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Optimal Tensile Properties of Biocomposites Made of Treated Amazonian Curauá Fibres Using Taguchi Method

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Natural fibres have many advantages over synthetic ones, making them attractive for reinforcing polymer materials. This work evaluates the use of an Amazonian plant, namely Curauá (*Ananas erectifolius*), as a reinforcement phase of biocomposites fabricated by cold pressing. Curauá fibres have been shown to be a promising fibre for composite materials, especially due to their higher elastic modulus than other plant species. An L9 Taguchi design is used to investigate the effect of fibre fraction, NaOH concentration and immersion time on the tensile properties of biocomposites. Statistical models are able of predicting and revealing the optimal composition of the biocomposites. The tensile strength of Curauá biocomposites is significantly affected by the fibre fraction, followed by the factors of immersion time and NaOH concentration. High tensile strength is obtained by adding 25 wt.% of Curauá fibres treated under different conditions. There is an interaction between NaOH concentration and the immersion time; a higher concentration requires less time or vice versa to achieve ideal roughness, promoting strong fibre/matrix adhesion.

Keywords: *Biocomposites, Natural fibres, Mechanical properties, Taguchi.*

1. Introduction

The use of natural fibres as reinforcement in composite materials has increased in recent years. The attractive features of natural fibres include low cost, lightweight, high specific modulus, contrary to the health hazards of composites reinforced with synthetic fibres such as glass, carbon and aramid fibres[1]. These advantages place natural fibre composites among high-performance composites with economic and environmental advantages[2,3]. Recently, there has been rapid research growth and innovation in natural fibre composites, especially due to sustainable circular economy requirements. In fact, many biotechnology achievements in materials science and composites have been reported in the literature for several years[4,5]. The most studied natural resources are lignocellulosic fibres. They are biodegradable, abundant and with high technical qualities, such as moderate mechanical properties, low density and low cost, making them suitable candidates for replacing synthetic fibres[6]. Vegetable fibres cover a wide range of applications, from the most traditional to the most complex. They are well known for their importance in the textile industry but have gained increasing participation in reinforcing polymeric materials. In addition, many researchers and various industries have invested in biocomposites for many applications using local natural fibres. On the other hand, vegetable fibres have some disadvantages and challenges to overcome, such as low processing and working temperature, low dimensional stability, variability of mechanical properties, cross-sections of complex geometries, sensitivity to the environmental effects of temperature and humidity, etc[7,8].

Natural fibres have low compatibility with non-polar polymeric matrices and high moisture absorption[9]. In addition, the contact surfaces between phases can act as defects or discontinuities in the material, impairing its properties[10]. To improve the mechanical properties of compounds containing these types of materials, it is necessary to modify the fibre surface through, for example, an alkaline treatment[11,12]. This procedure removes some of the lignin, wax and oils that protect the outer fibre surface, leading to depolymerization

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of the cellulose. This leads to reduced fibre hardness and increased surface roughness, enhancing its adhesion to the polymer matrix[13,14].

Curauá fibres is an Amazonian fibre, which has been little explored in the literature as a reinforcement phase for composite materials. Recent works show its potential for use in polymeric[15-17] and cementitious[18] matrix phases. The hybridisation of Curauá- with glass fibres[16] or aramid[17] has been considered for different applications, such as boats and bulletproof clothing, respectively.

A Taguchi method is used to identify the effects of fibre fraction, alkaline treatment concentration and treatment time factors on the tensile properties of Curauá/epoxybiocomposites. Analysis of Variance (ANOVA) is performed to indicate the largest contributing factor and provide models to estimate the responses within the experimental design.

2. Materials and Methods

Curauá fibres are collected in Santarém, in the State of Pará (Northern Brazil, Amazon region). Curauá fibres are extracted from the leaves of a plant, namely *Ananas erectifolius,* of the bromeliad's family (Figure 1a). A general chemical composition consists of 73.6% cellulose, 9.9% hemicellulose, 7.5 lignin and 0.9% ash[19].

