

The Effects of Sodium Carbonate and Bicarbonate Treatments on Sisal Fibre Composites

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This work investigates the effect of eco-friendly chemical treatments on the mechanical and physical properties of composite laminates based on sisal fibres. A 2³1 full-factorial design is conducted to test the influence of chemical solution types, fibre treatment time, and polymer matrix type on the mechanical and morphological characterisation of the composites. Chemical treatments remove impurities from fibre surfaces, and enhance fibre-matrix adhesion. The treatments, especially with sodium carbonate (Na₂CO₃), also progressively reduce the hemicellulose fibre content. Polyester composites made with sisal fibres treated with Na₂CO₃ for 96h achieve enhanced strength and stiffness under tensile, compressive and impact loads. The results evidence the feasibility and efficiency of the proposed eco-friendly treatments for natural fibres and the application of renewable fibre laminates in secondary structural applications.

Keywords: Epoxy, polyester, sisal, sodium carbonate, sodium bicarbonate.

1. Introduction

The need for materials with high mechanical performance with reduced environmental impact has driven several types of research on composites based on bio-sourced components. In addition to their mechanical performance, laminates made with natural fibres, such as flax, jute, sisal, coir and kenaf, are attractive due to their reduced cost, low density, and biodegradability and renewability^{1,2}. However, one of the significant drawbacks of natural fibres is their reduced adhesion to the polymer matrix. Natural fibres are hydrophilic, while polymeric matrices are generally hydrophobic^{3,4}. Despite their limitations, the application of these materials has risen in different sectors, such as the construction and automotive industries. The choice of the polymeric matrix is also an essential aspect of natural fibres laminates performance. The type of polymer is determined according to the degradation temperature of the natural fibres, generally limited to 200°C. Although thermoplastic polymers present improved recyclability, thermosetting polymers possess superior mechanical properties, and some of them can be cured at relatively low temperatures, such as epoxy and polyester⁵.

Sisal is one of the most abundant natural fibres, used in ropes, carpets, handicrafts, textiles and papers. Extracted from leaves of the sisal plant (*Agave sisalana*), the annual production of sisal fibres reached about 4.5 million tonnes, mainly in tropical countries, such as Tanzania and Brazil^{6,7}.

The abundance and high strength of sisal fibres motivated their use as composite reinforcement in several studies⁸.

Several chemical treatments have been applied to enhance fibre-matrix adhesion, such as mercerisation/alkalinisation, grafting, acrylation, acetylation and silanisation. The alkali treatment has been the most used, even though traditional alkali treatments are incredibly harmful to the environment. Eco-friendly mercerisation has been studied in recent years to reduce the environmental impact of treatment chemicals disposal. Fiore et al.⁹⁻¹¹ and Chaitanya and Singh¹² initially proposed sustainable fibre treatments based on sodium bicarbonate (NaHCO₃). Fiore et al.⁹ applied a statistical approach and the Weibull distribution to analyse the tensile performance of sisal fibres. The treatment with sodium bicarbonate for 24, 120, 240 hours increased the fibre elastic modulus by 63.23%, 115.01% and 138.44%, respectively. In contrast, sisal-fibre-reinforced PLA composites achieved an increase in tensile and flexural moduli of 48.8% and 39.3%, respectively, considering 72 hours of treatment with sodium bicarbonate¹².

Furthermore, Santos et al. studied the effect of sodium carbonate (Na₂CO₃)¹³ and sodium bicarbonate on the properties of coir fibres¹⁴. Both carbonates act as mild alkali in aqueous solutions and can be handled safely. Both alkali solutions release sodium (Na⁺) and hydroxide (OH⁻) ions. The OH groups present in fibres correspond mainly to alcoholic hydroxyls (weak acids). The breakdown of NaHCO₃ and Na₂CO₃ into hydroxide ions and carbonic acid in the presence of water renders a mild and strong

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alkaline nature for the aqueous solution, respectively^{9,12-15}. Therefore, it is expected that aqueous solutions of NaHCO_3 and Na_2CO_3 behave similarly to the NaOH solution while reacting with lignocellulose fibres, as shown for sisal^{9,12}, kenaf¹⁰, flax¹¹ and coir¹³⁻¹⁴ fibres. However, both alkaline solutions generally take longer than highly alkaline sodium hydroxide solutions¹², usually between 24 and 120 hours, to achieve the desired results.

This work investigates the effects of sodium bicarbonate and sodium carbonate eco-friendly treatments of sisal fibres on the mechanical properties of composite materials. Thermosetting polymers (epoxy and polyester) are used as a matrix phase to prevent damage to the natural fibres caused by thermoplastic fabrication, such as high temperature and compaction levels. Post-treatment morphological analyses are conducted on the fibres, and quantitative results are assessed statistically using the Design of Experiment (DoE) and ANOVA techniques.

2. Materials and Methods

2.1. Materials

Commercially available sisal fibre mats are supplied by Sisal Sul (São Paulo – Brazil). The matrix is based on two polymers: epoxy resin (Renlan M and hardener HY 956) and polyester resin with MEK (methyl-ethyl acetone) catalyst supplied by Huntsman (Brazil) and Reichhold (Brazil), respectively. Powdered sodium bicarbonate (NaHCO_3) and carbonate (Na_2CO_3) are sourced by Synth (Brazil) and Solvay (Brazil), respectively.

2.2. Design of experiments

A full-factorial design of experiments ($2^3 1$) is carried out to identify the effects of treatment type (NaHCO_3 and Na_2CO_3), treatment time (24 h, 96 h, 168 h), and polymer type (epoxy and polyester) on the mechanical properties of

sisal fibre laminates. The twelve experimental conditions are summarised in Table 1. The effect of each factor on the response is evidenced by the p -value obtained using the Minitab v.18 statistical software. A p -value less than or equal to 0.05 indicates that an individual factor or interaction is statistically significant considering a 95% confidence interval. An interaction indicates that the effect of a particular factor depends on the level of another factor. Two reference conditions based on untreated sisal fibre reinforced epoxy (REF 1) and polyester (REF 2) are also tested and compared to other conditions using Tukey's mean comparison test.

The predictability of the statistical model is determined by the value of R^2 (adj). A model with greater predictability is indicated with an R^2 (adj) close to 100%. The DoE findings are valid only for data that follow the normal distribution. The normality of the residuals is verified with the Anderson–Darling test. A p_{AD} -value greater than 0.05 indicates that the data followed a normal distribution, validating the DoE results¹⁶.

2.3. Manufacturing and testing

The sisal fibres are treated to remove dirt and ensure better bonding to the polymer. The aqueous solutions of 10% (w/v) Na_2CO_3 and NaHCO_3 ¹²⁻¹⁴ are stirred for 5 and 30 minutes, respectively, until total homogenisation. Table 2 presents the main characteristics of treatment solutions. The sisal fibres (as received) are soaked in the aqueous solutions at room temperature ($\sim 23^\circ\text{C}$). The fibres are removed at different time intervals (24, 96 and 168 h) and subsequently washed in running water at room temperature^{13,14}. The treated sisal fibres are oven-dried at 60°C for 5 hours. The dry fibres are stored in plastics bags until the composite is manufactured.

