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Agro-Based Biocomposites for Industrial Applications

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Leaf fibers are fibers that run lengthwise through the leaves of most monocotyledonous plants such as pineapple, banana, etc. Pineapple (Ananas comosus) and Banana (Musa indica) are emerging fiber having a very large potential to be used for composite materials. Over 150,000 ha of pineapple and over 100,000 ha of banana plantations are available in Brazil for the fruit production and enormous amount of agricultural waste is produced. This residual waste represents one of the single largest sources of cellulose fibers available at almost no cost. The potential consumers for this fiber are pulp and paper, chemical feedstock, textiles and composites for the automotive, furniture and civil construction industry.

Keywords Composites; nanocellulose; natural fibers; PALF; pineapple

Introduction

Environmental and economical concerns are stimulating research in the development of new materials for building construction, furniture, packaging and automotive industries. Particularly, there are a lot of attractiveness for new materials in which a good part is based on natural renewable resources, which prevent further stresses on the environment by depleting dwindling wood resources from forests or increasing the demand over fossil finite resources. Examples of such raw material sources are annual growth native crops/plants/fibers, which are abundantly available in tropical regions. These plants/fibers (like jute and sisal) have been used for hundreds of years for many applications such as ropes, beds, bags, etc.

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If new uses of fast growing, native plants can be developed for high value, non-timber based materials, there is a tremendous potential of creating jobs in the rural sector. These renewable, non-timber based materials could reduce the use of traditional materials such as wood, minerals and plastics for some applications.

The materials developed by the combination of native fibers with different plastics, such as Polyvinylchloride (PVC), Polypropylene (PP), and Polyethylene (PE) have wide application possibilities, having a potential of developing new industries in the near future using local crops, wastes, labor and helping to reduce the demand for tropical hardwoods (housing, furniture, pellets, etc.), and plastics.

The utilization of agricultural wastes from two most popular fruits around the world, banana and pineapple represents the biggest source of biomass for natural fiber production. The pseudo-stems of the banana plants and the leaves from the pineapple plants after the fruits are harvested represents a problem for many farmers and their utilizations will bring a new source of income for both production chains.

These fibers, which are also referred to as 'hard fibers', are the most commonly employed reinforcing agents in plastics. Natural staple fibers are found worldwide around the planet under different forms of vegetation. Some staple fibers occur naturally in the wild state and/or are cultivated as agricultural activity. The natural staple fibers can also be called as cellulosic staple fibers, since the cellulose is the main chemical component; or lignocellulosic staple fibers. The field of application of natural staple fibers is sufficiently ample, since classic applications in the field of textile industry, as reinforcement in thermoplastic polymeric matrices and thermo-setting and more recently as adsorbent material for the removal of toxic heavy metals from wastewater streams and others applications. In this paper, the pineapple and banana fibers will be considered.

After Thailand and Philippines, Brazil is the third largest producer of pineapple, contributing to about 7% of the total world fiber production, northeast region being the major contributor. There are two types of pineapple farming in the country. In the first, the plants are cut after the first crop leaving the stems for the next one, while having the fresh crop by the side. This brings down the investment cost with lower fiber yield. In the second method, only fresh plantations are grown. The fiber is mostly extracted using machine-decorticators [1]. The total pineapple area planted in Brazil is about 150,000 hectares, where is estimated a production of 1.5–2.0 tons of dry fiber/ha, depending on the crop variety and agricultural practices. This biomass has been used mainly for animal feeding. The main states that cultivate the fruits are: Minas Gerais, São Paulo, Paraíba, Rio de Janeiro, Bahia and Pará.

After India and Ecuador, Brazil is the third largest producer of banana. The country has studied this fiber extensively from various standpoints [1]. For the banana, the total cultivated area is about 65 millions hectares, with an average production of 1,500 kg/ha. But only 2% is exported, with the rest used for internal consumption. The main producer states are SP, with 17%, Bahia, 12%, Parana, 10% and Santa Catarina, 9%. These values represent an immense potential for biomass and natural fibers production.

The main challenge to use these agricultural residues is to develop a technology for production of bleached softwood from the leaves of the pineapple. Approximately, 95% of the pulp produced in the world today comes from wood fibers, and the major technological developments are dedicated to these fibers. There are some low level technologies available to use agricultural waste such as rice, wheat

and rye straw, sugar cane bagasse, bamboo, abaca, banana, sisal etc. Recently many works have been done to extract the nanocellulose for composite applications [2]. Nevertheless, little has been done about the utilization of long fiber derived from the leaves of pineapple.