The epoxy resin (2001, bisphenol-epichloridrine) with a density of 1.16 g/cm^3 and the epoxy hardener (3154, benzylic alcohol) with a density of 1.005 g/cm^3 are supplied by Redelease Company (Brazil). A resin/hardener ratio of 2:1 is considered. The datasheet indicates a tensile strength of 20 to 42 MPa.

Taguchi is a robust experimental design that analyses many parameters with a reduced set of experiments, recently implemented to manufacture green compounds[20]. The analysed factors, fibre fraction, solution concentration, and immersion time, are shown in Table 1, corresponding to the Taguchi matrix. A Taguchi design (L9) is used to identify the effect of the factors and levels according to Table 1.

First, the fibres are washed several times and dried in batches, as shown in Figure 1b.

Subsequently, the fibres are subjected to chemical treatment with sodium hydroxide at 2.5, 5.0 and 7.5wt% under different immersion times (2, 4, 6 hours) according to the Taguchi matrix (Table 1).

After removing the fibres from the solutions, they are washed several times with distilled water until reaching a neutral PH. Then, they are left at room temperature for 24 hours and oven-dried at 60°C for 8 hours. The fibres are cooled down in a desiccator and sealed in plastic bags until the composite is manufactured. Afterwards, before placing the fibres in the mould, they are oven-dried at 80°C for 1 hour to eliminate moisture.

The microstructural analysis is conducted using scanning electron microscopy model Zeiss Leo 435VP at 15 kV and 750 times magnification to verify the effectiveness of chemical treatment and surface modification of the fibres. The samples are coated with a thin layer of gold in an SCD 050 Sputter Coater metallizer manufactured by Bal-Tec.

A Shimadzu XRD-6000 X-ray is used to obtain diffractograms and crystallinity index (CI) of untreated and treated Curauá fibre.

The tensile specimens are manufactured in a male-female metal mould to compact the composite material, as shown in Figure 2a. The mould considers a cut-off depth of 3.2 mm, which corresponds to the thickness of the composite, following the protocols of ASTM D638[21]. Five specimens are fabricated for each experimental condition. The female mould is also used to obtain dog-bone shaped samples for unreinforced epoxy polymer without pressing.

A release wax (TecGlaze-N) is spread over the mould surfaces 1:30 hours prior to fabrication. The corresponding amount of resin and hardener is introduced into a Beaker and stirred by mixing for 15 minutes. A layer of polymer is placed in the cavity, followed by the fibres. Subsequently, the rest of the polymer is poured over the fibres. After 15 minutes of gel time, the male mould surface is used to apply a cold uniaxial pressure of 0.8 MPa. Then, the mould is placed in an oven at 60°C for 2 hours post-curing (according to the manufacturer's recommendations). After that, the mould is kept at room temperature for 24 hours to eliminate internal stress levels and then samples are taken from the mould. The treated Curauá fibre composites and reference samples, consisting of unreinforced polymer (Table 2) and untreated

Table 1. Factors and levels of the Taguchi Matrix.

Factor	Type	Levels	Values
A: NaOH (%)	Fixed	3	2.5, 5.0, 7.5
B: Immersion time (H)	Fixed	3	2, 4, 6
C: Fibre fraction (wt%)	Fixed	3	5, 15, 25

Figure 1. Curauá fibre: a) cultivation of curauá[15], b) curauá fibres after washing.

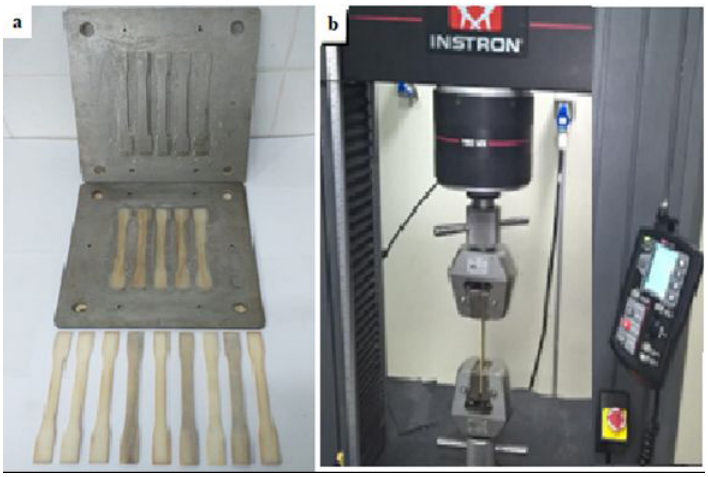

Figure 2. Test bodies manufacturing (a) and tensile testing (b).

