Journal of
**Engineering
Research**

MECHANICAL PROPERTIES OF RAMIE FIBERS AND THEIR POLYMER COMPOSITES: A REVIEW

Frederico Muylaert Margem
``Universidade Estadual do Norte Fluminense Darcy Ribeiro`` - UENF
Campos dos Goytacazes, RJ
http://lattes.cnpq.br/8712749538747455

Noan Tonini Simonassi
``Universidade Estadual do Norte Fluminense Darcy Ribeiro`` - UENF
Campos dos Goytacazes, RJ
http://lattes.cnpq.br/0091760384705916

Felipe Perissé Duarte Lopes
``Universidade Estadual do Norte Fluminense Darcy Ribeiro`` - UENF
Campos dos Goytacazes, RJ
http://lattes.cnpq.br/1944239448019813

Sérgio Neves Monteiro
``Instituto Militar de Engenharia`` - IME
Rio de Janeiro, RJ
http://lattes.cnpq.br/2962183322412029

Abstract: Natural fibers are attracting interest in engineering sectors due to specific advantages such as low density and cost, as well as renewability, biodegradability, recycling and CO2 neutrality. The objective of this work is to carry out a review on the composition processes of materials based on polymeric resins and lignocellulosic ramie fibers. This review must be able to provide a comprehensive view of the mechanical properties and applications for this composite, evaluating performance at limit levels of inclusion of lignocellulosic material. Finally, evaluations of this material over the last five years will also be visited in order to demonstrate the state of the art in the creation of this composite.

Keywords: natural fibers, polymer resin, polymer composite, ramie fibers.

INTRODUCTION

Natural fibers have been used by humanity for centuries in various applications in order to meet the basic requirement of shelter, food and clothing. In most countries, people have explored the possibilities of using natural fibers for a wide range of domestic and industrial applications (Chauam et al., 2013).

Scientists' attention has been attracted due to the advantages that these fibers offer when compared to more conventional reinforcement materials, and the development of natural fiber composites has been a topic of interest in recent years (Braga et al., 2018). In addition to being easily available, these natural fibers have low cost, low density and high specific properties, comparable to those of other reinforcing fibers, and are also biodegradable and non-abrasive.

There are some limitations, such as incompatibility with the polymer matrix, the tendency to form aggregates during processing, low resistance to moisture, which reduce the potential for using natural fibers as reinforcement in polymers (Simonassi et al., 2017).

Recently, automobile manufacturers have become interested in incorporating natural fiber composites into the interior and exterior parts of vehicles, aiming both to reduce the vehicle's total weight, thus increasing fuel efficiency, and to increase the sustainability of its manufacturing process. Many companies, such as Mercedes Benz, Toyota and Daimler Chrysler already use these composites in their automobiles and aim to expand this use (Westman et al. 2010).

Natural fibers of plant origin mainly consist of: cellulose, hemicellulose, pectin and lignin. The individual percentage of these components varies according to the different types of fibers. This variation can also be affected by growing and harvesting conditions. Cellulose is a linear polysaccharide of high molecular mass, 10 to 25 nm in diameter, indeterminate length and 30 to 100 cellulose molecules that are joined in parallel by hydrogen bonds, (Kraus et al., 2016) in addition to being the main structural constituent, being responsible for the stability and resistance of the fibers, and being distributed in all plants, from developed trees to primitive organisms. Hemicellulose is a completely amorphous polysaccharide, with a lower molecular weight compared to cellulose. The amorphous nature of hemicellulose results in it being partially soluble in water and alkaline solutions. Pectin, whose function is to hold the fiber together, is a polysaccharide just like cellulose and hemicellulose. Lignin is an amorphous polymer, but unlike hemicellulose, lignin is mainly composed of aromatics and has little effect on water absorption (Simonassi et al., 2017). In fiber, cellulose is associated with other substances, namely structural and envelopes, such as lignin and hemicelluloses, respectively, as can be seen in Figure 2, both in considerable quantities (Dence and

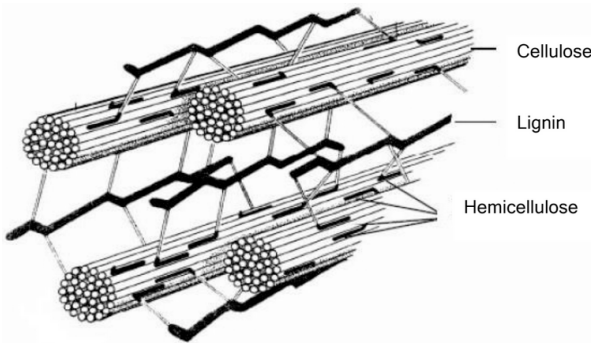Reeve, 1996). These substances are strongly associated and covalently linked (Girio et al., 2010).

Figure 1: Representation of the fiber of lignocellulosic materials and their components: cellulose, hemicellulose and lignin (Lynd *et al.,* 2012).

The hemicellulose molecules are almost parallel to the cellulose fibrils, while the lignin is presented in a random form, providing greater stability to the wall. Internally, the fibrils of the cellulose fraction are arranged like spirals, in order to provide strength and flexibility to the material. The third and final main fraction, hemicellulose, acts as a chemical link between cellulose and lignin. These characteristics result in flexible materials, but highly resistant to chemical species (Castro and Pereira Jr, 2010).

Cellulose, located in the walls of the fibers, has a gross molecular formula $(C_6H_{10}O_5)_n$, where n represents the number of glucose molecules (mers) that make up the chain and can have a value of up to 15,000 units. The value of n has a direct relationship with the degree of cellulose polymerization and this in turn with its physical resistance (D'Almeida, 1981).

The structure of the plant cell wall is composed of a microfibrillar reticulum included in a matrix of molecules joined together, stabilized by intramolecular hydrogen bonds (bonds between glucose units of the same molecule) and intermolecular

(between glucose units of adjacent molecules) and Van der Waals forming highly insoluble structures (Arantes and Saddler, 2011), as shown in Figure 2.
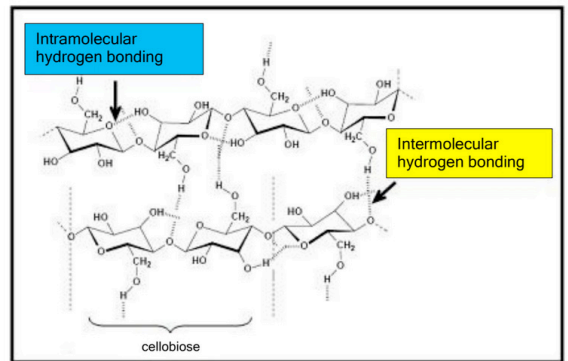

Figure 2: Chemical structure of cellulose (Morais, 2015).

Intermolecular bonds are responsible for rigidity and intra-molecular bonds are responsible for the formation of fibrils, highly ordered structures, which combine to form cellulose fibers.

Table 1 shows the proportion of chemical composition of some plant fibers. The amount of cellulose depends on the processing method and low levels of lignin indicate high malleability and roughness of the fiber (Gu et al., 2014).