After treatment, sisal fibre-reinforced epoxy (SFRE) and polyester (SFRP) composites are manufactured with a fibre volume fraction of 30%. This fibre volume fraction was set based on several preliminary tests to achieve a smooth surface without macropores. The grammage of sisal fibre is determined

Table 1. Experimental conditions, full-factorial design ($2^3 1$).

Conditions	Matrix Type	Treatment Type	Treatment Time (h)
C1	Epoxy	NaHCO_3	24
C2	Epoxy	NaHCO_3	96
C3	Epoxy	NaHCO_3	168
C4	Epoxy	Na_2CO_3	24
C5	Epoxy	Na_2CO_3	96
C6	Epoxy	Na_2CO_3	168
C7	Polyester	NaHCO_3	24
C8	Polyester	NaHCO_3	96
C9	Polyester	NaHCO_3	168
C10	Polyester	Na_2CO_3	24
C11	Polyester	Na_2CO_3	96
C12	Polyester	Na_2CO_3	168

Table 2. Na_2CO_3 and NaHCO_3 solutions characteristics.

Solution	pH	[OH]	Counterion
Na_2CO_3	11.80	6.42×10^{-3}	[Na+] = 1.868
NaHCO_3	8.30	2.04×10^{-3}	[Na+] = 1.190

as 900 g/cm^2 ¹⁷. A hybrid manufacturing process consisting of hand lay-up and uniaxial cold pressing is considered. This method is based on the procedures adopted by Santos and Oliveira et al.^{13,17-18}. Two sheets of waxed aluminium are used for the compaction process. An aluminium sheet is placed into a metal mould ($310 \times 310 \times 4 \text{ mm}^3$), being covered with a thin film of resin (40% of the total matrix mass) (Figure 1a). Such an initial polymer layer is applied to the mould surface to ensure surface wettability of the fibres and a proper composite surface finish, free of voids or imperfections. Then, the sisal fibre mat and the remaining polymer system are added to the mould (Figure 1b). The second aluminium sheet is laid over the fibres, and the metal mould is closed under a uniaxial pressure of 645 kPa (Figure 1c). The lid is fixed by steel bars to ensure sample thickness and applied pressure. The $310 \times 310 \times 2.5 \text{ mm}^3$ sandwich panels are removed after 15 hours and subsequently post-cured for 14 days in sealed bags to protect against moisture (Figure 1d).

After curing, the laminates are cut to specific sizes using a band saw (Makita LB1200F) to standard test dimensions. No coolant is used in cutting. Due to the low thickness of the laminates and random fibre orientation, no heat degradation or delamination is observed after cutting. Tensile, flexural, and compression tests are conducted on a Shimadzu AGX-Plus Universal Machine with a 100 kN load cell. Six (6) $250 \times 25 \times 2.5 \text{ mm}^3$ tensile samples are tested for each condition using a video-extensometer for strain measurement following ASTM D3039¹⁹. The flexural tests are performed according to ASTM D790²⁰, with samples 13 mm wide and 32 times

longer than the specimen thickness. Twenty (20) bending samples are tested for each experimental condition. The compressive test is performed using $90 \times 15 \times 2.5 \text{ mm}^3$ samples following the ASTM D6641/D6641M standard²¹. Based on ASTM standard protocols¹⁹⁻²¹ and other works reported in the literature^{12-13,17-18}, tensile, bending and compression tests are conducted at 2 mm/min. The impact test is performed on twenty (20) samples for each condition. $80 \times 10 \times 2.5 \text{ mm}^3$ samples are tested following ISO 179-1 guideline²² at 15 J impact energy on a Charpy Impact Tester (XJJ Series). Tests are conducted at controlled temperature ($\sim 23^\circ\text{C}$) and humidity (55-58%). The fracture mode of sisal-based composites is analysed with a Hitachi TM 3000 microscope.

The effect of chemical treatments on the surface of sisal fibres is observed in backscattered electron images obtained by scanning electron microscopy (Philips XL-30 FEG). FTIR Spectroscopy and X-ray diffraction are used to assess the removal of surface compounds and crystalline structures. Untreated and treated sisal fibre bundles are aligned and lacerated into micro-segments for FTIR and X-ray diffraction measurements. FTIR spectra are acquired using a Shimadzu IR Prestige-21 spectrometer with an attenuated total reflection (ATR) probe. Each sample is scanned from 4000 to 400 cm^{-1} wavelength with a 4 cm^{-1} resolution. X-ray diffraction is analysed using a Rigaku Ultima IV X-ray diffractometer operating with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). Diffraction patterns are obtained for 2θ values ranging from 5 to 40° in continuous scan mode at $1^\circ/\text{min}$. The crystallinity index (I_c) of the samples is calculated using Equation 1. I_{002} is the maximum diffraction intensity in the crystallographic

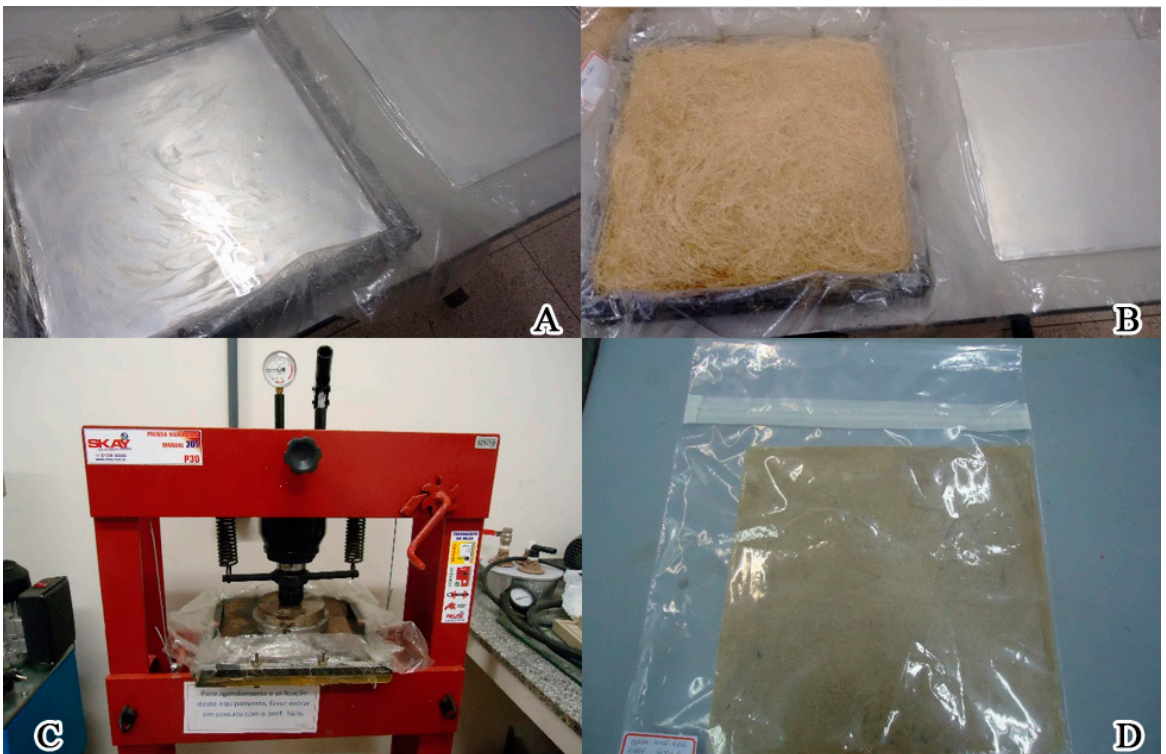


Figure 1. Manufacturing process steps: a) mould with aluminium surfaces covered by resin; b) sisal embedded with epoxy inside the mould; c) compaction pressure; d) composites sealed with bags (post-curing process).

plane (002) at an angle 2θ between 22° and 23° . I_{am} is the diffraction intensity of the amorphous material taken at a 2θ angle between 18° and 19° , where the intensity is minimal.

$$I_C = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

The thermal degradation of raw and treated sisal fibres is evaluated with varying treatment times, using a Shimadzu DTG-60H differential thermal analyser. Analyses are carried out under a nitrogen atmosphere at a constant flow (~ 100 mL/min), a heating rate of $10^\circ\text{C}/\text{min}$ and a temperature range of 30 to 800°C .

