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Valorization of cardboard waste in the production of polyurethane biocomposites: A new and environmentally friendly material for civil construction

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ABSTRACT

Cardboard has been widely used in various applications and industry sectors, such as in civil construction as a formwork for concreting circular columns. In addition to the versatility of the product, a vast amount of waste is generated by the manufacturing process. The objective of this work was to determine the properties of green polyurethane matrix thermosetting composites reinforced with cardboard tube waste for application as thermal insulation in buildings. Preliminarily, alkaline solutions of NaOH and Ca(OH)2 were applied to the residues to remove oils and waxes that affect the polymerization of vegetable polyurethane. The cardboard tube waste was characterized according to its chemical composition, basic density, infrared spectra, atomic force microscopy, Xray diffraction, and surface SEM images. The composites were produced with 10 % (wt%) treated cardboard waste and without surface treatment to replace vegetable polyurethane through the hand lay-up method. Specimens were obtained from the composites to perform tensile tests, determine the bulk density, water absorption, and thermal conductivity, and visualize the matrix-reinforcement interface via SEM. The data indicated that surface NaOH and Ca(OH)₂ treatments significantly increased the tensile strength of the composites by 76 and 187 %, respectively, compared with that of the polymer. For the composites, the use of cardboard waste significantly increased the thermal insulation, as proven by the thermal conductivity varying from 0.0607 to 0.0632 W/(m. K) and compatible with other insulating materials used in civil construction. Thus, composite polymers generated from cardboard tube waste are potential sustainable alternative construction materials.

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1. Introduction

Cardboard tubes are essential components in various industrial applications, encompassing diverse sectors. They are notable for their costeffectiveness, such as their compression strength and good performance against environmental variations [1]. The versatility of cardboard tubes is evidenced by their use in industrial operations, performing quality and integrity functions in the handling, transport and storage of raw materials and processed products. In addition to their functionality, the ability of these tubes to adapt to different industrial demands highlights their relevance in various contexts, such as paper production, textile manufacturing, polymer film processing, and civil construction designs [2].

However, as is inherent in all manufacturing industries, waste management has emerged as a crucial consideration for the cardboard tube industry. Effectively addressing this challenge is imperative not only to align with sustainable practices but also to mitigate the environmental impacts intrinsic to waste generation. Waste from industry poses an urgent global challenge, requiring commitment and in-depth analysis to find effective solutions [3]. The magnitude and complexity of industrial waste necessitate research and dedicated efforts to mitigate its environmental and social impact [4].

In addition to the environmental challenges inherent in this waste, inadequate management can lead to significant social impacts, such as food contamination and disease spread [5]. Therefore, the development of innovative technology strategies is crucial for addressing this problem and ensuring sustainable practices in the industry.

Polyurethane composites stand out as an effective matrix for reusing industrial and agricultural waste. Olcay and Kocak [6] evaluated the use of rice plant waste as a reinforcement in polyurethane foam after alkaline treatment to promote fiber—matrix adhesion. Compared with those of pure polyurethane foam, the mechanical and sound absorption properties of rice fiber composites improved, demonstrating the sustainable potential of agricultural waste for optimizing the properties of composites. Gomes et al. [7] investigated the production of sustainable artificial stone using granite waste and polyurethane resin derived from castor oil. By comparing its physical, mechanical and chemical resistance properties with those of natural granite, the results showed that artificial stone composed is suitable for application in civil construction, with an emphasis on the reuse of granite waste in the composition of sustainable materials.

Carvalho et al. [8] developed polyurethane biocomposites with castor oil and piassava (Attalea funifera) powder for high-performance coatings. An improvement in the flexural strength and flexural modulus was observed with the addition of 30 % Piassava powder. However, the impact strength decreased with increasing piassava powder content, and abrasive wear was also affected. Despite these considerations, wear values remain within the standards. This study highlights the viability of biocomposites as a sustainable option, although it suggests that improvements in the mechanical strength and adhesion between materials are needed. Some recent studies aimed at the production of polyurethane composites reinforced with lignocellulosic fibers and their results, which are important for applications as thermal insulation materials for buildings, are summarized in Table 1. Despite several studies on the reuse of waste with polyurethane, the application of waste from the processing industry has rarely been explored. Our work adds to this state of the art by producing rigid polyurethane composites reinforced with 10 % NaOH-treated cardboard waste fiber, whose thermal conductivity determined by a heat flow meter apparatus is 0.061 W/(m·K).