Table 2. Tensile strength of composites made with untreated fibres.

NaOH %	Immersion time	wt% fibre	Tensile strength (MPa)
0	0	5	29.33 ±0.42
0	0	15	51.4 ±0.58
0	0	25	73.5 ±0.72

Table 3. L9 Orthogonal Arrays.

Number of tests	NaOH %	Immersion time	wt.% fibre	Tensile strength (MPa)	S/N
Epoxy polymer	-	-	-	25.56±0.44	-
#1	2.5	2	5	34.44 ±0.44	30.7413
#2	2.5	4	15	62.54 ±0.48	35.9232
#3	2.5	6	25	93.7 ±0.81	39.4348
#4	5.0	2	15	64.55± 0.88	36.1979
#5	5.0	4	25	103.62 ±0.94	40.3089
#6	5.0	6	5	58.07 ±0.44	35.2790
#7	7.5	2	25	90.38 ±0.37	39.1214
#8	7.5	4	5	53.81±1.32	34.6173
#9	7.5	6	15	80.64 ±1.2	38.1310

fibre reinforced polymers (Table 3), are manufactured for comparison.

Tensile tests are performed on a universal testing machine (Instron 5984), with a 150 kN load cell and a 5 mm/min speed (Figure 2b). Figure 3 show a schematic drawing representing the experimental procedure.

3. Results and Discussions

Figures 4 and 5 show the micrograph of untreated and treated (with 5% NaOH for 4h) Curauá fibres, respectively, at the same magnification level. Untreated fibres reveal a smooth, compact surface with no fibrillation. In contrast, the treated fibres have a rougher surface, attributed to the chemical degradation of hemicellulose and lignin removal by the alkali treatment[22,23].

Figure 6 shows diffractograms of untreated Curauá fibres and treated with different concentrations of NaOH (at immersion times of 4h). X-ray diffraction shows a similar spectrum profile for untreated and treated fibres considering different NaOH concentrations for 4 hours of immersion time.

The presence of three distinct 2θ peaks at 16°, 22.5° and 35° correspond to the crystallographic planes of cellulose type I (0 0 -1), (0 0 2) and (0 4 0), respectively. The increase in NaOH concentration from 2.5% to 7.5% intensifies these peaks, attributed to removing wax, lignin and hemicellulose. When cellulosic compounds undergo alkaline treatments, there is a rearrangement in the internal structure of the fibre, forming a different type of crystalline structure, i.e., cellulose type I becomes type II, as reported in the literature[24,25].

The experimental data is transformed into a signal-to-noise ratio (S/N) to determine the optimal parameter configuration to maximise tensile properties. As Taguchi's analysis aims to maximise the tensile strength, the S/N ratio criterion chosen is the larger is better (LBT)[26].

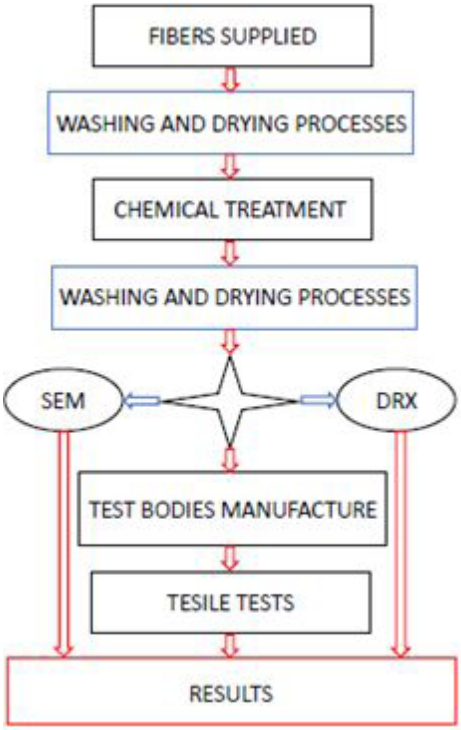

Figure 3. Schematic drawing representing the experimental procedure.