Fibers	Cellulose (%)	Hemicellulose (%)	Pectin (%)	Lignin (%)
Cotton	91,80	6,30	-	-
Jute	71,50	13,30	0,20	13,10
Linen	71,20	18,50	2,00	2,20
Sisal	73,10	13,30	0,90	11,00
Ramis	68,60	13,10	1,90	0,60
Coconut	36-43	0,15-0,25	3-4	41-45

Table 1: Chemical composition of some plant fibers (Adapted from Gu et al., 2014).

According to Dereje and collaborators (2017), the tensile strength and elastic modulus of the fibers are directly proportional to the cellulose content and inversely proportional to the angle of the microfibrils. The maximum

elongation at break increases with the angle, as the fracture work required to stretch the microfibrils is greater.

The use of these fibers presents some disadvantages, for example, the fact that they do not have uniform properties, presenting a large variation in the values of their properties, which are directly related to the composition of their constituents: cellulose, hemicellulose and lignin (Dereje et al., 2017). But there are also great advantages in using natural fibers, such as low specific mass; softness and reduced abrasiveness, recyclable, non-toxic and biodegradable; low cost and low energy consumption in production, thus studying the mechanical characteristics (Satyanarayana et al., 2007).

Table 2 shows a comparison of properties between vegetable fibers and glass fibers, highlighting the high attractiveness that the former have in terms of density, which makes it possible to produce materials that combine good mechanical resistance with low weight (Liu et al., 2012).

Fiber Type	Density (g/cm3)	Tensile strength (GPa)	Modulus of elasticity (GPa)	Elongation at break (%)
Ramie	1,5	0,5	27,2	1,8
Linen	1,2-1,4	0,25-0,39	12-26	1,2-1,4
Jute	1,45	0,25-0,5	11-35	0,8-3,1
Sisal	1,4	0,2-0,8	9,5-45	2-7
Curauá	1,4	0,48	9,7-11,8	2,2
Glass	2,5	3,4-3,5	72	3,3-4,8

Table 2: Comparative values of properties of some plant fibers with glass fiber (Liu et al., 2012).

The high availability of lignocellulosic fibers, combined with the need for a renewable source for the production of polymers, opens up a great opportunity for technological advances that add value to agro-industry products and, at the same time, act to fix carbon in nature. This implies helping to reduce CO2 emissions into the atmosphere during the production cycle, processing and use of agroindustry products, increasing the economic potential of agribusiness due to the possibility of trading carbon credits for the production chain, which emerged as a result of the clean development mechanism provided for in the Kyoto Protocol (Cardoso et al., 2008).

Table 3 shows the annual production of the main Brazilian crops that generate lignocellulosic fibers directly or indirectly (Silva et al., 2019).

Culture	Annual production (thousand tons)			
	2014	2015	2016	2017
Ramie (fiber)	1	1	-	-
Jute (fiber)	2	6	4	6
Malva (fiber)	10	20	14	20
Sisal (fiber)	199	207	248	215
Herbaceous cotton (seed)	3.798	3.666	2.884	3.661
Bay Coconut *	2.078	2.079	1.857	2.017
Pineapple *	1.477	1.528	1.658	1.682
Sugar cane	415.206	422.957	457.984	489.957
Rice (in paddy)	13.277	13.193	11.505	11.045

Table 3: Annual production of direct or indirect lignocellulosic fiber crops in Brazil (Silva et al., 2019).

* Annual production in millions of fruits.

THE RAMIE

Ramie was one of the main vegetable fibers used in the East to make clothing before the introduction of cotton, which took place in China approximately 1300 years before Christ. Although ramie appears to have been known in the East during the earliest recorded times, it apparently was not known in Europe, Africa, or America until much later. Authentic memories have not been found of the occurrence or use of this fiber in ancient Egypt, although statements mention its use initially by the Egyptians, it is believed that there was a certain confusion of ramie with linen (Robinson, 1940).

Ramie or Chinese grass consists of the wood of a species of nettle belonging to the natural order of Urticaceae (subdivision Bohmeria). The species known as Bohmeria nivea is the white-leaved ramie that has been cultivated in China since many years ago. The plants are shrubs that grow to a height of 1.2 to 2.4 m (4 to 8 ft). They are resistant and grow quickly, producing 3 to 4 crops per year (Bezerra et al., 2013).

Young immature ramie stalks do not contain fiber suitable for spinning; therefore, when 3% of the harvested green material appears at the end as degummed and dry fiber, it is considered a satisfactory result. The remaining unused material constitutes waste or raw material with multiple uses, but little explored (Spoladore et al., 1983).

Waldo (1948) already highlighted that the by-products obtained when industrializing the ramie plant could become more valuable than the textile fiber itself. Among these by-products, ramie flour (dehydrated and ground leaves) stands out, which has a high nutritional content. Another by-product that probably has potential for use is the shredded stem (woody part), as a source of cellulosic raw material.

Ramie fiber is a plant native to the southeast of São Paulo, but until the end of the nineties, much of the ramie culture was concentrated in Paraná, mainly in the municipality of Londrina, where the number of producers was around 130, these were mostly small producers, and cultivated an average area of 15 hectares each (Savastano et al., 1997).

Over the years, the cultivation of this plant has increasingly moved towards northeastern Brazilian states such as Pernambuco and Bahia, where the fiber is widely used as a raw material for artisanal products (BNDES, 2018).

At maturity, the plants are cut. The fibrous tissues are located near the bark of the tree, the stem, which is pulled manually from the earth. This is easily done by kneading. The stems are beaten against stones or with a wooden hammer. The fibers can possibly be separated manually in some places, or machines are used to replace human labor. In underdeveloped communities, the fibers are dried and bleached in the sun, as can be seen in Figure 3 (Bezerra et al, 2013).

Figure 3: Process of separating ramie fibers (a) and drying the fibers (b). (Sobreira, 2008).

Ramie fiber belongs to the family of long fibers, with an average length of 150 to 200 millimeters, like linen, jute, sisal, and hemp. It has high resistance, being considered three times greater than that of hemp, four times that of linen and eight times that of cotton (Zheng et al., 2013)

Observations made by scanning electron microscopy, SEM, revealed that ramie fibers are made up of a bundle of hollow fibrils of cellulose macromolecules covered and glued by a matrix of lignin and hemicellulose (Figure 4).

In addition to a large number of imperfections that are characteristic of lignocellulosic fibers, their properties are conditioned by the quantity and distribution of flaws.
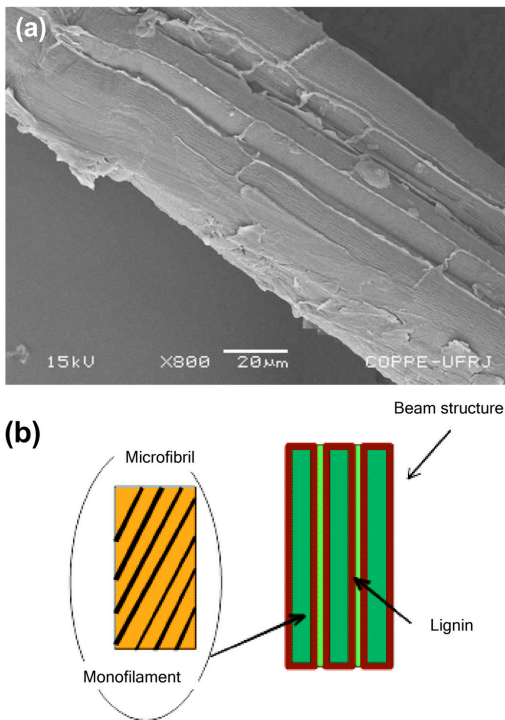
(a)

(b)

Figure 4: (a) micrograph obtained by SEM of the ramie fiber surface; (b) structural model of plant fiber (Gomes *et al.*, 2014).