This research was conducted with the purpose of providing a correct destination for cardboard tube waste. On the basis of the literature, the generation of a composite capable of combining cardboard waste with a green polyurethane adhesive, which can be used as a civil construction material, was established as a novel approach. As a methodology, the experimental results of several technological properties of the

Table 1

Summary of research on polyurethane composites reinforced with waste for use as thermal insulation for buildings.

Material	Method for determining thermal conductivity	Thermal conductivity (K) W/(m·K)	Ref
Polyurethane foam	Parallel hot wire	0.045	Cardoso [9]
Polyurethane foam with 12 % of cellulose fiber residue	Guarded hot-plate device	0.025	Silva et al. [7]
Rigid polyurethane with 10 % hemp fiber	Guarded hot-plate device	0.034	Sair et al.
Rigid polyurethane with 10 % NaOH-treated and untreated alfa fiber	Guarded hot-plate device	0.035	Sair et al. [11]
Rigid polyurethane composites reinforced with 1 % bleached curauá fiber	Guarded hot-plate device	0.033	Członka et al. [12]
Rigid polyurethane composites reinforced with 5 % NaOH-treated coconut fiber	Heat flow meter apparatus	0.028	Faria et al. [13]
Rigid polyurethane composites reinforced with 70 % of cotton fiber	Guarded hot-plate device	0.113	Gamaetal. [14]

composites produced were evaluated, such as apparent density, water absorption, tensile strength, impact strength, modulus of elasticity and thermal conductivity. Owing to the chemical treatment of the cardboard waste, three types of composites were produced (without treatment, NaOH treatment and Ca(OH)₂ treatment). The validation of the results was consolidated by discussion with data from other studies and prescriptions of standardizations. Therefore, this approach to creating environmentally responsible solutions establishes a link to the gap between the use of waste and the creation of new efficient materials for civil construction.

2. Materials and methods

2.1. Materials

Cardboard tubes that were damaged or outside of technical specifications were donated by a company that produces cardboard tubes and packaging. The cardboard tubes had dimensions of $77.4 \times 6.0 \times 100$ mm (diameter, thickness and length, respectively), were produced with 18 layers of recycled paper (grammage of ~182 g/m²) and were used to glue the layers of semialkaline sodium silicate adhesive for internal surfaces and polyvinyl acetate (PVA) adhesive for bonding the faces. The



Fig. 1. Waste paper tubes were processed in a hammer mill.

cardboard tubes were processed in a hammer mill to obtain fibrous residues (Fig. 1). The composites were produced only with fibers that passed through a 40 mesh (0.420 mm) sieve and were retained in a 60 mesh (0.250 mm) sieve.

After the grinding procedure, NaOH (Synth Ltda.) with 100 % purity and Ca(OH)₂ (Éxodo Científica Ltda.) A purity greater than 98 % was used for surface modification of the waste. The fibrous residues (modified and without surface modification) were dried in an oven (105 \pm 2 °C) for 24 h until they reached a moisture content of 3 %. The detailed procedure of the surface modifications can be found in Suardana et al. [15].

The two-component resin used as the composite matrix was a castor oil-based polyurethane (PU) obtained from Imperveg Company (Aguaí, Brazil). The polyol component derived from castor oil has a hydroxyl value of 166 mg KOH/g, an acid value of 2.5 mg KOH/g and a linoleic acid content of 90 % and remains liquid until a mass ratio (1:1.5) of the initiator methylene diphenyl diisocyanate (MDI) is added, at which point the polymerization and hardening process of the resin occurs. The polymer had an apparent viscosity (25 °C) of 430.63 mPa.s, a solids content of 79 %, a density of 1125 kg/m³ and a pH of 7.0.