3. Results

The mechanical results of sisal fibre-based laminates are shown in Table 3. Mean values and standard deviations for tensile modulus (E_T) and strength (σ_T), flexural modulus (E_F) and strength (σ_F), impact resistance (S_I) and compressive strength (σ_C) are reported for each DoE condition in Table 3. Additionally, reference conditions (laminates with untreated fibres) and responses for pristine epoxy and polyester

polymer are included in Table 3. Fibre inclusion increases the stiffness and impact resistance of sisal fibre composites compared to pure polymers. In contrast, composite strength exhibits a non-regular trend compared to matrix strength. The DoE responses obtained in mechanical tests are statistically analysed using the Analysis of Variance (ANOVA) technique. The ANOVA results are shown in Table 4. P-values less than 0.05 indicate that most responses are affected by a third-order interaction of the factors, except tensile strength and stiffness. The results of R^2 (adj) range from 91.33 to 97.09% , indicating excellent predictability of the subjacent statistical model used. Anderson–Darling tests also indicate p_{AD} -values greater than 0.05 for all responses, ensuring the validity of the ANOVA¹⁶. P-values in italics (Table 4) correspond to factors or interactions analysed using effect plots. When higher-order effects are significant, only interactions are analysed.

3.1. Tensile properties

Tensile modulus is affected only by the main factors, as shown in Table 4. The main-effect plots for the tensile modulus of sisal fibre composites are shown in Figure 2. Reference lines for untreated sisal fibre polyester (USFPC) and epoxy

Table 3. Mechanical properties of polymers and sisal based -epoxy and -polyester composites. The standard deviation is presented in parentheses.

Matrix phase	Fibre Reinforcement	E_T	σ_T	E_F	σ_F	S_I	σ_C
		[GPa]	[MPa]	[GPa]	[MPa]	[kJ/m ²]	[MPa]
Epoxy	Untreated	3.70 (0.02)	26.00 (0.86)	2.89 (0.14)	53.77 (1.47)	21.33 (0.15)	69.55 (6.20)
	NaHCO₃ - 24 h	4.70 (0.01)	34.04 (0.64)	3.13 (0.16)	58.41 (2.57)	20.82 (0.18)	63.74 (1.82)
	NaHCO₃ - 96 h	5.23 (0.34)	36.94 (0.46)	3.44 (0.04)	63.55 (0.62)	27.58 (0.69)	62.09 (2.96)
	NaHCO₃ - 168 h	3.86 (0.10)	31.80 (0.82)	2.88 (0.05)	55.71 (0.54)	22.06 (0.08)	48.82 (1.08)
	Na₂CO₃ - 24 h	5.12 (0.08)	37.73 (0.90)	3.44 (0.03)	60.72 (1.17)	18.93 (0.62)	69.00 (1.05)
	Na₂CO₃ - 96 h	5.76 (0.46)	38.74 (1.60)	3.80 (0.07)	65.76 (1.06)	19.69 (0.84)	73.45 (3.01)
	Na₂CO₃ - 168	4.50 (0.14)	30.61 (0.83)	3.04 (0.05)	59.52 (1.27)	18.47 (0.17)	64.03 (0.40)
	Polyester	Untreated	4.52 (0.19)	31.22 (3.17)	3.11 (0.05)	45.00 (1.94)	20.51 (0.36)
NaHCO₃ - 24 h		5.64 (0.15)	26.72 (0.86)	3.19 (0.12)	50.38 (1.83)	23.05 (0.97)	66.84 (0.98)
NaHCO₃ - 96 h		5.68 (0.29)	30.78 (0.92)	3.82 (0.16)	59.38 (0.99)	28.94 (0.16)	78.83 (0.84)
NaHCO₃ - 168 h		5.17 (0.25)	29.52 (1.95)	3.67 (0.15)	57.11 (1.48)	22.91 (0.53)	66.03 (5.24)
Na₂CO₃ - 24 h		6.23 (0.09)	34.83 (0.59)	3.96 (0.02)	67.59 (0.39)	22.76 (0.91)	80.71 (0.10)
Na₂CO₃ - 96 h		6.50 (0.14)	39.81 (0.36)	3.97 (0.05)	69.39 (2.18)	26.41 (0.23)	83.79 (0.20)
Na₂CO₃ - 168		5.39 (0.08)	36.15 (0.40)	3.78 (0.08)	57.34 (2.19)	23.48 (0.08)	79.80 (0.46)
Neat epoxy polymer		2.24 (0.11)	47.29 (2.00)	2.14 (0.04)	69.28 (3.9)	8.74 (1.4)	65.76 (1.88)
Neat polyester polymer	2.44 (0.14)	39.82 (3.00)	2.19 (0.08)	55.83 (2.90)	5.81 (0.31)	83.53 (3.02)	

Table 4. ANOVA (DoE) results for mechanical tests.

Factors and interactions		Tensile modulus	Tensile strength	Flexural modulus	Flexural strength	Impact strength	Compressive strength
P-Value	Matrix type (MT)	0.000	0.000	0.000	0.000	0.538	0.000
	Treatment type (TTy)	0.000	0.000	0.000	0.000	0.000	0.000
	Treatment Time (TTi)	0.000	0.000	0.000	0.000	0.000	0.000
	MT*TTy	0.946	0.000	0.391	0.000	0.001	0.884
	MT*TTi	0.082	0.000	0.000	0.132	0.266	0.003
	TTy*TTi	0.519	0.014	0.004	0.000	0.000	0.026
	MT*TTy*TTi	0.241	0.216	0.011	0.016	0.001	0.012
R^2 (adj)		91.33%	94.26%	93.47%	94.00%	97.09%	95.50%
A.D. (P-Value ≥ 0.05)		0.931	0.151	0.628	0.124	0.583	0.287

(USFEC) composites are added to this plot, revealing that both treatments are able to enhance the material stiffness. The polyester-based composites consisting of fibres treated with Na_2CO_3 for 96 hours have the highest modulus. Polyester-based composites exhibit 18.72% higher tensile modulus than epoxy-based composites (Figure 2, plot i), while conventional sodium bicarbonate treatment reduces its stiffness by 9.68% (Figure 2, plot ii) compared to the sodium carbonate treatment. The longer treatment time increases stiffness by 6.83% for up to 96 hours, presenting a significant drop of 18.31% for 168 hours (Figure 2, plot iii). Enhanced results for treatments up to 96 hours agree with previous findings, which indicated that treatments longer than 96 hours induce microstructural fibre damage and losses in lignin chains¹³. The tensile modulus improvement was also obtained by

Chaitanya and Singh¹² using sodium bicarbonate solution treatment. The alkaline treatment modifies the fibre surface due to the removal of external compounds, such as cellulose and hemicellulose, which causes a greater exposure of lignin (a natural phenolic polymer²³), and, consequently, makes it more compatible with polyester-based composites^{13,24}. The increased stiffness of polyester composites can be attributed to a better transfer of stresses between the polyester matrix and the stiff sisal fibres¹².