Each fibril has a complex, layered structure, consisting of a thin shell surrounding a second, thicker inner layer. This thicker layer determines the mechanical properties of the fiber. The fibrils form spirals along the fiber axis (Figure 4b).

The strength and stiffness of the fibers correlate with the angle between the fibril and this axis. The smaller this angle, the better the mechanical properties of the fiber (Bledzki et al., 1996).

Even with a large number of imperfections, ramie fiber arouses interest because it has cellulose in a more highly organized state, when compared to fibers such as linen, jute and cotton (Bezerra et al., 2013).

Ramie fiber is used to make rope, twine and fishing nets. It is also used for fabrics in the East, alone or with other fibers. In China it is used to make "grass cloth" and "summer white cloth". It can be bleached to a good white and dyed as satisfactorily as cotton.

Ramie fabrics have good market acceptance and can be considered a very close substitute for linen, with the advantage of being relatively cheaper. In general, it is sold to the end consumer as if it were linen or under the name "ramie linen", as it is difficult for people to distinguish between ramie and linen, whether in the form of ready-made clothing or fabric to be made (BNDES, 2018).

Ramie is grown almost exclusively for fiber production. Ramie fiber is used in addition to the manufacture of fabrics in bags, tapestry, ropes and string and can also generate cellulose for the production of paper money, due to its resistance. Furthermore, it can be used in the manufacture of hoses, tires and parachute wires (BNDES, 2018).

RESINS

It is known that the compatibility of the lignocellulosic material with the matrix plays a fundamental role in determining the properties of the composite. Lignocellulosic materials have polar hydroxyl groups on the surface due to the predominance of cellulose and lignin, and these polar groups are very easy to interact with polar polymer matrices, as in the case of phenolic resins (Rozman, 2018).

The raw material used in the preparation of phenolic resins (basically phenol and formaldehyde) is derived from fossil sources. Thus, lignin, being a macromolecule of natural origin and containing phenolic rings in its composition, presents the possibility of partially or completely replacing phenol in the manufacture of phenolic resins, forming an integrated network based on phenol and lignin, which could be an interesting alternative from an economic and environmental point of view (Razera, 2006).

The chemical composition of phenolic resins is dependent on the synthesis conditions, and in particular on the formaldehyde/phenol

molar ratio, type of catalysis, reaction time and temperature (Balcerowiak et al., 1998).

The properties of phenolic resins, which determine their main fields of application, are: rigidity, electrical insulation, chemical and thermal resistance, dimensional stability. Among the applications, we can highlight adhesives on wood plywood, surface coatings, molded electrical parts for making a series of small components, such as doorknobs, handles, electrical accessories and switches, automobile parts, battery boxes, precursor of carbon composites in the aeronautical and space industries, among others (Paiva, 2021).

Natural fibers are called hydrophilic and have low compatibility with hydrophobic polymer matrices, tending to form aggregates. To eliminate problems related to high water absorption, fiber treatment with aliphatics and cyclic structures has been an investigation. These structures contain functional groups that are capable of forming bonds with the reactive groups of the polymeric matrix, for example, the carboxyl group of the polyester resin. Thus, the attempt is to modify the fibers and improve the interfacial adhesion between the fiber and the polymeric matrix (Balcerowiak et al., 1998).

Epoxy and polyester polymer resins have been a good example for the development of new materials in recent times, as they offer a unique combination of properties that are unattainable with other thermoset resins (Bridson, 1966).

Table 4 illustrates the main characteristics and limitations of the most commonly used thermoset resins.

Resin	Characteristics	Limitations
Epoxy	- excellent property in composites - very good chemical resistance and electrical properties - good thermal properties low healing contraction	- long curing cycles - better properties obtained at high - curing temperatures
Phenolic	- excellent thermal properties - good fire resistance good electrical properties	- color
Polyester	- widely used - easy use - It cures at room temperature - excellent properties in composites - good chemical resistance good electrical properties	- styrene emission - contraction during healing - flammable
Polyamide	- excellent thermal properties - good properties in composites - good fire resistance good electrical properties	- color
Polyure-thane	- good properties in composites - very good chemical resistance - high hardness (impact resistance) - good abrasion resistance	- color - isocyanides as curing agents
Silicone	- excellent thermal properties - excellent chemical resistance - excellent electrical properties - resistant to hydrolysis and oxidation - good fire resistance - Non toxic	- membership - long curing cycles - cures only at high temperatures
Vinyl Ester	- good fatigue resistance - excellent properties in composites - very good chemical resistance - good hardness	- styrene emission - contraction during healing - flammable

Table 4: Main Characteristics and Limitations of Thermosetting Resins (Adapted from Bridson, 1966).

7

The epoxy resin family has good performance due to its high modulus of elasticity, low creep, and reasonable high-temperature performance, and is widely used in various fields, such as adhesives, coatings and matrix composites. The word epoxy comes from the Greek EP (over or between) and OXI (oxygen), the term means: oxygen between carbons, in general it refers to a group consisting of an oxygen atom linked to two carbon atoms as shown in Figure 5 (May and Tanaka, 1973).
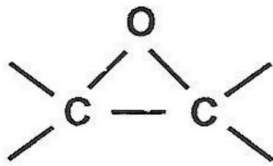

Figure 5: Epoxy ring (epoxy group) (May and Tanaka, 1973).

Before curing, they have thermoplastic characteristics, as when heated they soften and melt (Callister, 2000). The desirable properties of these resins typically appear after curing, which are converted into a thermoset system (Rangel, 2016).

Polyester resin generally has lower adhesive properties compared to epoxy resin. Many polyester resins are viscous, consisting of clear liquids of a polyester solution in a monomer that is usually styrene.

The addition of styrene in amounts above 50% helps to produce a resin that is easy to handle by reducing viscosity (Callister, 2000). Unsaturated polyesters are complex esters formed by the reaction of a dialcohol (glycol) and an anhydride or dibasic acid (diacid) with the release of a water molecule. Because the reaction occurs at both ends of the chain, it is possible to have very long molecules and obtain a multiplicity of ester groups. Polyester undergoes considerable molecular reorganization to reach the cured state, and can present a reduction of up to 8% in volume.

In the reaction of unsaturated polyester in its soluble phase with styrene monomer, which also has unsaturations, and which are liquid resin systems catalyzable at room temperature or with small elevation, the double bonds will be broken by the action of a catalyst (organic peroxide, heat or radiation), to react again with each other, giving rise to a three-dimensional polymer with thermostable characteristics, and therefore infusible and irreversible, Figure 6 (Silaex, 2024).
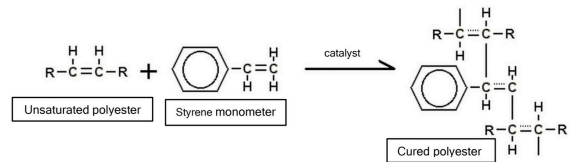

Figure 6: Curing process of a polyester resin (Silaex, 2024).