2.2. Characterization of the cardboard tube waste

The determination of the chemical components of the wastes was carried out after grinding the material in a knife mill, using the fraction that passed through the 40-mesh sieve (0.420 mm) and that was retained on the 60 mesh sieve (0.250 mm). The procedures for obtaining the chemical components were based on the following standardizations: total extractives (NBR 14853 [16]), insoluble lignin (NBR 7989 [17]) and ash (NBR 13999 [18]). The holocellulose component was obtained from the difference between the other components.

The basic density of the cardboard tube waste was obtained after saturation of the fibers and subsequent determination of the volume. The fibers were dried in an oven $(105 \pm 2 \degree C \text{ for } 24 \text{ h})$, where the basic density was obtained by the ratio between the dry mass of the fibers and their saturated volume, as described by Scatolino et al. [19].

2.3. Properties of wastepaper tubes subjected to surface modifications

Infrared spectra were obtained via a Shimadzu IR-Prestige21 spectrometer (model ATR-8200HA) equipped with an ATR-H horizontal attenuated total reflectance analysis accessory with a ZnSe crystal, with an incidence angle of 45°. The FTIR spectrometer was continuously purged with nitrogen. Thirty-two scans were collected with a resolution of 4 cm⁻¹ for each spectrum (4000–400 cm⁻¹).

Atomic force microscopy (AFM) analysis was carried out to evaluate the topography and roughness of the wastes subjected to different surface modifications. The test was conducted in dynamic force mode at room temperature with a scan speed of 2 s per line and 256 points per line. The cantilever DYN190AI model was used, with a nominal radius of 10 nm and an elastic constant of 48 N/m. The test evaluated an area of $10 \times 10 \,\mu$ m, which was evenly spaced on the surface of the samples, and the evaluations were carried out in triplicate. Typical topographic images and arithmetic average roughness graphs were obtained via Gwyddion software (Czech Republic).

Microstructural analysis of the wastes was carried out by scanning electron microscopy (SEM-FEG). The samples were covered with a layer of gold in an evaporator and analyzed on a Tescan Clara scanning electron microscope operating at 20 kV.

X-ray diffraction (XRD) analysis of the unmodified and modified cardboard tube waste fibers was performed on a Shimadzu XRD 7000 diffractometer with Cu-K\alpha radiation ($\lambda = 1.5418$ Å). The equipment used was a copper X-ray tube with a voltage of 40 kV and a current of 30 mA. The scattered radiation was detected in a 20 range of 5–100° at a scanning rate of 0.05°/s. The crystallinity index (CI) of the samples was calculated on the basis of the minimum intensity of peak 110 (amor-

phous region) and the maximum intensity that represents the crystalline portion of peak 200, according to Eq. (1).

$$CI = \frac{Ic - Iam}{Ic} x100$$
(1)

where CI is the crystallinity index, Ic is the maximum intensity of peak 200, and Iam is the minimum intensity of peak 110.

2.4. Composite production

The green polyurethane adhesive (control) IMPERVEG® AGT 1315, which is based on castor oil (free of formaldehyde), was synthesized by mixing the prepolymer with the polyol in a beaker at a ratio of 1:1.5 (according to the manufacturer's recommendations), with the aid of a mechanical stirrer at 150 rpm for 5 min. The polymer was poured into a metal mold with dimensions of $200 \times 200 \times 3$ mm, where it remained for 2 h, and was subsequently subjected to compression molding at room temperature via a hydraulic press (4.0 MPa, 24 h).

The composites were produced with 10 % (wt%) dry fibers obtained after surface modifications with NaOH and Ca(OH)₂ in different stages and without modification fibers. The production of the composites (Fig. 2) was carried out by mixing the fibers with MDI under constant stirring at 150 rpm for 5 min in a beaker. Then, the polyol was added, and the mixture was stirred as previously described for another 5 min. Afterwards, the material was poured into the metal mold and pressed, as previously described for the control. After the pressing period, the control and composites were transferred to a conditioned chamber at 20 \pm 3 °C and a relative humidity of 65 \pm 5 % until complete polymerization of the polymer. Composite production was based on the studies of Merlini et al. [20] and Faria et al. [13]. For each modification, 3 samples were produced.

The green polyurethane adhesive was synthesized similarly to the method used in the study of Faria et al. [13]. The prepolymer (MDI) reacts with the cellulose present in cardboard tube waste and forms two possible configurations, as shown in structures 1 and 2 (Fig. 3).

