it reduces costly and time consuming experiments to facilitate the choice of matrix and fiber to be used. Another important aspect is the choice of the best combination of constituent materials to satisfy the properties of the material and its application. Micromechanical composite models are derived based on the properties of the individual components of the composite and their arrangement. Other factors should be considered in choosing the best model to be used as the fiber orientation and the dimensions of the reinforcing phase [7].
In this article two models were compared the inverse rule of mixtures and Halpin-Tsai equations. The inverse rule of mixtures calculates the elastic modulus of the composite in two directions (E_2) and it is determined by assuming that the applied transverse stress is equal in both, the fiber and the matrix [7].

$$E_2 = \frac{Ef\,Em}{Vm\,Ef + Vf\,Em} \qquad \text{(Eq. 1)}$$

where: E_f, E_m, V_f and V_m, are the modulus and volume fractions of the fiber and matrix materials respectively.
The semi empirical equations developed by Halpin-Tsai are widely used for predicting the elastic properties (E_1) and the following form equation is used to predict the tensile modulus [7]:

$$E_1 = Em\left(\frac{1+\xi\eta Vf}{1-\eta Vf}\right) \quad \text{(Eq. 2)} \qquad \eta = \frac{\left(\frac{Ef}{Em}\right)-1}{\left(\frac{Ef}{Em}\right)+\xi} \quad \text{(Eq. 3)}$$

where: ξ, is a shape fitting parameter to fit the Halpin–Tsai equation to the experimental data. The significance of the parameter ξ is that it takes into consideration the packing arrangement and the geometry of the reinforcing fibers, then ξ is given by the following equation:

$$\xi = 2\left(\frac{L}{T}\right) \text{ or } \qquad \xi = 2\left(\frac{L}{D}\right) \qquad \text{(Eq. 4)}$$

where L refers to the length of a fiber and T or D is the thickness or diameter of the fiber.

3 RESULTS AND DISCUSSION

3.1. Density of composites

In Fig. 1 it is possible to observe the aaverage values of the experimental data densities and the theoretical density of the composites. It is noteworthy that the density of the composites obtained with piassava fiber have lower density to $CaCO_3$ composites with fibers, for which 60 wt% is 25% denser than the composite with piassava fiber. The lower density of plant fiber composites can be an advantage in applications requiring good performance and low mass, such as in the automotive and aerospace industry. The calculation of theoretical density was effective for contents up to 40 wt% but inaccurate for high fiber content of 60 wt%, most likely due to changes in the crystallinity of the composite, because the fiber acts as a nucleating agent. Almeida *et al.* [8] obtained similar results for the production of hybrid composites in blankets (30-70%) with curaua fibers and glass fibers, seeking to maintain the properties of composites with glass fiber alone, with the advantages of lower density and a higher ecological composites appeal only plant fibers.

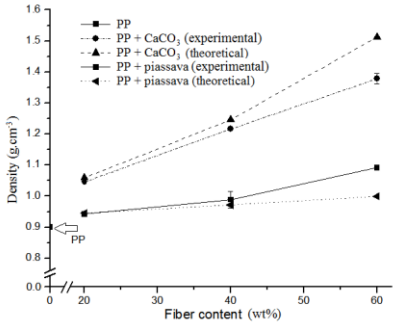

Fig. 1 – Determination of theoretical and experimental data density for PP and PP composites according to piassava fiber and $CaCO_3$ filler. The points are the mean ±SD of five determinations.

3.2.Tensile tests of composites

Fig. 2 shows there was an increase in Young's modulus (an indication of stiffness) with increasing natural fiber content. Compared with PP, all composites had a greater Young´s modulus at each of the fiber contents, although this was most marked for 60% (wt%) where there was an increase of 90% greater compared to PP. The observed increase in the Young`s modulus can be attributed to many things, and among them, we highlight the good surface adhesion, as can be seen in section 3.4. All composites with fibers had similar values of Young´s modulus when compared with composites containing $CaCO_3$. Pimenta *et al.* [5], who studied composites with 20% (wt%) sisal fiber subjected to different treatments, reported values for Young´s modulus 60-80% higher than for PP, probably because of changes in the morphology of the fibers caused by the various pre treatments of these.

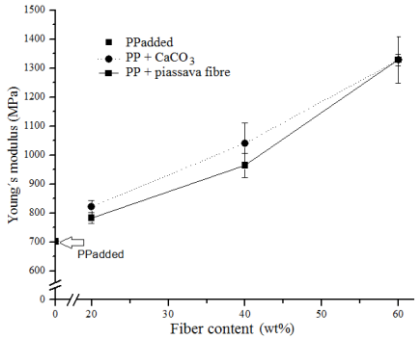

Fig. 2 – Young's modulus for PP containing additive and PP composites according to piassava fiber and $CaCO_3$ filler. The points are the mean ±SD of ten determinations.

