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Mechanical Characterization of Natural Fibers Composites submitted to extreme temperatures

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14. ABSTRACT
The present research focuses on the mechanical and thermal characterization of natural fibers, Curau, reinforced composites with respect to produce a low density composite material that can be used in extreme environment conditions such as low and high temperatures. The Curau plant is well-known in the Amazon Water Basin in the western region of Para State (Brazil) with excellent mechanical and physical properties. Experimental tests under different conditions will be performed to characterize this composite material manufactured with different Curau fiber concentration.

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Abstract
The research of natural fiber composites is growing due to the fact that the green materials combine low weight with good mechanical properties. In essence, this project focusses on the investigation of natural fiber composites when submitted to extreme temperatures, from very low to high. Curaua fiber arises as a competitive natural fiber due to its abundance, low cost and a variety of applications. Our main goal in this work is to study different weight fractions of Curaua fibers in order to obtain this natural composite material. Specimens of Curaua/Epoxy composites were tested in tensile and in flexion to observe the quasi-static mechanical properties and its physical properties due to temperature variation, from very low to elevated ones, were evaluated by DMA analyses. We found that an increase in the fiber quantity showed an increase in both the modulus and the strength, leading to a stiff and less ductile material. The results also showed an increase in the viscoelastic stiffness of the epoxy matrix by the incorporation of Curaua fibers. The interaction between Curaua fibers and epoxy matrix affects segmental mobility of the epoxy chains.

Archival publications during reporting period:

Amorim, F. C., Souza, J. F. B., Reis, J.M.L. The Quasi-static and Dynamic Mechanical Behavior of Epoxy Matrix Composites Reinforced with Curaua Fibers. Materials Research-Ibero-american Journal of Materials, v. 1, p. 1, 2018.

Amorim, F. C., Souza, J. F. B., Reis, J.M.L. Effects of Fiber Treatment on the Properties of Epoxy Curaua-Reinforced Composites. In: 2nd International Conference on Materials Design and Applications, MDA 2018, Porto, Portugal.

Reis, J.M.L.; Liese, T., Amorim, F.C., Mechanical properties of curaua/epoxy composites. In: 20th International Conference on Composite Structures - ICCS20, 2017, Paris, France.

1. Introduction

The applications of lignocellulosic fibers in reinforcement of composite structures are growing. Curaua fiber (Ananas erectifolius) is a Brazilian fiber development in the Amazon region (Para state) cultivated by small farmers. With an accelerated industrialization process the search for materials that can respond market needs is more often. Due to the fact that the industries are strongly competitive, this new material shall meet low cost, good mechanical and chemical properties.

Raw materials based on sustainability issues are a great solution for development of biocomposities considering the fact that they have an origin from renewable resources and ally some advantages such as biodegradability, high production and non-toxicity. Considering the properties of curaua, among natural fibers is the most competitive. This fiber is replacing glass and carbon fiber in some applications. Green materials gain attention for several applications for aerospace until the building industry because it combines some special features like low weight and price with good physical properties [1-3].

Automobile industries in a constant search of reduction of weight and CO_2 emissions are making panels and others interior parts with natural fibers [4-5].

Natural fiber polymer composites are materials that consist of a polymeric matrix with immersed fibers. The polymeric matrix can be in two types thermofixes and thermoplastics having the main function of ensuring the fiber integrity against chemical and environmental factors.

The fibers, with over mechanical strength, endure the load. An important mechanical aspect of composites is the load transfer by matrix to the fibers.

The reduction in interfacial mechanical properties between fiber and polymer matrix commonly decreases the fiber's ability of to be a reinforcing component considering the hydrophilic character of lignocellulosic fibers.

Some disadvantages of Curaua, as all natural fiber, are related to the composition (cellulose, hemicellulose, lignin and waxes) and the elevated capacity of moisture absorption which contribute to the poor adhesion between the polymeric matrix and fibers. The properties of natural fibers have a hard dependency of its chemical composition [6-8]. In order to improve the adhesion between Curaua/Epoxy, chemical treatment with $5\,wt\,\%$ aqueous NaOH solution for $2, 4,\ 6,\ 8,\ 12,\ 24\ and\ 48\,h$ at $23\ °\mathrm{C}$ is applied to the natural fibers. Other treatment of natural fiber involves the exposure in hot water at $80\ °\mathrm{C}$ for $1\,h$ and then after both treatments dried in air for $48\,h$. These procedures improve the mechanical interaction between hydrophobic epoxy resin and hydrophilic fibers, removing the waste components (lignin, hemicellulose) from the fibers [9-12].