With the addition of polyol, MDI did not react with cellulose to form green polyurethane (structure 3), as shown in Fig. 4. Fig. 5 illustrates the polymerization mechanism of cellulose present in the cell wall of fibers with vegetable adhesives (structure 4).

The polymerization mechanism of the adhesive starts with mixing the prepolymer with the cardboard waste, resulting in prepolymerembedded particles linked by weak chemical bonds. The vegetable polyol derived from castor oil is subsequently added to the mixture, and the polycondensation reaction starts. As the lignocellulosic particles are embedded in the prepolymer, the hydroxyls that make up the particles form urethane bonds in contact with the polyol. In contrast, the prepolymer on the surface of the particles in contact with the polyol forms adhesive bonds.

2.5. Characterization of composites

2.5.1. FTIR

Infrared spectra were obtained via a Shimadzu IR-Prestige21 spectrometer (model ATR-8200HA) equipped with an ATR-H horizontal attenuated total reflectance analysis accessory with a ZnSe crystal, with an incidence angle of 45°. The characteristic spectra of the resin and composites provide information regarding the chemical groups observed in the pure resin and in the composites produced with different fiber modifications. The FTIR spectrometer was continuously purged throughout the nitrogen analysis. A total of 32 scans were collected with a resolution of 4 cm⁻¹ for each spectrum (4000–400 cm⁻¹).

2.5.2. Raman spectroscopy

Raman spectra were acquired in triplicate with a confocal Raman microscope (alpha 300, WITec GmbH, Ulm, Germany) equipped with a



Fig. 2. Composite production steps and cutting scheme of the samples for characterization.



Fig. 3. Scheme of the reaction of MDI and cellulose from cardboard tube waste. Adapted from Maurya et al. [21].



Fig. 4. Reactions involving polyol and MDI for the formation of green polyurethane. Adapted from Maurya et al. [21].



Fig. 5. Polymerization mechanism involving vegetable polyol and MDI reacting with cellulose from cardboard tubes. Adapted from Maurya et al. [21].

10x air objective (NA = 0.25, Carl Zeiss GmbH, Jena, Germany). A linearly polarized laser with a wavelength of 532 nm (Crysta Laser, Reno, NV, USA) and a power of 10 mW was focused on a diffraction-limited spot size of $0.61 \times \lambda/NA$. Each Raman spectrum was the average of 20 accumulations acquired with a 0.1 s exposure time. Raman light was detected with a backlit, air-cooled charge-coupled device (CCD) detector (DV401_BV, Andor, Belfast, UK) with a spectral resolution of 6 cm⁻¹. A baseline was created for each analyzed spectrum via Origin Pro 8.5 software (OriginLab, USA) to remove residual fluorescence, followed by smoothing. As the cardboard tube waste fibers showed intense autofluorescence, preventing characterization by Raman spectroscopy, the analysis was performed on the composites only.

2.5.3. X-ray diffraction

X-ray diffraction (XRD) analysis of the resin and composites was performed on a Shimadzu XRD 7000 diffractometer with Cu-K α radiation ($\lambda = 1.5418$ Å). The equipment used was a copper X-ray tube with a voltage of 40 kV and a current of 30 mA. The scattered radiation was detected in a 2 θ range of 5–100° at a scanning rate of 0.05°/s.

2.5.4. Apparent density

The apparent densities of the composites and pure polymers were calculated from the quotient between the mass and volume of the samples. For this purpose, a caliper was used to obtain the dimensions of the samples, and a precision balance was used to measure the mass. The apparent densities of five samples of each composition were analyzed.

2.5.5. Void content

The void contents in the pure polymer and composites were determined by considering their theoretical and experimental densities, which were calculated via Eq. 2 [22].

$$Void content = \frac{\rho_{theorical} - \rho_{experimental}}{\rho_{theorical}}$$
(2)

To calculate the void content, the theoretical density was obtained via Eq. 3. The experimental density used was obtained as described in Section 2.5.4.

$$\rho \text{theoritical} = \frac{1}{\left[\frac{W_f}{\rho_f} + \frac{W_m}{\rho_m}\right]} \tag{3}$$

where W_f and W_m are the volumetric fractions of the cardboard tube fibers and green polyurethane, respectively, and ρ_f and ρ_m are the densities of the cardboard tube fibers and green polyurethane, respectively.