The increase in the amount of untreated fibres produces an increase in tensile strength (Table 2), but to a lesser extent than composites with treated fibres (Table 3). This can be attributed to improved adhesion of the fibres to the matrix phase, amplifying this effect. Based on the strength of epoxy polymer (25.56 MPa, Table 3), an increase of up to 3 times in tensile strength can be achieved due to the incorporation of treated or untreated fibres, revealing their reinforcing effect.

Table 2 also shows the S/N ratios for all experimental conditions. Figure 7 and 8 show the main effect plots of each factor for the mean S/N ratios and the mean tensile strength, respectively. The greater the gradient of the lines, the greater the effect. The effect of the fibre fraction factor is greater than that of treatment factors. A higher percentage of fibre leads to an increase in tensile strength. The results presented in Table 3 also reveal a combined effect between NaOH% and immersion time. A high strength composite can be obtained by combining a lower NaOH concentration with a longer immersion time (#3, Table 3), or a higher NaOH% with a shorter immersion time (#7, Table 3). Taking into account these findings, sample #5 (Table 3), composed of 25% Curauá fibres treated with 5wt.% NaOH for 4 hours can be considered a promising experimental setup since it combines mid-levels of NaOH% and time and a high amount of fibres. Neutralising NaOH solutions before their disposal in nature can be considered an economic and environmental issue. Longer manufacturing times are also avoided to reduce production costs. Furthermore, composites made with a higher amount of fibres and a lower amount of matrix are desired to minimise production costs, especially in natural fibre composites, where the latter is substantially cheaper than a polymer system.

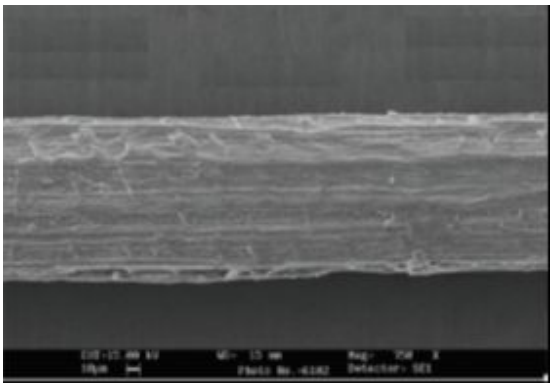

Figure 4. SEM micrograph 750x of untreated Curauá fibres.

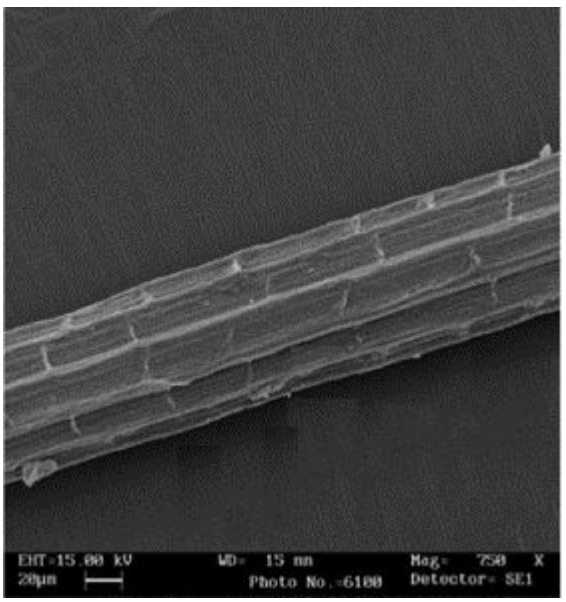

Figure 5. SEM micrograph 750x of treated Curauá fibres with 5% NaOH for 4 h.