Literature Review

Environmental and economical concerns are stimulating research in the development of new materials for construction, furniture, packaging and automotive industries. There is a tremendous interest for pharmaceutical industry as well as the material's companies. In applications such as ropes, new materials such as nylon have replaced locally grown fibers like sisal and jute. The advantages of these plants are they are fast-growing and renewable and sometimes is also a source of food supply for animals and even humans.

There is a significant deficit of bleached softwood in the Brazilian market. Brazil has only a producer of this type of fiber, with a daily capacity of 200 tons per day. Much of the domestic demand for softwood bleached is supplied by imports from Argentina, Chile and Canada. Bleached softwood is required to produce white papers and packaging that require high mechanical strength [3].

The limited production of bleached softwood in Brazil is due to the low availability of softwood (pine, bamboo, etc.) and its high production cost compared to, for example, bleached hardwood Eucalyptus pulp. The Brazilian business community has focused on the production of bleached hardwood eucalyptus, because the cost of production is at least the half of that of long fibers. The causes of the lower cost of short fibers are derived from the increased productivity of forest plantations over most of the long fibers and the highest yield of converting wood into pulp. Moreover, the international market is hungry for hardwood pulp, which guarantees good prices for these fibers, compatible with those of long fibers.

Pineapple and banana fibers have a higher cellulose content than other fruit plants, which is probably related to the relatively higher weight of the fruit they support and the fact that they are less perishable. Other fiber sources such as corn stover, bagasse, wheat, rice and barley straw, and sorghum stalks all contain nearly the same amount of cellulose. Fibers in these crops support relatively smaller weights in comparison with bananas and pineapples.

The cultivation of pineapple generates post-harvest residues with the significant amount of fibers that are usually wasted and in many cases cause inconvenience to farmers to dispose them. Fibers derived from pineapple leaves are long and slender, with excellent characteristics for use in pulping processes. It is estimated that the production of pineapple fiber per hectare per annum reaches figures of around 15–20 tons per hectare. This productivity is similar to that achieved by softwood at its mature age. In addition, the fibers of the pineapple are from agricultural residues that would be discarded, since the main objective of the crop is the production of food articles (juice, pulp, jelly, etc.). Other by products are been studied mainly the enzyme bromelin with its many applications. Therefore, these fibers are very low cost, around US\$ 10 per ton in the field, compared to the softwood costs of about US\$ 80 per ton in the field [3]. In Brazil, pineapple, one of the contributors for agricultural economic activity of the country, has the potential to produce about 19,600 tons of fibers from about 1011 leaves produced on 58,794 ha, with collection and extraction of fibers done in the rural sector, thus providing jobs and improving

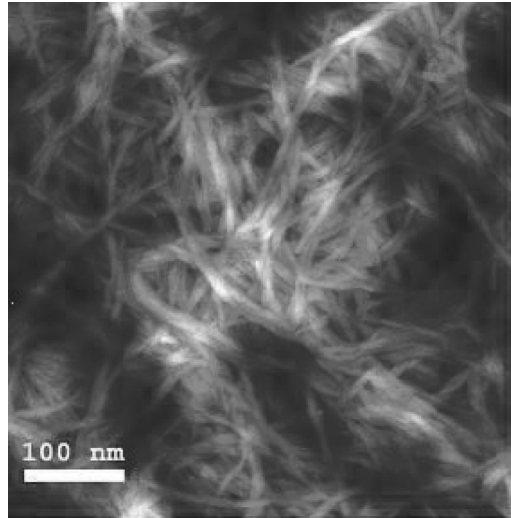


Figure 1. AFM image of cellulose nanofibrils extracted from pineapple leaf fibers by steam explosion process.

the living conditions of the rural population [4]. Pineapple leaf fibers can be utilized for the production of cellulose nanofibrils. The nanocellulose embedded in the pineapple leaf was successfully extracted using high pressure steaming coupled with acid treatment. Figure 1 shows the AFM image of cross-linked fine cellulose nanofibrils extracted from pineapple leaf fibers.

Recently green composites were fabricated using pineapple leaf fiber and soy based plastic [5]. In another interesting study involving bio composites, the effect



Figure 2. Composite spare-tire carrier for Mercedes-Benz A-class mini car made from banana fiber reinforced composites.

Table 1. Chemical composition of a banana rachis

Items	Percent (Dry Mass)
Holocellulose	79.9
Cellulose	64.4
Lignin	13.3
Ash	2.1
Extractives	4.7

of alkali treatment on the thermal properties of Indian grass fiber reinforced soy protein green composites was studied by the same group [6]. Pineapple has also found their way as a potential reinforcement in natural rubber [7] and jute fiber [8].