2.5.6. Water absorption

The water absorption content after 24 h of immersion of the pure polymer and composites was obtained on the basis of the D570–22 standard [23]. A total of 24 samples with dimensions of 30.0×12.0 mm were used, with six samples for each composition.

2.5.7. Tensile strength

The tensile tests of the resin and composites were performed according to standard D638–14 [24]. The composites were cut with a laser to obtain type 1 samples, which were evaluated with a universal testing machine (INSTRON, Paraná, Brazil) equipped with a 20 kN load cell and a set test speed of 2 mm/min. Five samples of each composition were used to obtain the strain and maximum load, tensile strength (LRT), Young's modulus (E), and toughness (TE). The proportionality limit was obtained at the last point where the tangent line touches the elastic section of the stress—strain curve. The mechanical properties were obtained via Eqs. (4), (5) and (6), as described in D638–14 [24], and (7), as described by Garcia [25]. Fig. 6 presents a typical stress—strain curve showing the E calculation range.

$$LRT(MPa) = \frac{Q_{máx}}{A_0}$$
(4)

$$E(MPa) = \frac{\Delta\sigma}{\Delta\epsilon}$$
(5)

$$LOP(MPa) = \frac{Q_{lp}}{A_0}$$
(6)

$$TE(N.mm/mm^3) = \frac{Energy}{b.h}$$
(7)



Fig. 6. Typical stress—strain curve showing the range of E calculations.

where $Q_{m\dot{\alpha}x}$ is the maximum load (kN), A_0 is the initial cross-sectional area of the sample (mm²), $\Delta\sigma$ is the variation in stress in the region of elastic deformation, $\Delta\epsilon$ is the variation in deformation associated with stresses, Q_{lp} is the maximum load at the upper point of the linear section of the stress—strain curve (kN), and TE is the energy absorbed during the tensile test divided by the cross-sectional area of the sample.

2.5.8. Impact strength

The impact strength was determined via composites measuring 6.1 cm long and 1.2 cm wide, following the guidelines of the D256 standard [26]. Tinius Olsen was used as the model Impact 104 equipment (Horsham, PA, USA) with a hammer of 2.82 J by the IZOD method. To determine the composite impact strength, five samples of each composition were analyzed.

2.5.9. Surface morphology

Microstructural analysis of the surface of the fractured composites was carried out by scanning electron microscopy (SEM-FEG). The samples were covered with a layer of gold in an evaporator and analyzed on a Tescan Clara scanning electron microscope operating at 20 kV.

2.5.10. Thermal conductivity

The thermal conductivity of the composites was obtained with the aid of two rectangular expanded polystyrene boxes with a thickness of 25 mm containing a 25 W incandescent lamp connected to a thermostat that maintained the incident temperature of the sample at 60 °C. To obtain the data, a TC-08 (Pico Technology) thermocouple data logger connected to a computer containing PicoLog 6 software was used for 3 h, which is useful for stabilizing the temperature of the thermocouple in the upper chamber for the compositions studied. For each composition studied, three specimens with dimensions of 127×12.7 mm were used. Prior to the analysis of the composite samples, expanded polystyrene foam (EPS) samples with dimensions of 127×12.7 mm were selected as representative common contemporary insulation materials for comparison and calibration of the apparatus. A sketch of the experimental equipment is shown in Fig. 7. The detailed methodology for determining the thermal conductivity of composites can be found in Faria et al. [13].

2.6. Statistical analysis

The data were analyzed with a completely randomized design to evaluate the properties of the composites and subjected to ANOVA with LSD at 5 % significance to evaluate the effects of surface modifications



Fig. 7. Experimental mechanism for determining the thermal conductivity. Adapted from Faria et al. [13].

on the properties of the composites. The data were processed via the software Sisvar 5.6.

3. Results and discussion

3.1. Evaluation of the physical and chemical properties of the cardboard tube fiber waste

The constitutive properties of lignocellulosic fibers, such as their density and chemical constitution, strongly influence the performance of composites, especially their physical characteristics and mechanical and thermal resistance. Table 2 presents the results for the basic density and chemical components present in fibers from cardboard tube waste.