All these findings corroborate a strong adhesion of the fibre/matrix interface due to the increase in the surface roughness of the fibres. In other words, the alkaline treatment enhances composite strength by removing or reducing non-cellulosic components (hemicellulose, lignin, pectin, and waxy substances) from the fibres. However, the individual effect of NaOH%, shown in Figure 7, does not reveal any substantial increment in strength from 5wt.% to 7.5wt.%, which suggests a threshold level of NaOH related to excessive alkaline surface wear or weakening of cellulose or its partial degradation.

The effectiveness of the alkaline treatment is evidenced by the SEM micrograph of sample #5 (Figure 5), with a substantial modification of the fibre surface compared to the untreated samples (Figure 4), corresponding to the higher tensile strength shown in Table 3. Beltrami et al.[27] also achieved similar results by treating Curauá fibres with 5% NaOH for 4 hours of immersion. In this case, increases of 30% and 12% in flexural strength and impact resistance, respectively, were obtained for composites of treated fibres.

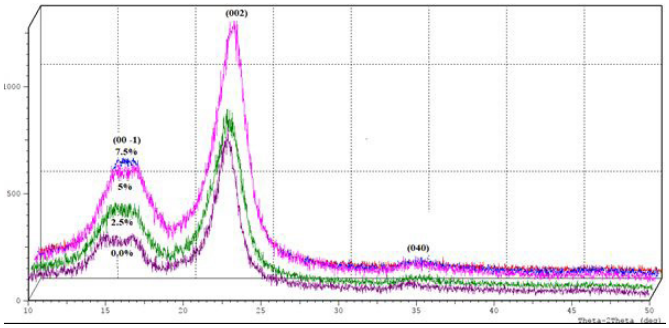

Figure 6. Diffractograms of untreated Curauá fibres and treated with different NaOH concentration (at immersion times of 4h).

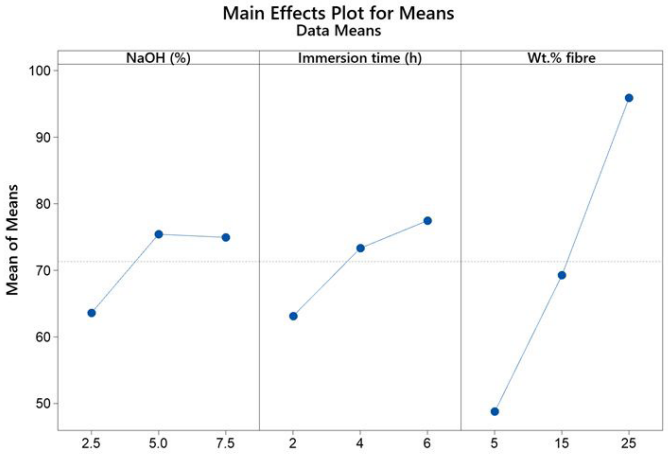

Figure 7. Main effect plots for the mean tensile strength (MPa).

Table 4. Analysis of Variance (ANOVA) of tensile strength.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Regression	3	3834.5	1278.16	51.12	<0.0001
NaOH	1	194.4	194.37	7.77	0.0395
Immersion time	1	308.7	308.74	12.35	0.0170
Wt.% fibre	1	3331.4	3331.38	133.23	<0.0001
Error	5	125.0	25.00		
Total	8	3959.5			
R-sq = 96.84% R-sq(adj) = 94.95% R-sq(pred) = 91.26%					

In addition, DRX diffractograms of untreated and treated Curauá fibres also corroborate the effectiveness of their chemical treatment (Figure 6). Sample #5, corresponding to the highest tensile stress (Table 3), evidences a higher peak in Figure 6, which means an increase in the crystallinity index especially attributed to the removal of wax, lignin and hemicellulose. Oliveira et al.[28] reported the effects of alkaline treatment on coir and Curauá fibre composites. The alkaline treatment increased the crystallinity index from 53% to 67% between pristine and treated coir fibres. Likewise, an increase from 61% to 81% was reported for Curauá fibres. Furthermore, the temperature at which coir fibres started to degrade increased from 255 to 272°C, while Curauá fibres increased from 275 to 314°C. Vilson et al.[29] also reported an increase in the thermal stability of Curauá fibres treated in NaOH solution.