The different nature of the epoxy resin curing reaction leads to little reorganization, implying a smaller reduction, approximately 2% of its volume. In epoxy resins, the curing reaction occurs only at the ends of the polymer chain through reactive epoxy groups. In polyester resins, the curing reaction is more complex because many processes occur simultaneously. (Silaex, 2024).

COMPOSITES

A composite can be defined as a material formed by two or more materials with different characteristics and aspects, however, when analyzed macroscopically, it is homogeneous (Gay, 2021).

Composites represent a case of greater importance within the group of immiscible polymeric mixtures. It can be said that composite materials constitute a class of heterogeneous, multiphase materials, which may or may not be polymeric, in which the properties of the whole are superior to those of each individual component, with one of the discontinuous components providing the

main resistance to resistance. effort, and the other, continuous, is the means of transferring this effort. The interface between them has a dominant influence on their characteristics. They are generally used as engineering materials, formed by reinforcement elements in a variable degree of order, which are distributed in a flexible matrix (Plasmet, 2024).

A composite exhibit, in addition to the inherent properties of each constituent, intermediate properties resulting from the formation of an interfacial region (Chawla, 1987). The phases of composites are called matrix (which can be of three types, ceramic, polymeric and metallic) and the disperse phase (generally fibers or particles that serve as filler).

The matrix is generally a continuous material that involves the dispersed phase. The properties of the composite are a combination of factors such as the geometry of the dispersed phase, distribution, orientation and also the interfacial compatibility between the constituents of the mixture (Chawla, 1987).

The adhesion of one material to another is associated with the establishment of interactions that can be of the following types: electrostatic, hydrogen bonds, covalent bonds or Van der Walls forces. The nature of these interactions is associated with the chemical affinity between the matrix and the dispersed phase. Generally, the fillers (dispersed phase) are hydrophilic in nature while the polymer (matrix) is hydrophobic in nature (Chawla, 1987).

There are countless applications for these materials, including the automobile industry (manufacturing of bumpers, truck bodies), aeronautics (helicopter propeller), nautical (boat manufacturing), chemistry (tanks for storing chemical products), among other industries (Albuquerque, 2019).

These materials, in addition to combining high mechanical resistance with good ductility, allow the product to have better dimensional stability and mechanical resistance, and in certain cases, greater tenacity with the incorporation of fillers (Freire et al., 2014).

The combination of high-performance polymers with ceramic or polymeric fibers with a high elastic modulus and mechanical resistance allows the production of new composites with a group of specific properties (per unit weight) superior to steel, aluminum and others. These composites generally have high modulus/weight and strength/weight ratios that are superior to those of ceramic, polymeric and metallic materials (Santos, 2006).

POLYMERIC COMPOSITES

Polymeric composites (also called reinforced plastics) are materials formed by a polymer matrix and a reinforcement (usually a fiber). Among the advantages of polymer composites are: low weight, resistance to corrosion and high temperatures and excellent mechanical properties, when compared to conventional engineering materials (Santos, 2006).

In Brazil, the alternative of replacing synthetic fibers with natural fibers is viable due to the fact that the country's economy is based on agriculture, where raw material is obtained from renewable sources, which can be used in polymer composites (Barros, 2016).

The combination of low specific mass with high values of resistance and stiffness that advanced polymer composites provide, allows this class of materials to be used in the aeronautical and space industries to replace traditional metallic materials, as these can offer structural components high resistance to resistance. fatigue and corrosion, low thermal conductivity, acoustic and thermal insulation and ease of obtaining complex geometries,

ensuring greater performance in service (Barros, 2016).

The mechanical properties of composites are affected by two phases: the structural phase, generally has high mechanical resistance and is represented by a fibrous material; the matrix phase, in general, is capable of great elongation and is typically made of a plastic, non-brittle material. Nowadays the use of composite materials is something that is gradually growing, and that is why there is concern about replacing synthetic material with natural material. Natural fibers have been studied for decades, regarding their constitution, mechanical properties and their possible uses. The advantages of using natural fibers over synthetic fibers are: biodegradable, low cost, low density, good tenacity, good thermal properties and reduced use of instruments for their treatment or processing.

Vegetable fibers are an ecological alternative in relation to their biodegradability, which favors the decomposition of the composites with which they are associated, and the fact that these residues are not pollutants, which are advantageous aspects for some applications (Nothenberg, 2016).

Composite materials are basically classified into two groups, which are fiber-reinforced composites and particle-reinforced composites or particulate composites (Figure 7). Fiber-reinforced composites can be characterized with continuous, long, or short fibers, and in relation to their arrangement, these can be parallel, unidirectional, bidirectional in the form of fabric, and can also be randomly oriented, with continuous or chopped fibers. (Nothenberg, 2016).
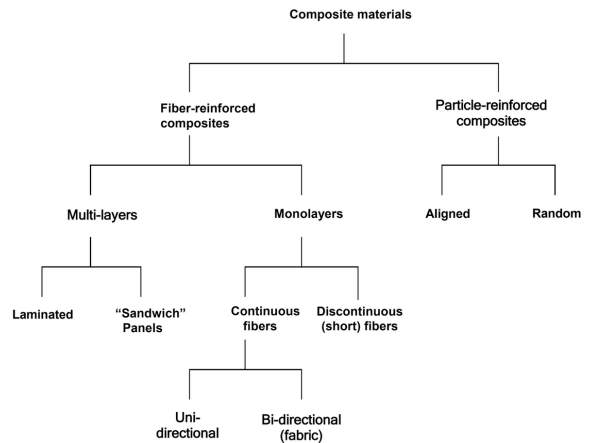
Figure 7: A classification scheme for the various types of composites (Adapted from Callister, 2000).

The volumetric and mass fractions of the fibers must be properly studied, as there is a minimum and maximum range that will influence the reinforcement. Generally, increased reinforcement promotes mechanical properties, although high reinforcement loading may favor fiber agglomeration and low matrix dispersion (Satyanarayana, 1984). Fiber orientation is also another significant factor in the mechanical properties of composites. It is known that oriented fibers have tensile strength along their axis and stress transfer in the manufactured composite is favored.

The discontinuity of the natural fiber, when used as reinforcement, also has a strong influence on the tensile strength and toughness of the composites. Factors such as fiber length and orientation are decisive in improving their properties. An example is the tensile strength of composites with discontinuous fibers, which is lower when compared to composites with continuous fibers (Zarate et al., 2020).

For the composite to benefit from the maximum level of fiber strength, the fiber length must be equal to or greater than its critical length, defined as the minimum fiber length required to obtain the highest fracture resistance of the composite (Zarate et al., 2020).