2. Materials and Methods

2.1. Materials

To make Curaua/Epoxy composite the natural fibers and polymer resin were mixed and cured for one week at room temperature prior to testing. The composite resultant was post-cured for 8h at 80°C in order to accelerate the curing process and improve some properties of composites.

The epoxy resin used in this work was provided by Epoxyfiber®. Based on diglycidyl ether of bisphenol A and an aliphatic amine hardener. The epoxy resin has low viscosity and the mix ratio to hardener of 4:1. Resin properties by the manufacture are shown in Table 1.

Table 1 - Properties of Epoxy resin at room temperature.

Property	Epoxy
Viscosity at 25°C μ (mPa.s)	12000-13000
Density ρ (g/cm^3)	1.16
Heat Distortion Temperature HDT (°C)	100
Modulus of Elasticity E (GPa)	5.0
Flexural Strength (MPa) (ASTM D790)	60
Tensile Strength (MPa) (ASTM D638)	73
Maximum Elongation (%)	4

Curaua fiber (*Ananas erectifolius*) from Para state is a type of lignocellulosic fiber. The fiber has a diameter of 50 μm and a length of 6 mm. The Curaua fibers are shown in Fig. 1. The mechanical properties of Curaua fiber are presented in Table 2.

Fig 1. Curaua fibers.

Table 2 - Properties of Curaua fiber.

Property	Curaua	Reference
Density ρ (g/cm^3)	1.4	[13]
Modulus of Elasticity E GPa)	11.8	[13]
Tensile Strength (MPa) (ASTM D638)	500-1150	[13]

Maximum Elongation (%)	3.7-4.3	[13]
Fiber diameter (μm)	50	[-]
Fiber length (mm)	6	[-]

2.2 Methods

Mechanical tensile and flexural tests at different weight % were performed by Shimadzu®AG-X universal testing machine according to ASTM D3039/D3039M-14 [14] and ASTM D790-10 [15], respectively. The tensile tests were performed with a cross-head speed of 2 mm/min and the three-point bending with a speed of 1.5 mm/min. Four specimens were tested for each type of mechanical testing.

The dynamic mechanical analysis –DMA was used for measuring the temperature influence in elastic properties of all formulations of natural fiber composite. Tests were performed with three-point bending configuration and the span of the supports was 40 mm, according to ASTM D7028 [16]. The samples were scanned from -50°C to 180°C with a heating rate of 2°C/min at some frequencies: 0.01, 0.1, 1, 10 and 100 Hz.

2.3 Chemical Treatment

The Curaua fibers were treated with different NaOH concentrations (1%, 3% and 5 wt%) and immersion time (24, 72 and 168h) at room temperature. These parameters were combined forming a 3 x 3 result matrix. Thereafter, the Curaua fibers were washed in running water for 30 min (post-treatment), dried in an electric oven at 80ºC for 24h and the fibers were reprocessed. It is possible to see that 5 wt% NaOH solution removes more residues than others concentrations at the same immersion period.

3. Results and Discussion

3.1. Untreated composites

The tensile and three-point bending test results of composite with different content of Curaua fiber are presented in Table 3.

From Table 3 it is visible that the tensile and flexural maximum strength and stiffness are dependent on quantity do fiber. As fiber content increases the tensile and flexural modulus increase. Although the fibers improve the strength of a composite, with the addition of fiber the tensile and flexural strength decrease compared to the epoxy matrix.

Fig. 2 shows the tensile and flexural stress vs. strain curves for Curaua/epoxy composite with 0, 30, 40 and 50% of the fiber. The graphics presented in Fig. 2 shows the hard fiber content dependency. Both modulus of elasticity and maximum strength are fiber-dependent.

The curves showed in Fig. 2 present the strong influence of quantity of fiber with modification in stiffness and strength of composite.

Table 3 - Mechanical results.

Fiber content (%)	Maximum Tensile Strength (MPa)	Modulus of Elasticity (GPa)	Maximum Flexural Strength (MPa)	Flexural Modulus (GPa)
0	53.84	1.73	85.39	2.71
30	20.20	2.27	52.02	2.94
40	25.95	3.45	59.00	4.06
50	30.29	4.24	67.45	4.37