The surface modifications performed on the fibers increased the basic density, with significant differences detected between the treated fibers and those without surface treatment, with values in the range of 0.057 and 0.074 g/cm³ for fibers without surface modification and those modified with a solution of NaOH, respectively. This slight increase can be attributed to the densification of the cell wall of the fibers by the removal of substances with low molar weights, such as waxes, greases, oils and pectin. In a study of kenaf fibers treated with alkaline solution, Hashim et al. [27] reported that the behavior was similar to that observed in this study. The authors noticed an increase in the basic density of the fibers subjected to different NaOH contents and

Table 2

Basic density and chemical components of modified and unmodified cardboard tube waste fibers.

Property	Without treatment	NaOH- treatment	Ca(OH) ₂ - treatment
Basic density (g/ cm ³)	0.057 (0.009) a	0.074 (0.003) b	0.071 (0.008) b
Total extractives (%)	9.44 (0.64) b	6.95 (0.40) a	6.95 (0.37) a
Ash (%)	13.61 (0.21) b	4.40 (0.17) a	18.22 (0.20) c
Holocellulose (%) Insoluble lignin (%)	53.78 (0.84) a 23.17 (0.92) c	79.49 (1.16) b 9.16 (0.97) a	57.49 (1.30) a 17.34 (0.92) b

The values in parentheses represent the standard deviation. Averages followed by the same letter indicate no significant difference according to the LSD test (p > 0.05).

immersion times in solution, showing the densification of the fibers, with a consequent reduction in diameter and cross-sectional area.

Table 2 shows a reduction in the contents of total extractives and insoluble lignin. Alkaline treatments partially remove the chemical compounds that are located on the outside of the cell wall of the fibers, such as lignin and some substances that make up the total extractives, such as waxes, oils, greases, etc. [28]. The fibers obtained from cardboard tube waste come from recycled paper; that is, during kraft pulping, the nonvolatile extractives are removed under alkaline conditions; thus, many of the extractives have already been removed for paper production.

Surface modifications significantly reduced the content of total extractives present in the fibers originating from the cardboard tube waste. Owing to their hydrophobic nature, the extractives present in lignocellulosic materials act to inhibit the polymerization of the polymer, in addition to covering the surface of the plant fiber, reducing surface roughness and consequently reducing the wettability and spreading of the polymer, resulting in surface inactivation and a consequent decrease in mechanical properties due to low fiber—matrix interactions [29]. Alkaline treatments resulted in a 26 % reduction in extractives present in the fibers. Sousa et al. [30] reported an extract of 24.4 % for cellulosic pulp from yacon *(Smallanthus sonchifolius)* stem fiber waste without surface treatment and 1.3 % for pulps after treatment with a solution containing 5 % NaOH, a decrease of 95 %.

The ash content decreased from 13.61 % to 4.40 % for the untreated fibers and those treated with NaOH solution, respectively. This 68 % reduction compared with that of unmodified fibers occurred mainly because of the intensity of the NaOH treatment, which was able to remove a large portion of the inorganic materials contained in the fibers. Wooden lignocellulosic materials generally have ash contents of up to 2% in their chemical constitution [31]. The high ash content of untreated fibers is due to the presence of sodium silicate adhesive used in the production of cardboard tubes because of its inorganic nature and high melting point above 1100 °C [32]. Therefore, the final ash content found in fibers subjected to alkaline treatment with NaOH is due to the amount not removed during extraction with the alkaline solution. On the other hand, the fibers subjected to treatment with Ca(OH)₂ presented the highest average ash value, which was higher than the content for fibers without surface treatment. This difference can be explained by the deposition of CaCO₃ during the alkaline treatment on the surface of the fibers, resulting in an increase in inorganic materials and a consequent increase in ash content.