The main limitation in finding new applications for plant fiber composites is due to the high moisture absorption of these fibers, which causes the formation of voids during the processing of these materials. Voids can occur for two reasons: firstly, due to the incomplete wettability of the resin on the fibers, resulting in the formation of air bubbles that can become trapped due to the high viscosity of the resin; second, due to the presence of volatile compounds that form in the curing process of thermoset resins. (Zarate et al., 2020).

Polymeric composites can be thermoplastic or thermoset. In Table 5 we have a comparative table between the main characteristics of thermoplastic and thermoset polymers. The main difference between them is their characteristic behavior when the temperature increases. Thermoplastic composites are polymers capable of being molded several times due to their characteristics of becoming fluid under the action of temperature and then solidifying when there is a decrease in temperature. Thermosets do not become fluid due to the presence of cross-links between the macromolecular chains (Cantwell and Morton, 2021).

Comparison between properties of Thermoplastic and Thermorigid materials	
Thermoplastic	**Thermosets**
Mechanically Recyclable	**Not mechanically recyclable**
Unlimited storage time	**Limited time during storage**
High viscosity when melted	**Low viscosity during processing**
Low creep resistance	**High creep resistance**
Use temperature limited to T_g and T_m.	**High thermal and dimensional resistance**
Low thermal stability	

Table 5: Main characteristics of thermoplastic and thermoset polymers (Cantwell and Morton, 2021).

Thermosetting polymers are most commonly used for structural use in composite materials as they have some advantages over thermoplastics, such as high thermal stability, high rigidity, high dimensional stability, good thermal and electrical insulation properties, resistance to creep and deformation under loading. (Cantwell and Morton, 2021).

The most used and cheapest thermoset resins are polyesters, polyurethanes, vinyl esters and phenolic resins; being mainly used to compose composites reinforced with glass fibers. Epoxy resins have a higher cost and are widely used in aerospace applications as they have better mechanical properties and better resistance to moisture than polyesters, polyurethanes and vinyl resins.

THE STATE OF THE ART

PULLOUT TEST WITH POLYESTER MATRIX

Simonassi 2017 carried out numerous pullout tests on ramie fiber with a polyester matrix. Table 6 summarizes these results.

L (mm)	Voltage resistance (MPa)
1	1069.3 ± 644.4
2	1462.4 ± 506.1
3	1176.1 ± 571.0
5	1539.8 ± 673.8
10	1448.0 ± 625.3
20	1588.7 ± 630.6
30	1688.9 ± 515.9

Table 6: Average tensile strength for each length of ramie fiber embedded in a polyester matrix (Simonassi 2017).

In addition to the pullout tests, the results of conventional tensile tests were also considered, and an average stress of 1803.2 ± 679.1 MPa was obtained.

The results of pullout tests with polyester matrix, carried out for ramie fibers with diameters ranging from 1 to 30 mm, are shown in Figure 8.
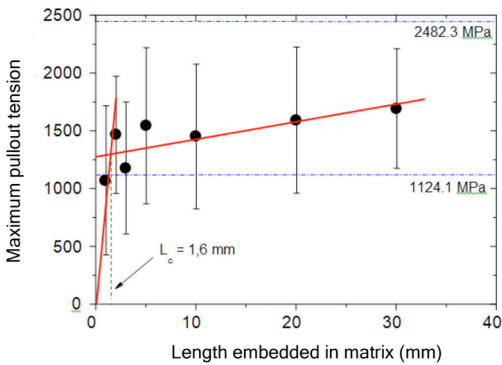

Figure 8: Variation in pullout tension as the length of fiber embedment in the matrix varies (Simonassi 2017).

The critical length (Lc) of the ramie embedded in the polyester matrix can be seen in the dashed line, and as already mentioned that for the fiber to benefit from its maximum resistance, the length of the fiber must be equal to or greater than its length critical, then good results can be found for ramie fiber as its length varies from 150 to 200 millimeters, which is up to ten times greater than the critical length of 1.6 millimeters found in this work.

The large scatter noted in Figure 8 associated with the error bars is due to the non-uniform characteristics of lignocellulosic fibers (Wambua et al, 2003).

With the value of L_c, the shear strength of ramie fiber with polyester matrix was obtained using the equation below:

$$\tau_i = \frac{r\sigma_f}{2\ell_c} \qquad (1)$$

As natural fibers are generally not circular, the value of r can be a source of error, but the average radius value for ramie fiber used was 0.055mm, which gives the following result:

$$\tau_i = 3.10 \pm 1.17 \text{MPa} \qquad (2)$$

Comparing this value with other lignocellulosic fibers embedded in polymer matrices, it can be assumed that the interface of ramie fiber with polyester is strong. As an example, piassava/polyester fiber can reach values of t_i = 2,8 MPa (Aquino et al., 2013), and sisal/polystyrene fiber has t_i = 2,2 MPa (Aquino et al., 2013). On the contrary, the interface of synthetic fibers with polymer matrix is comparatively strong. For example, fiberglass/polypropylene has t_i = 15,2 MPa and carbon fiber/polypropylene, t_i = 19,2 MPa (Aquino et al., 2013).

The appearance of the ramie fiber before and after the pullout test can be seen in Figure 9 through SEM images.
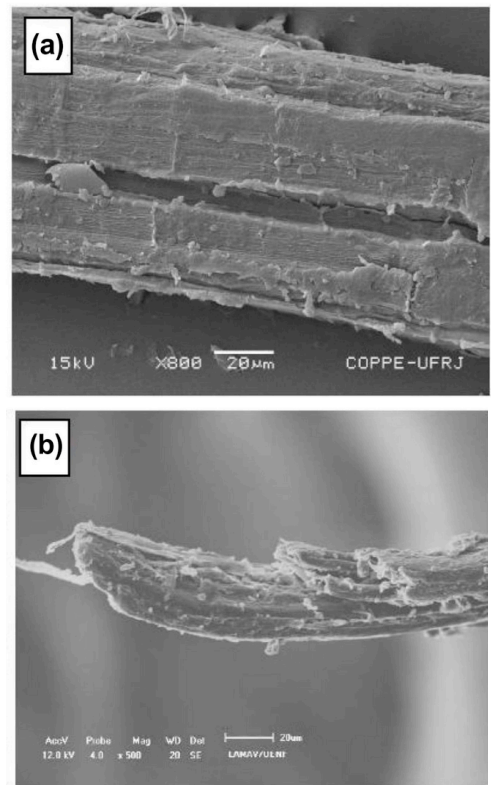

Figure 9: Typical appearance of ramie fiber (a) before testing and (b) after testing.

In Figure 9 (a) it is important to note the heterogeneous shape that is characteristic of natural fibers. In Figure 9 (b) it is important to

note that among the countless fibrils, filaments and fibers that were torn from the matrix, traces of polyester resin can be observed on their fibrillar surface.

FLEXURE TEST WITH POLYESTER

The Table 7 presents the average values of flexural strength and total displacement until failure of polyester composites with different volume fractions of ramie fibers.

Volumetric fraction of ramie (%)	Flexural strength until rupture (MPa)	Total displacement until rupture (mm)
0	64.67 ± 30.23	4.98 ± 2.42
10	70.04 ± 14.80	6.35 ± 1.21
20	58.41 ± 10.36	20.79 ± 13.23 (3 specimens did not break)
30	21.05 ± 12.02	(No test specimen broke)

Table 7: Flexural strength and total displacement for ramie fiber composites.