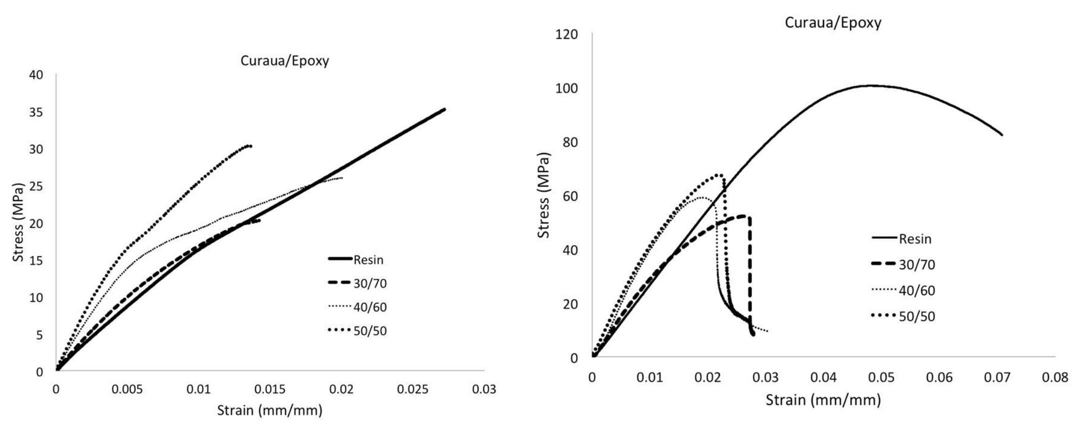

Fig. 2. Typical tensile and flexural stress vs. strain curves of Curaua/Epoxy composite.

The DMA results of 1Hz analysis are presented in Fig. 3. The specimens were tested under -50°C to 180°C. It shows a typical E' dependence on temperature of crystalline material, with the first drop due to the glass transition. High crystallinity is due to high E' value. Table 4 shows the storage modulus (E'), Tan Delta and glass transition temperature (Tg) of composite Curaua/Epoxy with different content of fiber. The increase in fiber quantity improves de Tg of the composite.

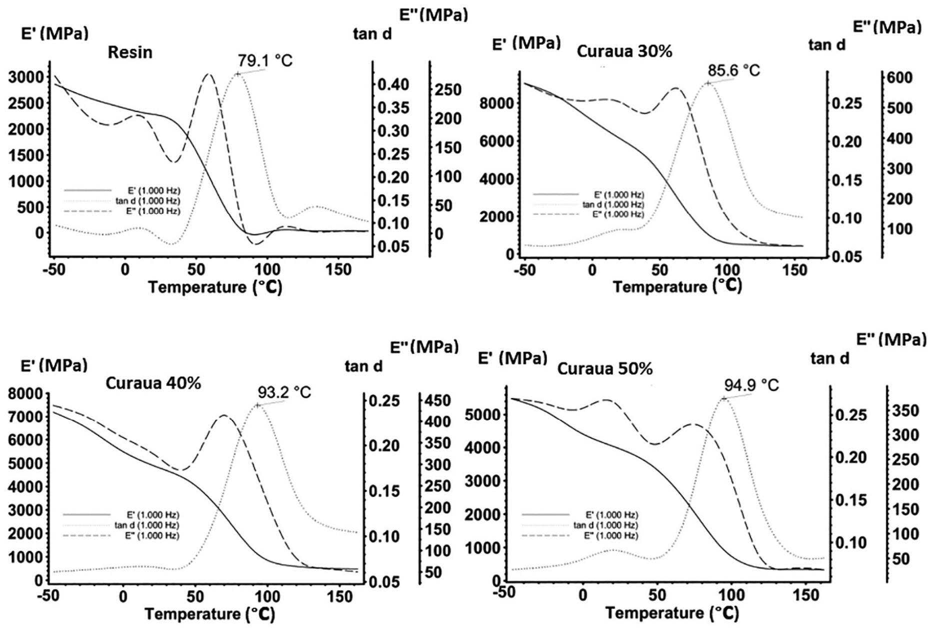

Fig. 3. DMA results of Curaua/Epoxy composite.

Table 4 – DMA results of different content of Curaua fiber.

Property	0	30%	40%	50%
E’ (GPa)	2.20	4.89	3.89	3.29
Tan Delta	0.422	0.276	0.245	0.269
Tg (°C)	79.1	85.6	93.2	94.9

3.2 Treated composites

The tensile and three-point bending test results of composite with Curaua fiber (50% fiber content) treated with different NaOH concentration (1%, 3% and 5 wt%) and immersion time (24, 72 and 168h) are presented in Tables 5 and 6.

Table 5 – Tensile properties of Curaua/Epoxy composite.