Tensile strength is affected by the main and second-order interaction effects, as shown in Table 4. Figure 3 (plot i) shows that epoxy-based composites consisting of fibres treated with NaHCO_3 provide 18.14% higher strength than polyester composites. In contrast, the alternative treatment with sodium carbonate (Na_2CO_3) increases the strength of

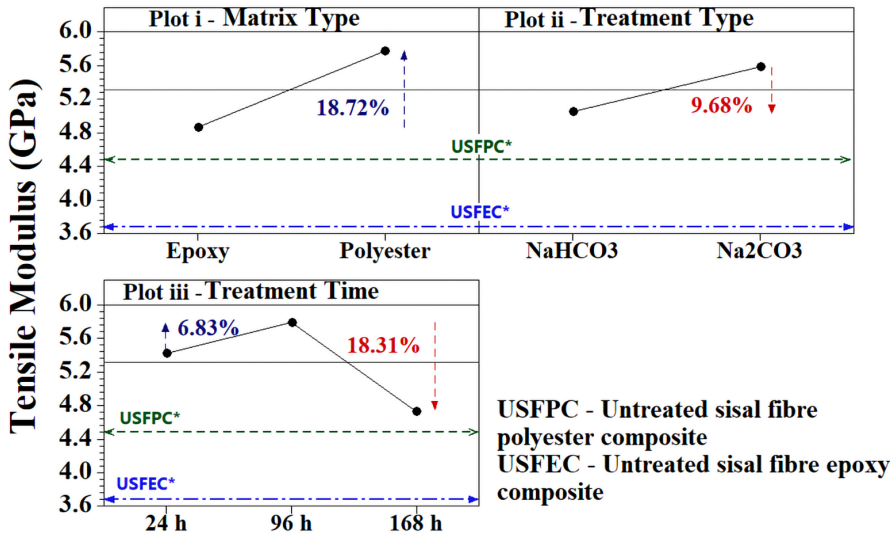


Figure 2. Main effect plots for the mean tensile modulus.

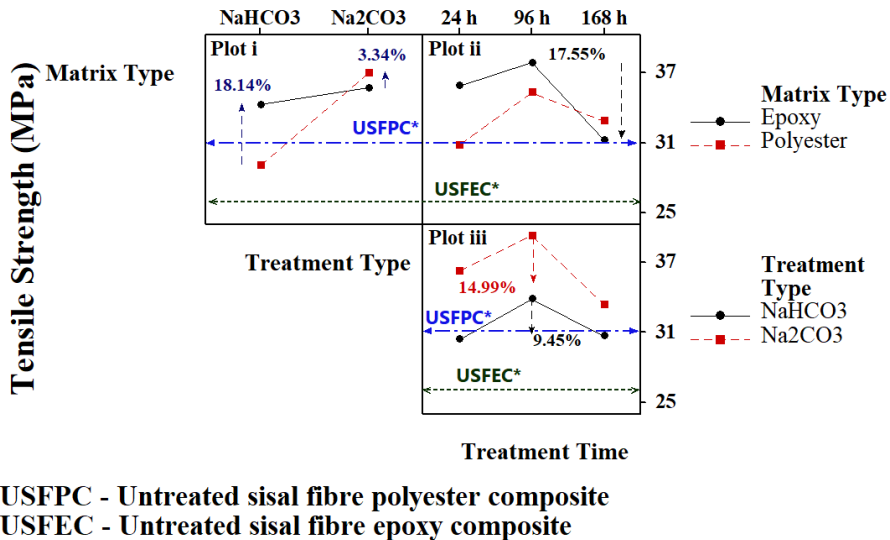


Figure 3. Tensile testing plots for DoE: tensile strength interaction plots for i) Matrix type x Treatment Type; ii) Matrix type x Treatment time, and iii) Treatment Time x Treatment Type.

polyester-based laminates, as shown in Figure 3 (plot i). The 96-hour exposure time provides improved strength for both polymers, as shown in Figure 3 (plot ii). Fibre degradation, due to the longer exposure time, is more pronounced in the epoxy polymer, reaching the lowest strength observed after a drop of 17.55% (Figure 3, plot ii). Similar behaviour is observed for both solutions considering different treatment times (Figure 3iii). Laminates fabricated with treated fibres using Na_2CO_3 for 96 hours presented increase strength. The reference lines for USFPC and USFEC shown in Figures 3i and 3iii reveal that the NaHCO_3 solution slightly impairs the tensile strength of composites made with the polyester matrix. According to Santos et al.¹³, the fibre-to-fibre stress transfer at fibre intersections is crucial in a random network system of composite fibres. Waxes can enhance fibre slide at fibre intersections. Thus, removing wax layers and other impurities with both sodium carbonate and bicarbonate solutions may improve the axial stress transfer, hence the composite strength. Sodium carbonate establishes a more aggressive alkaline environment (pH 11.80) than sodium bicarbonate (pH 8.30) and more deeply remove more external layers of the fibre. This behaviour will be discussed in more detail in Section 3.5.

3.2. Flexural testing

Flexural properties also exhibit significant third-order interactions with P-values below 0.05. The third-order interaction plots for flexural strength and stiffness are shown in Figure 4. Based on the reference lines (USFPC and USFEC), all treatment settings are beneficial for bending properties. Higher strength and stiffness values are obtained, for both matrices, when sisal fibres are treated with sodium carbonate. Polyester based composites have 14.04% and 4.48% higher flexural stiffness and strength, respectively, than epoxy laminates (Figure 5a plot i). It is noteworthy that the Na_2CO_3 fibre treatment hinders the impact performance of epoxy composites when compared to the baseline USFEC. The treatment time factor presents similar behaviour for both polymers, reaching higher results for fibres treated for 96 h (Figure 5a plot ii). While the flexural and tensile properties exhibit better interaction for sodium carbonate and 96h treatment time, impact resistance presents better results for sodium bicarbonate. Panels made with fibres treated with sodium bicarbonate have 22.60% enhanced strength for 96 h treatment compared to Na_2CO_3 (Figure 5a plot iii). Fibre treatment with Na_2CO_3 improves the bonding interface between the reinforcement and matrix, as discussed in Figure 4a (plot iii), affecting the failure mode, especially under dynamic loads²⁵. Rather than a pull-out mechanism, sample failure is characterised by fibre rupture¹³⁻¹⁴, which significantly reduces the amount of energy absorbed during impact, especially after fibre treatment with sodium carbonate. Similar behaviour was obtained by Santos et al.¹³ using sodium carbonate treatment and coir fibres reinforced composites.

chemical solution. Higher increments are observed for both strength (14.87%) and stiffness (18.05%) for sodium bicarbonate compared to sodium carbonate up to 96h (Figure 4a,b, plot iii). Longer treatments with sodium carbonate, on the other hand, are more harmful to fibres (higher alkalinity), with reductions of up to 12.37% (stiffness) and 13.53% (strength) (see Figure 4a and 4b, plot iii).