3.3. Micromechanical models

Fig. 3 shows the relationship between the experimental data values for Young's modulus of the composite with PP and piassava fibers and the theoretical values obtained from the modeling equations of the inverse rule of mixtures and Halpin-Tsai equations (equations 1 2, 3 and 4).

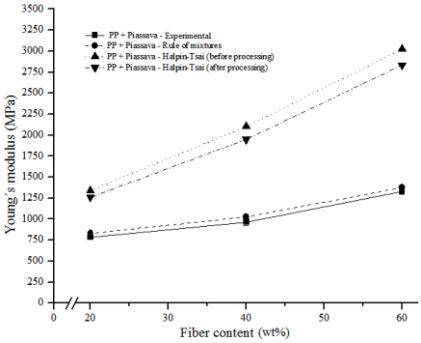

Fig. 3 – Determination of modulus for rule of mixtures and Halpin-Tsai equations for composites with piassava fiber.

The results observed in Fig. 3, show that the model the inverse rule of mixtures proved to be very efficient in predicting for Young's modulus and that dispersion of short piassava fibers, even in high concentrations, are randomly dispersed. This is probably due to the randomness of sample preparation, which consisted in using mixer with internal camera mixing process, allowing the direct feeding of the matrix, fibers and additives in a single stage. The good dispersion of the additives, especially the processing additives (Licolub H12 and calcium stearate) contribute to good dispersion and homogeneity of the mixture and hence to good distribution of stresses throughout the matrix/fiber. Facca *et al.* [7] evaluated several models for Young's

modulus of the composites with wood, hemp and rice in different particle size fibers and considered the model of Halpin-Tsai one of the most approximate to the experimental data and emphasize that many factors influence the fact that a model is best applied in a certain condition, such as type of fiber or particle reinforcement, fiber alignment and orientation, shape and size of these fibers, as well as the fiber content and participation of the matrix in the transmission efforts, among other features.

3.4. Scanning electron microscopy (SEM) of composites

Fig. 4 shows the photomicrographs of composite with piassava fibers in the levels 20, 40 and 60 wt%. In Fig. 4 for composites with 20 and 40 wt% of fiber piassava it can´t be observed absence of fibers on the surface, with the occurrence of pull-out effect on the surface, indicating presence of fibers on the surface of the composite and a good interaction between the fiber and the matrix, but with the transfer of forces in the composite are more marked by the matrix phase. In Fig. 4 for 60 wt% shows the presence of fixed fibers of the composite surface with a larger fiber matrix interaction, which confirms the best result for Young's Modulus (Fig. 2) in composites with high fiber content of 60 wt% fiber and in this case the transfer of forces in the composite was more pronounced for the reinforcing phase. Another highlight is the maintenance of febrile geometry of the building, even after the processing of these. Bledzki *et al.* [4] in their work found that composites with 40 wt% of fibers without treatment presented some effect of pull out, like similar images shown in this work. Elzubair *et al.* [3] observed that the fibers display also a superficial array of parenquimatic cells with spinulose bodies known as silica bodies or tylosis. Another highlight is that the piassava fibers have similar values of cellulose and lignin (Table 1) and according Morandim *et. al* [9] the higher the cellulose content in fiber, present in a composite, the greater the probability of good mechanical properties because cellulose is responsible for increasing the tensile strength of the fibers and that despite high levels of lignin generally reduce adhesion at the interface, the incorporation of additives coupling (PP-g-MA) help this adhesion and improve the mechanical properties, because the compatibilizer has good interaction with the lignin, which is the less polar component of lignocelluloses fibers.

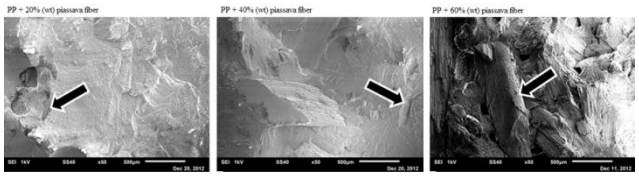

Fig. 4 - Photomicrographs of PP composites with 20, 40, 60 wt% piassava fibers.

4 CONCLUSIONS

The results demonstrate the feasibility of using piassava fibers to prepare environmentally friendly composites. The additives used in the composites (processing and compatibilizer), especially PP-g-MA were adequate for preparation of composites with hydrophobic fibers. The results for Young's modulus suggest that even at high concentrations (40 and 60 wt%) of piassava fiber can be used to increase stiffness values. The inverse rule of mixtures equation was an adequate mechanism for predicting the Young`s modulus and it was possible to verify in this work a good adhesion between the hydrophilic fibers and hydrophobic polymer matrix does not prevent the incorporation of high levels (60 wt%) of natural vegetable fibers in PP composites were obtained surfaces with satisfactory interaction at the interface in the high levels of fibers with the matrix. These results also show that the method of processing was efficient and economically viable once there was no need to alter the superficial fibers (pretreat, washing or pre-drying) and this lack of intermediate steps reduced the amount of energy needed and facilitated preparation of the composites with short fiber.

Acknowledgements
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