Based on the results presented in Table 7, Figure 10 shows the curve of variation in flexural strength as a function of the volume of ramie fibers.
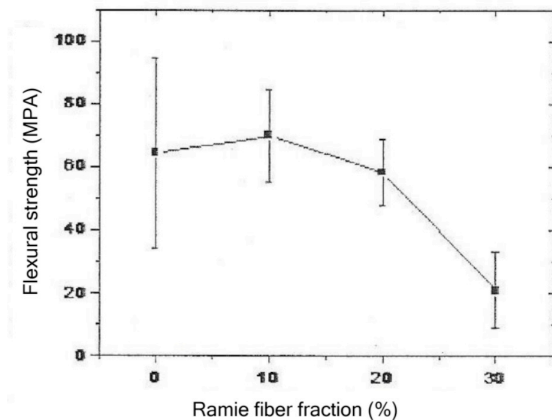

Figure 10: Variation in flexural strength depending on the volumetric fraction of ramie fibers.

It can be seen in the Figure that the flexural strength increases slightly when the ramie fiber fraction is 10%, while for higher volumetric fractions the resistance of the composites is reduced, as for composites with incorporation of up to 10% of fiber the rupture is transverse, however, for larger amounts of fiber the rupture is not necessarily nucleated at the midpoint, but rather through cracks nucleated at the fiber/matrix interfaces, and this propagation path will be preferential due to the low interfacial shear tension between the fiber. ramie and polyester matrix (Margem et al., 2010).

Figure 11 shows SEM micrographs of a typical rupture for composites with 10% ramie fiber.
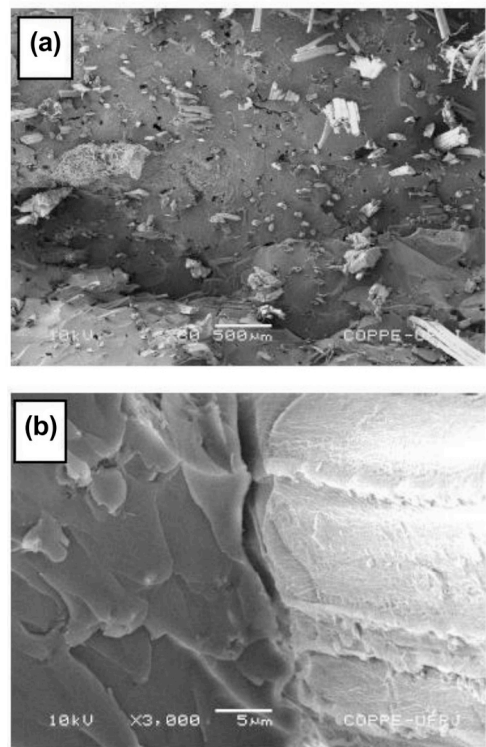

Figure 11: Micrographs of the fracture of a test specimen with 10% ramie fibers in a polyester matrix. With lower magnification (a): general view of the fracture and with higher magnification (b): showing detachment of fibers at the interface (Margem et al., 2010).

In Figure 11 (a), it can be seen, with lower magnification, torn fibers and voids corresponding to the holes from which other fibers were removed from the transversely fractured polyester matrix. With greater

magnification, in Figure 11 (b), it is revealed that the interface between the ramie fiber and the polyester matrix is not continuous. In fact, most of the interface presents a separation of the fiber surface and the polyester matrix. This fact certainly occurs due to the interfacial shear tension found for this type of compound.

Figure 12 shows a micrograph of a typical rupture for composites with 30% ramie fiber added. Figure 12 (a), at lower magnification, shows the general appearance of a longitudinal rupture, which is characteristic of sample delamination. Figure 12(b), at higher magnification, shows interfacial detachment, associated with very low shear stress resistance.
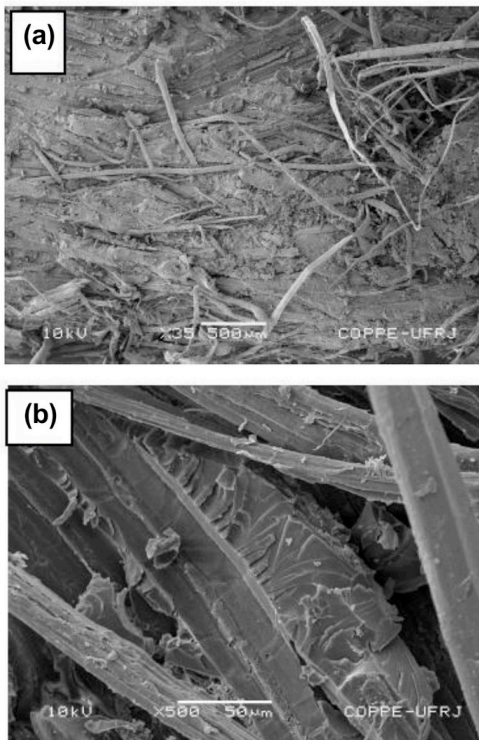

Figure 12: Micrographs of the fracture of a specimen with 30% ramie fibers;

(a) general view and (b) detail of the fiber/ matrix interface demonstrating longitudinal detachment (Margem et al., 2009).

CHARPY IMPACT TESTS ON POLYESTER MATRIX

The variation of Charpy impact energy as a function of the amount of ramie fiber in the polyester composite is shown in Figure 13.
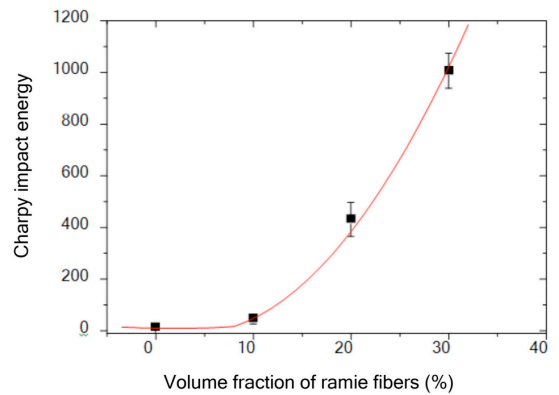

Figure 13: Variation of Charpy impact energy of polyester composites with different volume fractions of ramie fibers (Margem et al. 2009).

The increase in impact energy in Figure 13 is correlated with an exponential equation between the impact energy, E, and the fraction of ramie fibers, F:

$$E = 2, 68.\exp(F) \qquad (4)$$

Figure 14 presents SEM details of the surface broken by Charpy impact of a specimen with 30% by volume of ramie fibers.
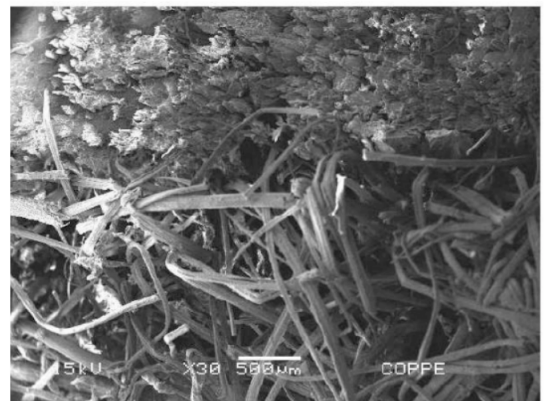

Figure 14: Impact fracture of the composite specimen with 30% by volume of ramie fiber, with polyester matrix (adapted from Margem et al. 2010).