The increase in sisal fibre modulus with sodium bicarbonate^{9,12} and sodium carbonate reflects on higher flexural modulus of the epoxy and polyester composites¹³⁻¹⁴. The flexural strength is influenced by the fibre-matrix interface^{9,12-15}. The enhancement in fibre roughness and the removal of surface waxes and impurities improve fibre-matrix adhesion. The consequent more efficient energy distribution along the surfaces leads to an increase in the load to failure of the composites, and higher flexural strength.

3.3. Impact testing

Impact resistance reveals a third-order interaction effect, as shown in Figure 5. Compared to NaHCO_3 , the treatment with Na_2CO_3 shows a slight reduction in impact resistance for polyester composites and a considerable reduction (18.99%) for epoxy laminates (Figure 5a plot i). It is noteworthy that the Na_2CO_3 fibre treatment hinders the impact performance of epoxy composites when compared to the baseline USFEC. The treatment time factor presents similar behaviour for both polymers, reaching higher results for fibres treated for 96 h (Figure 5a plot ii). While the flexural and tensile properties exhibit better interaction for sodium carbonate and 96h treatment time, impact resistance presents better results for sodium bicarbonate. Panels made with fibres treated with sodium bicarbonate have 22.60% enhanced strength for 96 h treatment compared to Na_2CO_3 (Figure 5a plot iii). Fibre treatment with Na_2CO_3 improves the bonding interface between the reinforcement and matrix, as discussed in Figure 4a (plot iii), affecting the failure mode, especially under dynamic loads²⁵. Rather than a pull-out mechanism, sample failure is characterised by fibre rupture¹³⁻¹⁴, which significantly reduces the amount of energy absorbed during impact, especially after fibre treatment with sodium carbonate. Similar behaviour was obtained by Santos et al.¹³ using sodium carbonate treatment and coir fibres reinforced composites.

3.4. Compressive testing

A third-order interaction effect is evidenced for the compressive strength, as shown in Table 4. The summary of

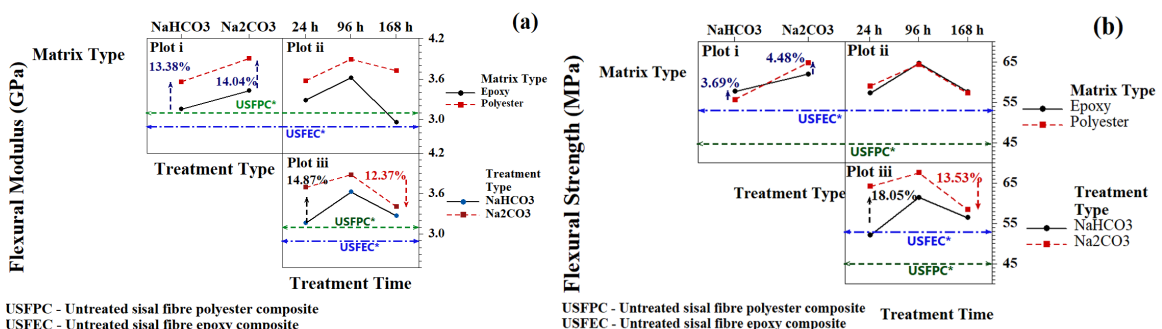


Figure 4. Flexural testing plots for DoE: interaction plots for flexural a) modulus and b) strength.

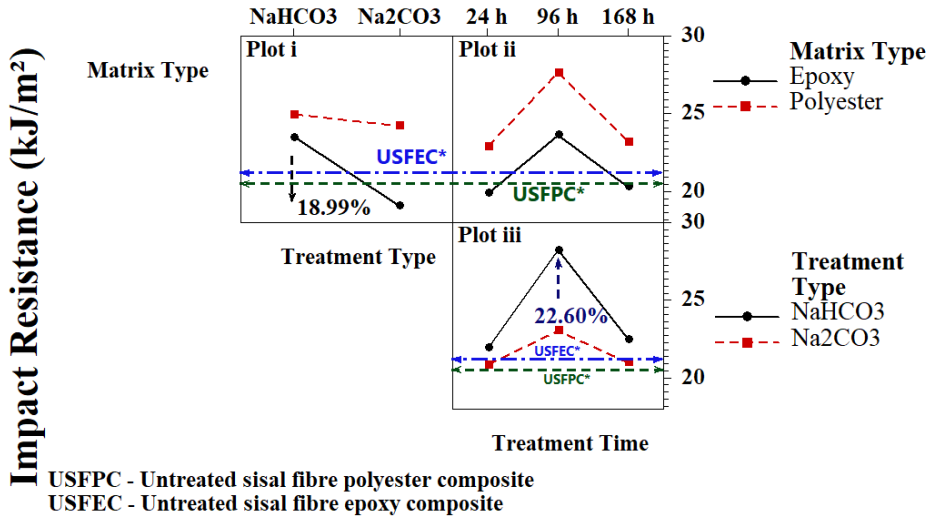


Figure 5. Impact testing (out of plane) interaction plot.

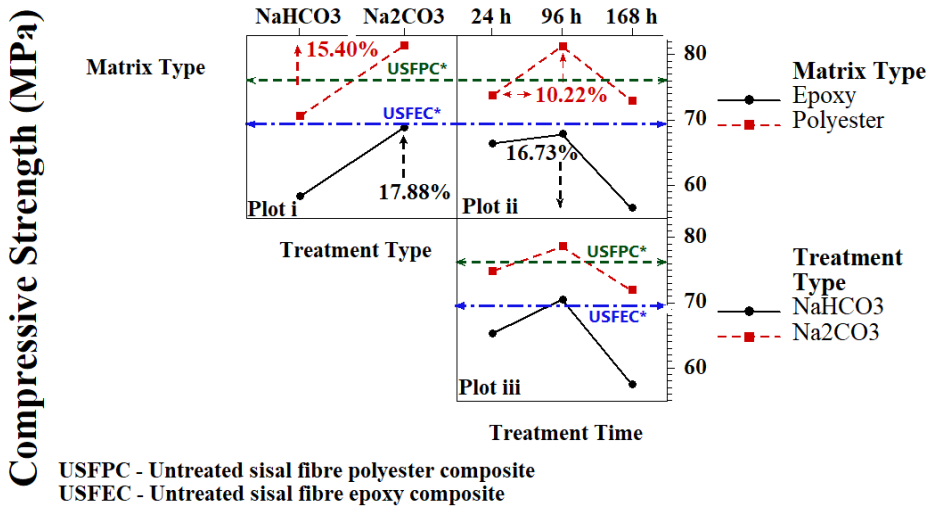


Figure 6. Compressive strength, interaction plots.

interactions is shown in Figure 6. The compressive strength is 15.40% and 17.88% higher for composites (both polymers) made from sisal fibres treated with sodium carbonate (see Figure 6 plot i) relative to sodium bicarbonate. However, fibre treatment is only favourable when combining Na_2CO_3 and polyester composites, as revealed by the reference conditions (USFPC and USFEC) made with untreated fibres (plot i). The treatment time factor is more favourable at 96 h, mainly for polyester polymer laminates (increment of 10.22%, plot ii). Epoxy-based composites show a significant reduction (up to 16.73%) when the fibres are subjected to longer treatments (Figure 6.ii). Both treatments reveal improved strength when the fibres are treated for 96 h (Figure 6 plot iii). The compressive behaviour is dominated by the mechanical properties of the matrix in fibre-reinforced composites. Polyester composites reveal higher compressive strength

since polyester presents superior compressive strength compared to epoxy (Table 3).