	Maximum Tensile Strength (MPa)			Young´s Modulus (GPa)		
	24h	72h	168h	24h	72h	168h
1%	26.90±1.64	28.00±2.59	24.66±2.43	2.86±0.07	2.50±0.11	2.49±0.13
3%	26.99±3.41	28.67±3.82	27.37±1.63	2.87±0.23	2.71±0.26	2.70±0.12
5%	29.21±2.28	30.21±4.28	27.94±0.82	2.89±0.20	2.73±0.13	2.74±0.04

Table 6 – Flexural properties of Curaua/Epoxy composite.

	Maximum Flexural Strength (MPa)			Flexural Modulus (GPa)		
	24h	72h	168h	24h	72h	168h
1%	60.24±4.55	61.62±5.36	57.12±4.05	4.76±0.47	5.03±0.28	4.66±0.38
3%	60.41±2.53	62.97±3.21	59.09±2.54	4.84±0.36	5.03±0.35	4.73±0.41
5%	61.99±6.16	63.30±4.55	59.41±4.14	5.29±0.47	5.74±0.57	4.03±0.44

From Tables 5 and 6 it is visible that the tensile and flexural maximum strength and stiffness are dependent of NaOH concentration and immersion time. As NaOH wt% content increase the tensile and flexural modulus increase and tensile and flexural stiffness also increase. Although the immersion time improves the strength and stiffness of composite, there is an optimal time (72h) where the properties reach their best values, after this period of time occurs the degradation of the Curaua fibers and thus the mechanical properties decrease.

Overall, composites reinforced with Curaua fibers immersed for 72h in a 5% wt% aqueous solution are stiffer and high strength, tensile and flexural, compared to untreated Curaua fiber composites [17].

It can be seen a typical E' dependence on temperature of crystalline material, with the first drop due to the glass transition. High crystallinity is due to high E' value. Table 7 shows the storage modulus (E'), glass transition temperature (Tg) and loss modulus (E'') of Curaua/Epoxy composite with chemical treatment of 1, 3 and 5 wt% NaOH at different immersion periods (24, 72 and 168h).

The increase in NaOH wt% up to 5% and immersion period for 72h improve the storage modulus (E') and unaltered the glass transition temperature (Tg). Higher loss modulus is also observed for the composites reinforced with Curaua fibers immersed in 5% of NaOH for 72h. Loss modulus (E'') or dynamic loss modulus, is related to the predisposition of the material to dissipate energy applied to it [18], a viscous response of the materials. The dynamic loss modulus is often associated with "internal friction" and is sensitive to different kinds of molecular motions, transitions, relaxation processes, morphology and other structural heterogeneities. Therefore, better surface treatment leads to increase fiber/matrix bonding resulting in better mechanical properties.

Table 7 – DMA test results of Curaua fiber composites.

	Storage Modulus E' (GPa)			Glass Temperature T_g (°C)			Loss Modulus E'' (GPa)		
	24h	72h	168h	24h	72h	168h	24h	72h	168h
1%	4.65	5.46	3.91	83.4	89.0	85.3	1.18	1.60	0.98
3%	4.85	6.41	4.12	91.4	70.5	70.7	1.44	1.55	1.03
5%	5.59	6.83	4.31	89.5	89.2	86.9	1.47	1.84	1.30

After all exposure periods, it can be observed that high frequencies led to higher storage modulus, which are related to the composite stiffness.

4. Conclusions

The influence of fiber content in Curaua/Epoxy composites was analyzed. The glass transition temperature assessed by DMA analysis displaying that the values have a strong relation with rigidity of the chemical structure of the matrix. Extreme temperatures -50°C to 180°C were used to evaluate stiffness and phase change of the composite. The composite material exhibited the viscoelastic behavior when shows dependency of test rate. The elastic characteristics related to storage modulus (E') are more evident at higher frequencies. Increase in fiber content increase stiffness, tensile and flexural strength. The results of the mechanical tests presented a good agreement between traditional and DMA flexural tests.

The influence of fiber treatment with NaOH solution in Curaua/Epoxy composites was analyzed. The increase in NaOH content in a chemical solution and the increase in a period of immersion improve the tensile and flexural properties until the optimal time of the 72h, after this time the degradation process of the fibers is more intense. The best NaOH concentration was 5 wt% since it removed all residues of the fibers and exhibited the good mechanical properties.

The DMA analysis shows that the DMA properties have a strong relation to the chemical treatment with NaOH and the immersion time. Extreme temperatures -50°C to 180°C were used to measure stiffness and phase change of the composite. The resultant composite material exhibited the viscoelastic behavior when shows dependence on test rate. The elastic characteristics related to storage modulus (E') are more evident at higher frequencies.

Increase in fiber treatment NaOH concentration increase stiffness, tensile and flexural strength.

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