It is important to note in figure 14, observed in the region where the fracture propagated following the fiber/matrix interface, evidence of interfacial detachment. This behavior corroborates the rupture mechanism through cracks that propagate preferentially between the fiber and the matrix due to the weak interfacial resistance (Margem et al., 2009).

CONCLUSION

The mechanical properties of the newest tests of polymer composites with ramie fibers demonstrated that the adhesion relationship between the hydrophilic fiber and the hydrophobic matrix considerably increases the material's capacity to absorb energy, especially when this energy is expended instantly, as a impact or blow, it was also found that the increase in volume of this type of material in a polymeric matrix has a limit, which is defined mainly by the inability of the resin to impregnate a high volume of fibers, which ends up generating areas of accumulation of material stress and fatigue. The literature shows that volumes of up to 30% of fibers are very well accepted by the polymeric matrix and highlight the composite with high energy capabilities, but it also demonstrates that volumes greater than 40% of fibers deteriorate the material, making it more fragile than pure resin., consequently null in a reinforcement process. It is clear, however, that new research with this composite will take place in the near future, indicating appropriate uses for it, and new ways of taking advantage of these interesting properties.

THANKS

REFERENCES

CHAUHAN, A., CHAUHAN, P. (2013). Natural Fibers Reinforced Advanced Materials. *Chemical Engineering & Process Technology.*

BRAGA, FABIO O.; MILANEZI, THIAGO LARA; MONTEIRO, S. N.; LOURO, L. H. L.; Gomes, A.V.; LIMA JR, E. P.. Ballistic comparison between epoxy-ramie and epoxy-aramid composites in Multilayered Armor Systems. Journal of Materials Research and Technology-JMR&T, v. 7, p. 541-549, 2018.

SIMONASSI, NOAN TONINI; PEREIRA, ARTUR CAMPOSO; Monteiro, Sergio Neves; MARGEM, FREDERICO MUYLAERT; Rodríguez, Rubén Jesus Sánchez; DEUS, Janine Feitosa de; VIEIRA, CARLOS MAURICIO FONTES; DRELICH, JAROSLAW. Reinforcement of Polyester with Renewable Ramie Fibers. Materials Research-Ibero-american Journal of Materials, v. 20, p. 51-59, 2017.

WESTMAN, M. P., FIFIELD, L. S., SIMMONS, K. L., LADDHA, S. G., KAFENTZIS, T.A. (2010). Natural Fiber Composites: A review. U. S. Department of Energy.

KRAUS, J. LOURO, R. RP.; ARDUIN, M.; ESTELITA, M. E. (2016). A célula Vegetal. In. A Ppezato-da-gloria, B.; Carmello-Guerreiro, S. M. (Ed) Anatomial Vegetal. 2 ed. Viçosa: UFV, p.32-67.

SIMONASSI, NOAN TONINI; PEREIRA, ARTUR CAMPOSO; Monteiro, Sergio Neves; MARGEM, FREDERICO MUYLAERT; Rodríguez, Rubén Jesus Sánchez; DEUS, Janine Feitosa de; VIEIRA, CARLOS MAURICIO FONTES; DRELICH, JAROSLAW. Reinforcement of Polyester with Renewable Ramie Fibers. Materials Research-Ibero-american Journal of Materials, v. 20, p. 51-59, 2017.

DENCE, C. W.; REEVE, D.W. (1996). Pulping bleaching: Principles and Pratice. Atlanta: Tappi.

GIRIO, F.M., FONSECA, C., CARVALHEIRO, F., DUARTE, L.C., MARQUES, S., BOGEL-ŁUKASIK, R. (2010). Hemicelluloses for fuel ethanol: A review. Bioresource Technology. 101:4775–4800.

LYND, L.R.; WEIMER, P.J.; VAN Zyl, W.H. (2012). Pretorius, I.S. Microbial Cellulose Utilization: Fundamentals and Biotechnology. Microbiology and molecular biology reviews. American Society for Microbiology., n.3, v.66., p.506-577.

CASTRO, A. M.; PEREIRA Jr, N. (2010). Produção, propriedades e aplicação de celulases na hidrólise de resíduos agroindustriais. Química Nova (Impresso), v. 33, p. 1-12.

D'ALMEIDA, M. L. O. (1981). Celulose e papel: tecnologia de fabricação de pasta celulósica. 2. ed. São Paulo: IPT-SENAI, v. 1.

ARANTES, V. & SADDLER, J.N. (2010). Access to cellulose limits the efficiency of enzymatic hydrolysis: the role of amorphogenesis. Biotechnology for Biofuels, v. 3, n.4.Disponível em www.biotechnologyforbiofuels.com/content/3/1/4. Acesso em fevereiro de 2011.

MORAIS, S.A.L.; NASCIMENTO, E.A.; MELO, D.C. (2015). Chemical analysis of Pinus oocarpa wood PARTE I – quantification of macromolecular components and volatile extractives. Revista Árvore, v. 29, n. 3, p. 461-470.

H. Gu, M. Miao, Optimising fibre alignment in twisted yarns for natural fibre composites, J Compos Mater, 48 (24) (2014), pp. 2993-3002

Dereje Kebebew Debeli, Zhao Qin &JianshengGuo (2017),"Study on the Pre-Treatment, Physical and Chemical Properties of Ramie Fibers Reinforced Poly (Lactic Acid) (PLA) Biocomposite", Journal of Natural Fibers, DOI: 10.1080/15440478.2017.1349711

SATYANARAYANA, K.G.; GUIMARÃES, J.L.; WYPYCH, F. Studies on lignocellulosic fibers of Brazil. Part I: Source, production, morphology, properties and applications. Composites: Part A, v. 38, p. 1694-1709, 2007.

K. Liu, H. Takagi, R. Osugi, Z. Yang Effect of lumen size on the effective transverse thermal conductivity of unidirectional natural fiber composites Compos Sci Technol, 72 (2012), pp. 633-639

CARDOSO, A. A., MACHADO, C. M. D., PEREIRA, E. A. (2008). Química Nova na Escola. nº 28, 9.

SILVA, R., HARAGUCHI, S. K., MUNIZ, E. C., RUBIRA, A. F. (2019). Aplicações de fibras lignocelulósicas na química de polímeros e em compósitos. Química Nova. 32, 663.

ROBINSON, B. B., (1940). Ramie Fiber Production. Division of Cotton and Other Fiber Crops and Diseases, Department of Agriculture.

BEZERRA, C. M., GONÇALVES, D. C. S., FREITAS, D. O., SOUTO, K. K. O., BARBOSA, R. X., FERREIRA, T. R. (2013). Fibras Celulósicas. Universidade Federal do Rio Grande do Norte. Departamento de Engenharia e Produção Têxtil.