3.5. Fracture analysis

The typical fracture of the composites after tensile, bending, impact and compression tests are shown in Figure 7 from left to right for different conditions: (a-b) untreated sisal fibre composites, (c-d) NaHCO_3 -treated fibre composites and (e-f) Na_2CO_3 -treated fibre composites. The fracture modes obtained for all samples are very similar for each test set. Tensile specimens are split into two halves (left), while compressive samples reveal only an apparent crack (right). The bending and impact samples are substantially bent after testing, but, in most cases, fibres hold them as a single piece.

Figure 8 shows the fractures of tensile samples made from Na_2CO_3 treated fibres with (a) polyester and (b) epoxy matrices. There is no significant difference between them;

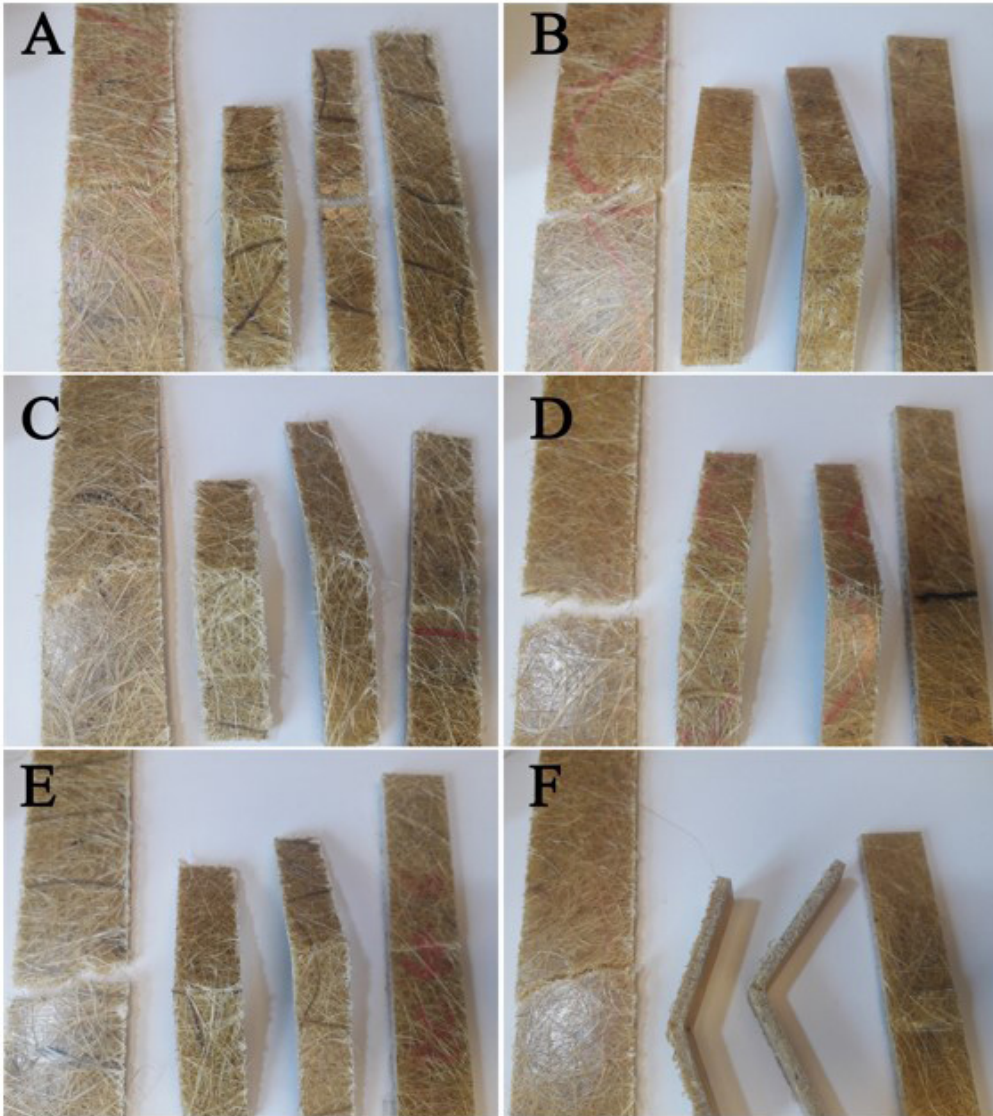


Figure 7. Typical composite fractures composed of (a) untreated fibres and polyester, (b) untreated fibres and epoxy, (c) NaHCO₃-treated fibres and polyester, (d) NaHCO₃-treated fibres and epoxy, (e) Na₂CO₃-treated fibres and polyester and (f) Na₂CO₃ treated fibres and epoxy for tensile, bending, impact and compressive samples as shown from left to right.

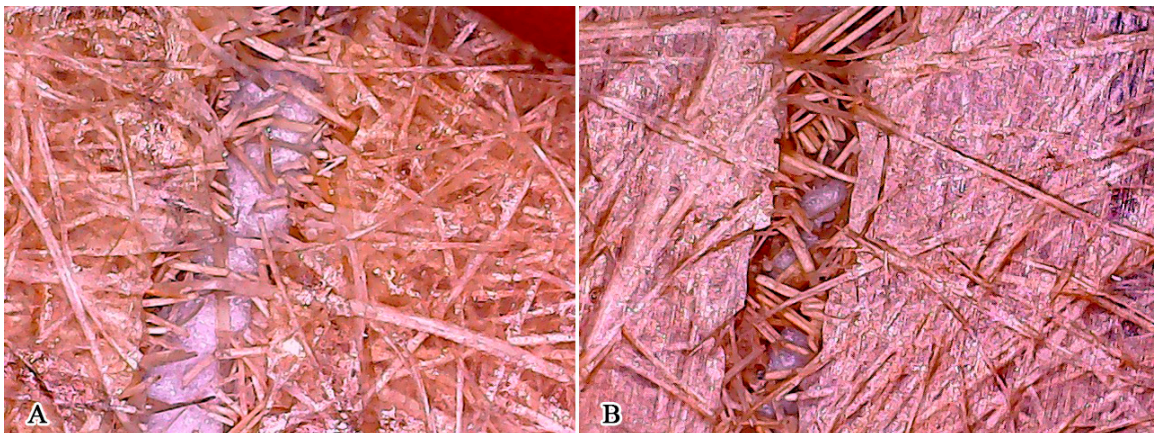


Figure 8. Tensile fractures of (a) polyester and (b) epoxy composites composed of treated fibres with Na₂CO₃ for 96h.