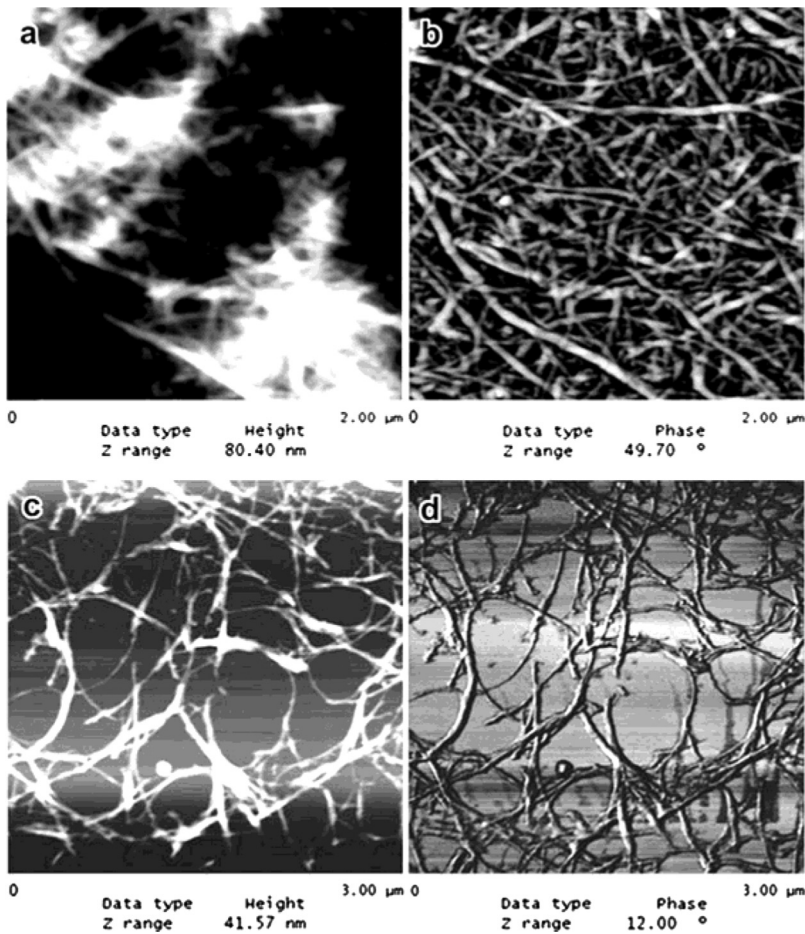


Figure 3. AFM micrographs of cellulose microfibrils and microcrystals from banana rachis: (a, b) peroxide/homogenization treatment; (c, d) peroxide/organosolv treatment (a, c: topographic images; b, d: phase images).

Researchers have chosen pineapple leaf fibers for the preparation of hybrid composites. The composite systems chosen were sisal/glass and pineapple/glass fiber reinforced polyester composites. Composites were prepared by varying the concentration of glass fiber and by subjecting the bio-fibers to different chemical treatments. The authors observed that water uptake of hybrid composites was less than that of unhybridized composites [9].

The banana plants generate the rachis, which is the part of the plant where the fruits are linked to the pseudo stem and the fiber leaves, which comes from the pseudo stem. Both materials can be used in industrial applications. DaimlerChrysler's composite spare-tyre carrier on the Mercedes-Benz A-Class mini car won this category. In this component, banana fiber replaced glass as reinforcement for the polypropylene matrix (Fig. 2). This is said to be the first large-scale use of a natural-fiber-based composite for the exterior of an automobile.

The rachis has high cellulose content, and can be used for handmade paper, cardboard boxes, biogas, organic compost and the most valuable one, in textile fibers. The pseudo stem is also the excellent source of cellulose fibers from the banana plants. The pseudo stem is a bundle of huge leaf stems wrapped around a soft central corm. Initially, the leaves develop in a circular pattern around a central growing region and emerge as a shoot from the underground corm. Eventually, these leaves mature as overlapping leaf sheaths, made up of the leaf base, and the petiole that supports the blade. The banana fibers are produced from these leaf sheaths extracted mechanically in most cases, since the pseudo stem is removed after the banana fruit harvesting, which allows the sprout to grow. From these pseudo stems is possible to extract several types of fibers, each one with particular characteristics. The pseudo stem is constituted of three layers: the external, where the mechanical bundles are found. These mechanical bundles are unique in such a sense that they are responsible to sustain the plant, sometimes up to four meters height. These fibers are among the longest of the hard fiber's group after abaca. The banana fibers were extracted from the leaves, but the rachis is also a source of pulp material, whose