SPOLADORE, D. S., JUNIOR, R. B., TEIXEIRA, J. P. F., ZULLO, M. A. T., AZZINI, A. (1983). Composição química das folhas e dimensões das fibras lenhosas em rami. 35ª Reunião Anual da Sociedade Brasileira para o Progresso da Ciência, Belém (PA), 1983.

WALDO, W. G. (1948). A fibra de rami e seus sub-produtos, uma cultura em expansão. Revista de Agricultura de Porto Rico, Porto Rico, USA.

SAVASTANO Jr., H. LUZ, PHC. NOLASCO, A.M; Seleção de Resíduos de alguns tipos de fibras vegetal, para reforço de componentes de construção. In: Encontro Nacional Sobre Edificações e Comunidades Sustentáveis, 1. Canela, nov Anais. Porto Alegre, Antac, 1997, P107-12.

BNDES (2018). – Produção e consumo de algodão e as indústrias de fiações de algodão e linho no Paraná. Informe Setorial– Banco de Desenvolvimento Econômico e Social – BNDES, site oficial – www.bndes.gov.br

SOBREIRA, G, Imagens de colheitas e plantios de fibras em geral, Terrastock, Banco de Imagens e Fotos. Fotografia de Gerson Sobreira. Pecuária, Agricultura, Rural. Stock Photos, Agriculture & Livestock Photography, 2008.

Z.Y. Zheng, Y. Li, W.D. Yang, Absorption properties of natural fiber-reinforced sandwich structures based on the fabric structures, J Reinf Plast Compos, 32 (20) (2013), pp. 1561-1568

GOMES, A., GODA, K., OHGI, J. (2014). Effects of alkali treatment to reinforcement on tensile properties of Curaua fiber green composites. JSME Intern. Journal, 47 A, p.541-546.

BLEDZKI, A K, REIHMANE, S., GASSAN, J. (1996). Properties and modification methods for vegetable fibers for natural fiber composites, J. Appl. Polym. Sci., 59, p.1329-1336.

ROZMAN, H. D. (2018). The Effect of Lignin and Surface Activation on the Mechanical Properties of Rubberwood-Polypropylene Composites. Journal of Wood Chemistry and Technology, v.18, n.4, p.471-490.

RAZERA, I. A. T. (2006). Fibras lignocelulósicas como agente de reforço de compósitos de matriz fenólica e lignofenólica. Tese de doutorado em Ciências (Físico-química) da Universidade de São Paulo – Instituto de Química de São Carlos, 2006.

BALCEROWIAK, W., HETPER, J., KALEDKOWSKI, B., GRYTA, M. (1998). A new approach to the determination of heat of phenolics resol synthesis. Thermochimica Acta, v. 320, p. 209-214.

PAIVA, J. M. F. (2021). Compósitos de Matrizes Termorrígidas Fenólicas e Lignofenólicas Reforçadas com Fibras Vegetais. Tese de doutorado em Ciência e Engenharia dos Materiais – Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, 266f.

BRIDSON, J.A. (1996). Handbook of Plastics Materials, Van Nostrand Co., p 451– 483.

MAY, C.A., TANAKA, Y. (1973). Epoxy Resins, Chemistry and Technology. Marcel Dekker.

CALLISTER, W.D. (2000). Materials Science and Engineering- 2n Introduction, Jonh Wiley and Sons, Canadá.

RANGEL, S.A. (2016). Nanocompósitos baseados no sistema epoxídico DEGBA/DETA modificado com uma resina epoxídica de silsesquioxano. Dissertação de Mestrado em Ciências dos Materiais -São Paulo- SP, Universidade Estadual Paulista- UNESP, 70p.

SILAEX (2024) http://www.silaex.com.br/poli%C3%A9ster.htm, Visitado em 07/03/2024.

GAY, D. (2021). Matèriaux Composites, Editions Hermes Paris, France.

PLASMET (2011). Plásticos e Metais, Suporte Técnico, http://plasmet.com.br/site/menus/suporte_tecnico/Compositos.pdf>, Acessado em 10 de março de 2024.

CHAWLA, K. K. (1987). Composite Materials. Science and Engineering, Springer- Verlag, New York.

ALBUQUERQUE, J. A. C. (2019). O Plástico na Prática: Manual de Aplicações. Porto Alegre: 2ª ed.; Editora Sagra Luzzato.

FREIRE, E., MONTEIRO, E. E. C., CYRINO, J. C. R. (1994). Propriedades Mecânicas de Compósitos de Polipropileno com Fibra de Vidro. Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro. Polímeros: Ciência e Tecnologia – Jul/Set, 2014.

SANTOS, A. M. (2006). Estudo de compósitos híbridos polipropileno/fibras de vidro e coco para aplicações em engenharia. Dissertação de Mestrado em Engenharia, Programa de Pós-Graduação em Engenharia Mecânica, Setor de Tecnologia. Universidade Federal do Paraná.

BARROS A.R de F. (2016). Compósitos híbridos: desenvolvimento de configuração e efeito de umidificação. Dissertação de Mestrado em Engenharia Mecânica. Universidade Federal do Rio Grande do Norte, Natal, Dezembro.

NOTHENBERG, M. (2016). Cresce o interesse pelo uso de fibras naturais. Revista Plástico Moderno, Ed. QD. Ltda., n. 263, p. 6-15.

ZARATE, C.N.; ARANGUREM, M. I.; REBOREDO, M. M. (2000). Effects of fiber length in resol/sisal composites. In: International Symposiumon Natural Polymers and Composites, 3., São Pedro, 2020. Proceedings. São Paulo, USP/UNESP/Embrapa, p.362-366.

CANTWELL, W. J. E MORTON, J. (2021). The impact Resistance of Composites Materials – a Review. Composites; vol. 22, n.5.

WAMBUA, P., IVENS, I., VERPOEST, I. (2003). Natural fibers: can they replace glass and fiber reinforced plastics? Composites Science and Technology, 63,1259-1264

AQUINO R. C. M. P., MONTEIRO, S. N., d'ALMEIDA J. R.M. (2013). Evaluation of the Critical Fiber Length of Piassava (Attalea funifera) Fibers using the Pullout Test. J. Mater. Sci. Letters, 22, 1495-1497.

MARGEM, F. M. M. (2009). Análise das características estruturais e propriedades de compósitos poliméricos reforçados com fibras de rami. Tese de doutorado em Engenharia e Ciência dos Materiais. Universidade Estadual do Norte Fluminense. Campos dos Goytacazes, Dezembro, 2009.

MARGEM, F. M. M., NETO, J. B., MONTEIRO, S. N. (2010). Ensaios de pullout de fibras de rami em matriz epoxídica. Em: 65o Congresso Anual da ABM. Jul. 2010, Rio de Janeiro, Brasil, p. 1-9.

MARGEM, F. M. M., MONTEIRO, S. N., NETO, J. B., RODRIGUEZ, R. J. S., SOARES, B. G. (2010). The dynamic-mechanical behavior of epoxy matrix composites reinforced with ramie fibers. Revista Matéria, v. 15, n. 2, pp. 164 – 171.

SOARES, B. G. (2010). The dynamic-mechanical behavior of epoxy matrix composites reinforced with ramie fibers. Revista Matéria, v. 15, n. 2, pp. 164 – 171.