Table 4 shows the ANOVA for tensile strength. P-value less than or equal to 0.05 indicates the factor significantly affects the response. Tensile strength is significantly affected by the factors. F–value indicates the contribution of each factor to the response. Fibre weight fraction (133.23) is the main factor affecting the response, followed by immersion time (12.35) and NaOH concentration (7.77). In addition, the contribution of the error term has been reported to determine whether the results are due to the investigated factors or due to the residual error (Res. error). The model obtained from ANOVA indicates that the coefficient of determination R-Sq of 96.84 shown in Table 3 indicates the data are well fitted in the regression models.

The standardized effect of the factors is examined by preparing a Pareto chart (Figure 9), which depicts the most influential factor in the response. The analysis suggests that

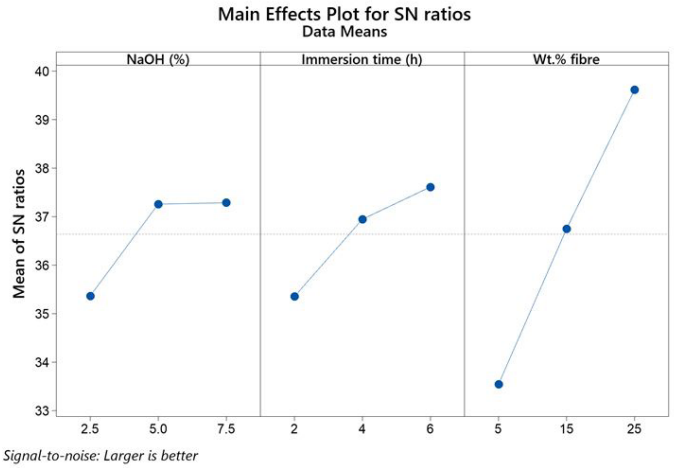

Figure 8. Main effect plots for the mean S/N ratios of tensile strength.

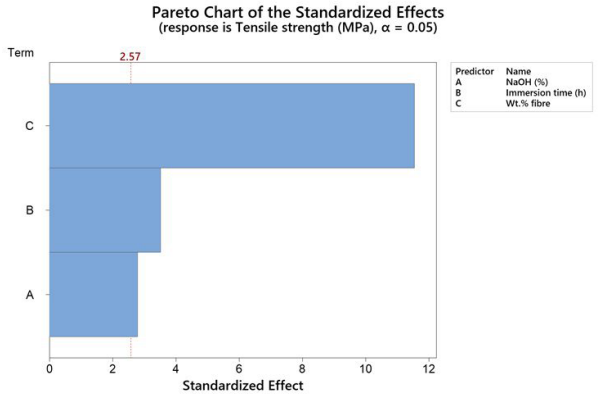

Figure 9. Pareto chart of the standardized effects.

the fibre amount is the most effective factor, significantly contributing to the tensile strength. The other factors show less influence on the strength of Curauá biocomposites. Regression analysis is performed by evolving a mathematical model established in the relationship between the control factors and the output response. This regression model (Equation 1) is notable for predicting tensile strength using new factor levels exclusively within the experiment design setup.

$$Regression\ Equation\ of\ tensile\ stress\ = \\ 10.23\ +\ 2.277\ A +\ 3.59\ B\ +\ 2.356\ C \quad (1)$$

4. Conclusion

Fibre content is the main factor affecting the tensile strength of biocomposites, followed by immersion time and NaOH concentration. The highest tensile strength (103.62 ±0.94 MPa) is obtained when the biocomposites are composed of 25 wt.% of Curauá fibre treated with 5 wt.% NaOH for 4 hours, which represents a 3-fold increase compared to the neat epoxy polymer. Alkaline treatment has been shown to effectively increase adhesiveness between phases and, in turn, strength. Different combinations between NaOH concentration and immersion time allowed to obtain composites with high tensile strength. When the NaOH concentration is high, a shorter immersion time is enough, or vice versa, to obtain high tensile strength. The results imply that above 7.5wt.% of NaOH, a reduction in strength is expected due to the excessive effect of the alkaline treatment.

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