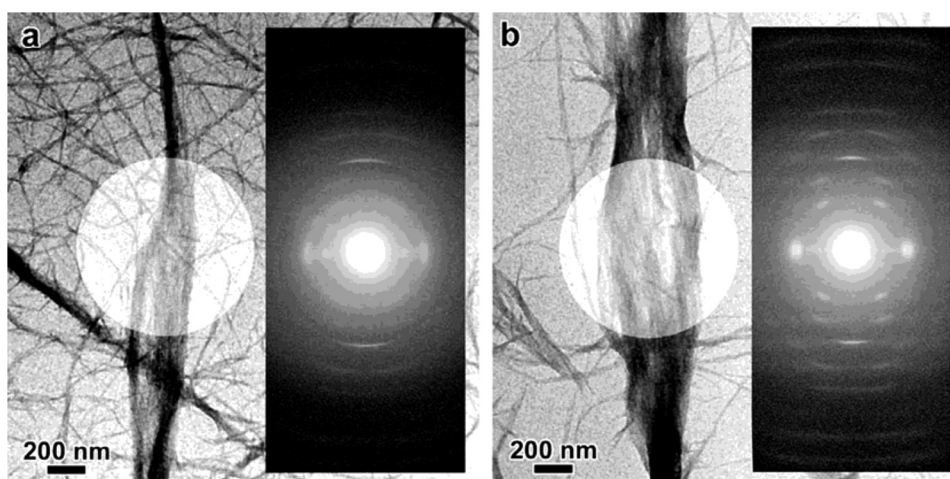


Figure 4. TEM images of unstained bundles of cellulose microfibrils prepared using alkaline treatments KOH-5 (a) and KOH-18 (b). Inset: corresponding cellulose I and cellulose II fiber electron.

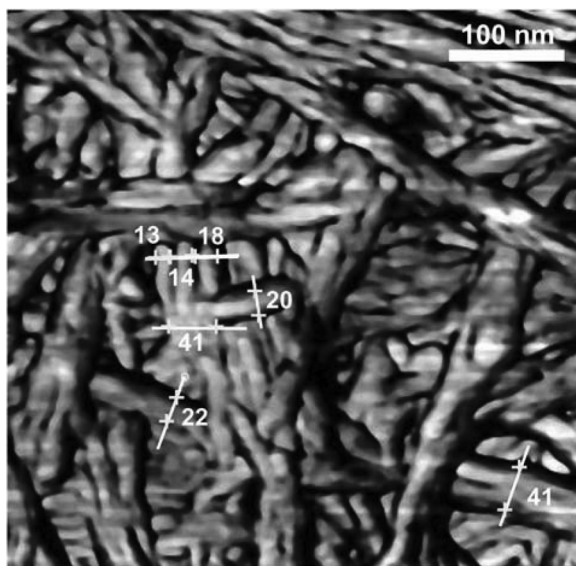


Figure 5. TEM images of unstained bundles of cellulose microfibrils prepared using alkaline treatments KOH-5 (a) and KOH-18 (b). Inset: corresponding cellulose I and cellulose II fiber electron.

composition is shown in Table 1. Researchers found banana rachis as a good source for cellulose microfibrils. Zuluaga *et al.* [10] extracted microfibrils of cellulose from banana rachis using chemical and mechanical treatments. The peroxide alkaline bleaching followed by mechanical homogenization allowed preparing suspensions of more or less individualized long microfibrils as shown in Figure 3. Alkaline treatments for isolation of cellulose microfibrils from vascular bundles of banana rachis were studied by Zuluaga *et al.* [11] (Fig. 4). Researchers also proved pseudo stem as an excellent source for cellulose nanofibrils. Cherian *et al.* [12] extracted microfibrils of cellulose from banana pseudo stem using high pressure steam coupled with acid treatment. The AFM morphology of the separated fibers is shown in Figure 5. The separated nanofibrils were found to have an average length and diameter between 200–250 nm and 4–5 nm, respectively.

Results and Discussion

The first activity to use the natural fibers in industrial applications is to determine its chemical composition, which is shown in Table 2. In this table is shown the chemical composition for both fibers used in this paper.

The pineapple fibers were used to make non-woven mats using polypropylene as the matrix and the banana fibers were tested as the reinforcement agent in composites using polypropylene as the matrix using the extrusion process. This process has been applied by many researchers and the natural fibers properties are found to be the most important parameter [13].