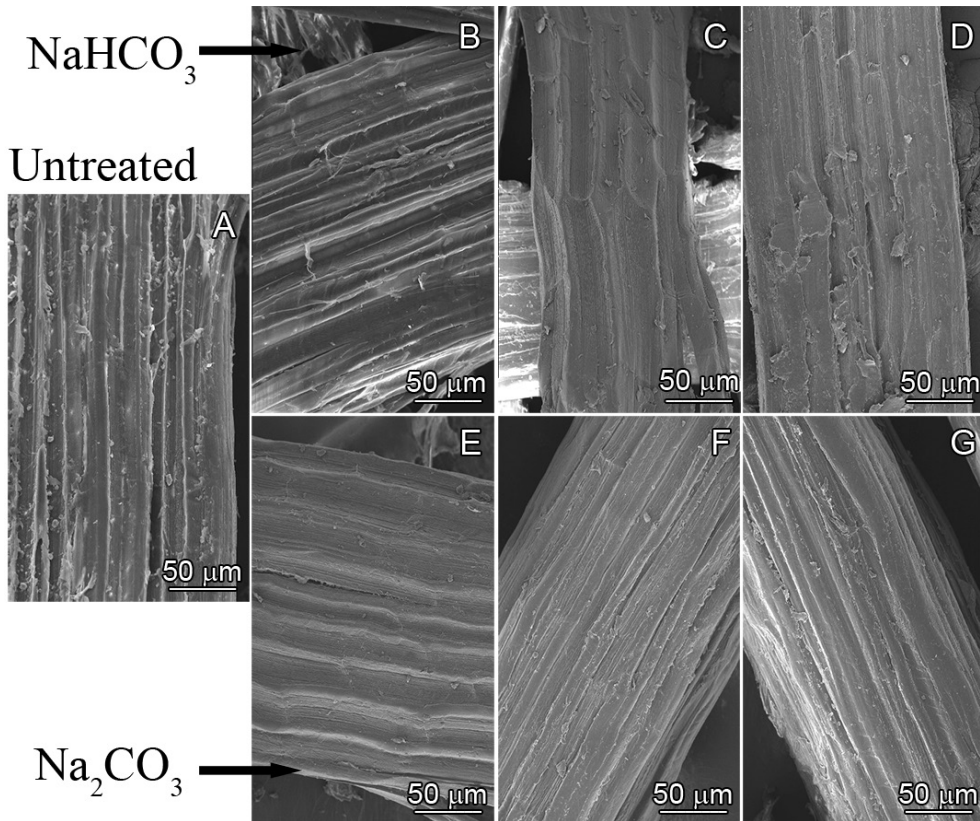


Figure 9. SEM images of sisal fibres: a) untreated; treated with NaHCO_3 b) 24 h, c) 96 h and d) 168h; treated with Na_2CO_3 e) 24 h, f) 96 h and g) 168 h.

fibre pull-out and matrix rupture are mainly evidenced. In general, a greater amount of matrix in the rupture region is obtained by epoxy composites, attributed to their enhanced surface adhesion.

3.6. SEM, FTIR, X-ray diffraction and thermal analysis

SEM micrographs of untreated and treated sisal fibres are shown in Figure 9. Untreated fibres exhibit noticeable surface impurities (Figure 9a), e.g., natural waxes and oils, as reported in the literature⁹. In the manufacturing process of the composite laminates, impurities negatively affect the adhesiveness with the polymer matrix¹⁰. Figures 9b to 9g show the surfaces of sisal fibres after different treatment settings. In general, micrographs do not show any detectable impurity on the fibre surface due to the cleaning effect of both solutions. With sodium carbonate treatment at intermediate exposure times, greater surface roughness is obtained, which justifies the greater adhesion and mechanical properties of fibrous composites treated with Na_2CO_3 .

Comparative FTIR spectra in the range of 400–2.250 cm^{-1} of untreated and treated (NaHCO_3 and Na_2CO_3 solutions) sisal fibres with varying treatment times (24, 96 and 168 h) are shown in Figure 10. The letter “a” represents the spectrum of untreated sisal fibres. The characteristic peaks around 1.735 and 1.245 cm^{-1} indicate the presence of hemicellulose in the fibre composition^{12,26}. The intensity of hemicellulose-related peaks shows marginal reduction for conditions

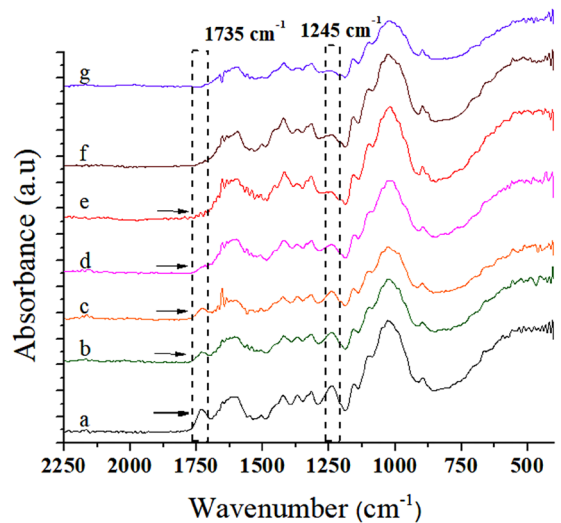


Figure 10. Comparative FT-IR analysis of sisal fibre: a) untreated; treated with NaHCO_3 for b) 24 h c) 96 h and d) 168 h; treated with Na_2CO_3 for e) 24 h f) 96 h and g) 168 h.

treated with NaHCO_3 for 24 and 96 h (Figure 10b and c). Peak reduction is more evident after 168 h of treatment (Figure 6d). Chaitanya et al.¹² and Santos et al.¹⁴ also reported similar FTIR findings for NaHCO_3 -treated sisal and coir fibres, respectively. Na_2CO_3 intensifies the peak reduction

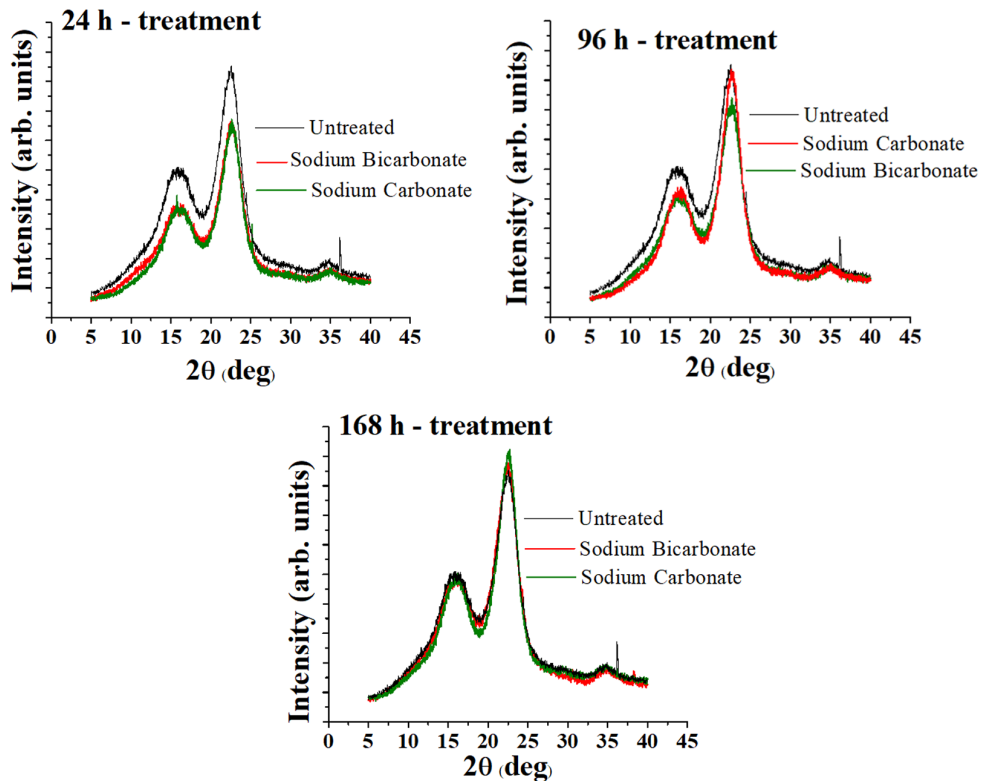


Figure 11. Comparative X-ray diffraction pattern of untreated and treated sisal fibres for 24 h (a), 96 h (b), and 168 h (c).