The fiber components were mixed on a dry weight basis and mixed by hand prior to the picker, which cuts the fibers to 5 cm in length, also giving more mixing. After the picker, the mixture goes to the cards, where more mixing can be obtained, and

Table 2. Chemical composition of some natural fibers

Items	Pineapple	Banana
Extractives Hot Water	5.5	6.4
Lignin Klason (%)	10.5	32.8
Hemicellulose (%)	7.1	12.1
Cellulose (%)	73.4	44.2
Ashes (%)	2.0	2.2

finally it goes to the needle machine. The mats were cut and pressed at different temperature, densities, pressure and time of heating and cooling. The heating time was 30 to 180 seconds. The pressure varies from 3.25 MPa up to 9.8 MPa. The pressure time in the cold press was 20–30 seconds. The samples were taken from the boards using a pressing knife. The parameters evaluated were EMC (Equilibrium Moisture Content), bending (ASTM D790M-93), tension (ASTM D638M-89) and dimensional stability.

The moisture content (MC) in the air at uncontrolled conditions, after 10 days of pressing was found to be very low for all the treatments, and therefore, it will not be considered as a variable. The results obtained varied from 1.6 to 2.8%, showing that there was no significant variation among the treatments, and according to the objectives of obtaining a stable composite. When the natural fiber content was 60% with the blend of 40% polypropylene, a strong increase in tensile strength was observed, much more than the tensile modules (Table 3). The thickness was not important for the levels studied (1.8–3.0 mm), showing, that it is closely related to basic weight, but it is not so sensible to small variations. Above 3.0 and below 1.5 mm, the properties have a significant reduction. The pressure at the values tested, varying from 3.25 MPa up to 9.8 MPa, at the forming press (cool) was not significantly different. The heating pressure was used only to compress the mats and to carry the heat throughout, with values varying from 0.82 to 3.67 kg/cm³.

Composites were also compounded in a twin-screw extruder, model ZSK-25, Coperion, L/D ratio of 25, at 300 rpm and the temperature profile of 190, 190, 180, 180 and 190°C. This equipment was used to compound the natural fibers with the resins and subsequent formation of pellets. The feeding process was one in which both components are introduced at the same time to avoid overheating. The ratio used was 50/50 PALF/Polypropylene. The extruded pellets were dried at 105°C for 4 hours to eliminate residual humidity from the fiber before the injection moulding of the samples.

Table 3. PALF fibers in non-woven mats

Ratio, PALF/PP (%)	Tension strength, MPa	Tension modulus, GPa	Flexural strength, MPa	Flexural modulus, GPa
80/20	18.98	1.16	12.67	1.12
70/30	20.13	1.42	22.73	2.83
60/40	48.73	3.12	21.77	2.23
50/50	42.17	3.42	31.01	2.32

Table 4. Tensile properties

Polypropylene matrix	PALF/PP	PP
Tensile strength (Mpa)	25	35
±SD	.83	
Young modulus (Gpa)	2.8	1.1
±SD	.09	

The sample specimens were moulded at 190°C in an automatic injection moulding machine, Sandretto, 65 Micros. Prior to mechanical testing, the samples were conditioned at 40 (5)% relative humidity, 25 (2)C for 40 hours. The mechanical properties were evaluated according to ASTM standards. Notched Izod Impact tests were made using a CEAST Resil 25 pendulum type impact machine according to ASTM Standard D-256. At least ten specimens of every composite were tested to obtain the impact strength. The other testing properties were performed following ASTM standards: tensile testing (ASTM D638); flexural testing (ASTM D790); and impact testing (ASTM D256).

The natural fibers are a source of environmental materials, but high variation in properties can be a problem for industrial applications [14]. Table 4 shows the tensile strength and tensile moduli for the injection molded samples in PP matrix. The flexural strength was found to be increased when compared to the net resin, showing a significant improvement due to the addition of the PALF fibers into the composites (Table 5). For the property unnotched impact resistance, it was observed a large difference between the polypropylene and the PALF. The notched resistance was found to be improved by the addition of the PALF, as can be seen at Table 6.

Table 5. Flexural properties

Polypropylene matrix	PALF/PP	PP
Flexural strength (Mpa)	34	28
±SD	.44	
Young mod (Gpa)	1.9	.95
±SD	.23	

Table 6. Impact resistance

Polypropylene matrix	PALF/PP	PP
Impact Resistance	51	21
Notched	1.44	0.88
Impact Resistance	140	538
Unnotched	2.28	1.7

Conclusions

By the obtained results, both residues can represent interesting sources of the raw material for industrial applications, mainly for production of composite materials and special papers, chemical feedstock's (bromelin enzyme) and fabrics. The development of new value added products and opening of new market niches are expected to have a positive impact in the pineapple and banana production chain. The beneficiaries will be the small producers that will end up with a commodity that nowadays has an almost zero value.

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