Table 5. X-ray diffraction analysis: crystallinity index (I_c).

Treatment	2θ		I_c
	22°-23°	18°-19°	
Untreated sisal	4267	1675	60.75%
Sodium bicarbonate - 24h	3322	1242	62.61%
Sodium bicarbonate - 96h	3704	1351	63.53%
Sodium bicarbonate - 168h	4394	1612	63.31%
Sodium carbonate - 24h	3355	1196	64.35%
Sodium carbonate - 96h	4619	1433	68.98%
Sodium carbonate - 168h	4185	1248	70.18%

(Figure 10e to g) compared to NaHCO_3 for all treatment times, indicating a partial removal of hemicellulose and waxes from the fibre surface. A greater amount of OH^- ions, released by the Na_2CO_3 solution (see Table 2), leads to greater removal of the wax layer and hemicellulose, affecting the surface wettability and mechanical properties of the resulting composite laminates¹³.

The X-ray diffraction analyses are shown in Table 5. Figure 11 presents the diffraction patterns of untreated and treated sisal fibres after 24 h, 96 h and 168 h (Figure 11 a to c). The intensity of the amorphous phase identified by 2θ between 18° and 19° is significantly reduced with fibre treatment, especially for shorter treatment times of up to 96 h (see Table 5 and Figure 11). It evidences an effective caustic action on the fibre surface, removing impurities, waxes and segments of amorphous components, i.e. hemicellulose and some amount of lignin. A higher crystallinity index is observed for fibres treated with sodium carbonate during

168 h (Table 5), contrasting with the moderate increase obtained with sisal treated with sodium bicarbonate.

The thermogravimetric (TGA) and differential thermogravimetric (DTG) curves are shown in Figure 12, items a and b, respectively. Sisal fibres have three stages of thermal degradation. The drops described by the TGA curves as a function of temperature represent the weight loss (%) of treated and untreated sisal filament samples. The first stage takes place at 30 to 120°C ^{12,14}, corresponding to water removal from environmental humidity. Fibres treated with Na_2CO_3 show a similar trend compared to sisal fibres treated with NaHCO_3 . The susceptibility of the fibres to moisture is gradually reduced with increasing treatment time. A similar observation was reported by Chaitanya et al.¹², analysing sisal fibres treated with NaHCO_3 . Therefore, this implies that long exposure times in carbonate solutions (168 h) can change the hydrophilicity of sisal fibre surfaces. The thermal degradation of sisal fibres begins after 230°C and corresponds to the removal of hemicellulose (230 to 295°C), cellulose (300 to 400°C) and

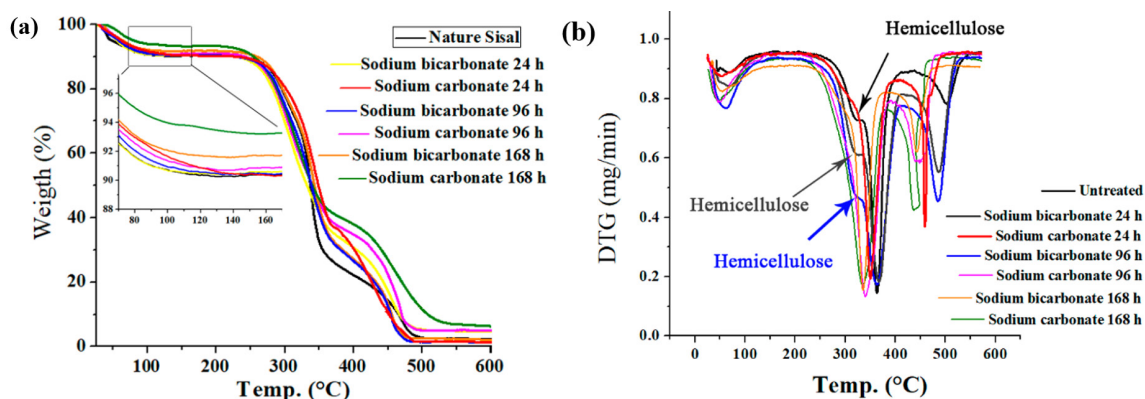


Figure 12. (a) TGA and (b) DTG thermographs of sisal fibres untreated and treated with Na_2CO_3 and NaHCO_3 (24, 96 and 18 hours).

lignin compounds on the fibre surface (above 400°C)^{9,12,27}. A hemicellulose *shoulder peak* can be seen in the DTG curves of untreated and NaHCO_3 treated fibres (24 and 96 h). The absence of this broad peak for the other fibres corresponds to the pyrolysis of hemicellulose, which is more pronounced for the treatment with 168 h- NaHCO_3 and Na_2CO_3 at all-time levels.

4. Conclusions

This work investigates the effect of carbonate treatments of sisal fibres on the properties of laminate composites based on epoxy and polyester polymers. The main conclusions are described below:

- The tensile modulus is higher for laminates made with polyester polymer and sisal fibres treated with Na_2CO_3 for 96 h. Tensile strength is superior when fibres are treated with Na_2CO_3 , especially for epoxy.
- The flexural modulus is higher for polyester polymer composites reinforced with treated sisal fibres, especially using Na_2CO_3 in the intermediate treatment time (96 h). In contrast, an interaction effect between the type of treatment and matrix is evidenced for the flexural strength response, revealing less variation. Longer treatments lead to a severe reduction in strength and stiffness.
- Impact resistance is reduced when sisal fibres are treated with Na_2CO_3 , mainly for epoxy polymer composites, attributed to the stronger fibre-matrix interface. Fibres treated with NaHCO_3 for 96 h reveal enhanced impact results due to the fibre pull-out mechanism, especially when the polyester polymer is used.
- Fibre treatment is only favourable for compressive strength when combining Na_2CO_3 and polyester composites. Compressive properties are substantially increased with Na_2CO_3 treatment, especially for 96 h.
- SEM analyses reveal a smooth fibre surface with no visible contaminants for both tested solutions. In addition, FTIR spectroscopy indicates progressive removal of hemicellulose from the fibres with NaHCO_3 with longer treatments and no visible peaks for the hemicellulose when fibres are treated with Na_2CO_3 . Similar conclusions are also obtained from XRD patterns and thermogravimetric analysis of sisal fibres.

These results evidence the applicability of the proposed composite in the field of sustainable structures, ensuring enhanced mechanical performance with a chemical treatment less harmful to nature.

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