Surface modification with NaOH provided the highest holocellulose contents for the fibers. This result is very satisfactory, as higher cellulose contents present in the fibers result in increased tensile strength. However, fibers modified with Ca(OH)₂ and without surface modification presented statistically equal holocellulose contents. Owing to the lower intensity of the Ca(OH)₂ treatment, few variations in the chemical composition in relation to that of the untreated fibers were observed. Surface treatment with NaOH promotes the removal of some of the hemicelluloses present in the fibers, thus reducing hydrophilicity due to the dissociation of NaOH into sodium (Na+) and hydroxide (OH-) ions dissolved in water. Therefore, the OH- ions released into the solution improve the dimensional stability of the composites when subjected to water [33]. The treatment depolymerizes the cellulose in the fibers and thus opens short crystallites.

3.2. Effects of surface modification on the properties of cardboard tube waste

The FTIR/ATR spectra for cardboard tube waste without and with surface modifications are shown in Fig. 8. Importantly, important changes occurred in the cardboard tube waste subjected to alkaline treatments. The absorption peak at 3328 cm^{-1} showed a significant reduction for fibers treated with NaOH and Ca(OH)₂, and this peak is typical of the O-H functional groups of cellulose [34]. Thus, alkaline



Fig. 8. ATR/FTIR spectra of the cardboard tube wastes.

treatments break many of the hydrogen bonds in the hydroxyl group (O-H) present in the fiber structure through ionization of the O-H group to form an alkoxide [35]. The decrease in peak intensity at 3328 cm⁻¹ is also related to the removal of residual sodium silicate adhesive used in the production of cardboard tubes through alkaline treatments, since the literature reports a Si-OH stretching vibration peak at 3356 cm⁻¹ [36].

In addition, other characteristic peaks of cellulose, such as those at 2898 cm⁻¹, which are attributed to the absorption of C-H and to the polymers found in vegetable fibers and extractives, were observed [37]. The peak at 1623 cm^{-1} is attributed to the aromatic units of lignin, the peak at 1441 cm⁻¹ is attributed to C-C absorption, and the peak at 1021 cm⁻¹ is attributed to the absorption of C–O–C bonds, which are typical of samples containing cellulose with hydroxyl, carbonyl and methyl functional groups [38]. Concomitantly, in the ATR/FTIR spectrum, there are other peaks identified as typical of cellulose, as well as belonging to the sodium silicate present in cardboard tube waste, as seen in the low-intensity peak at 2109 cm^{-1} , which is attributed to the hydrogen bond in the sodium silicate structure [39]; at 1623 cm⁻¹, there are peaks designated to the occurrence of water and O-H stretching modes; the peak at 1021 cm⁻¹ is attributed to the asymmetric stretching of the siloxo bond; and at 823 cm⁻¹, there is Si-OH bending vibration [36].

Typical topographic images and arithmetic average roughness (AR) graphs for the cardboard tube wastes subjected to different treatments (Fig. 9) show an increase in the surface roughness of the cardboard tube waste fibers, with NaOH treatment being responsible for the highest average roughness value.

Treatment with alkaline agents such as Ca(OH)₂ and NaOH, also known as mercerization, increases the surface roughness of fibers. This effect is linked to the removal of compounds such as extractives, hemicelluloses and lignin, which alter the organized structure of cellulose and increase the surface area, increasing the roughness [40]. In this case, the greater roughness shown by the NaOH treatment may be associated with its greater performance in removing lignin (Table 2).

In addition to the solubilization and hydrolysis of hemicelluloses and lignin, mercerization can also alter the crystallinity of cellulose, weakening the crystalline region and consequently increasing the amorphous portion. The breakdown of the crystalline structure, associated with the presence of water, causes swelling in the structure, increasing the distance between the cellulose molecules, which culminates in increased roughness.

A greater roughness is associated with an increased surface area, which optimizes the interaction with the polymer matrix. The verified trend in the AFM analysis is confirmed by the SEM micrographs



Fig. 9. Surface topography and arithmetic average roughness (Ra) of the cardboard tube waste fibers. (a) Unmodified fibers; (b) NaOH-treated fibers; (c) Ca(OH)₂-treated fibers.



Fig. 10. SEM micrographs of the cardboard tube waste fibers. (a) Unmodified fibers; (b) NaOH-treated fibers; (c) Ca(OH)₂-treated fibers.

(Fig. 10). The removal of accidental (extractive) components and low-molar-weight substances, as shown in Table 2, together with the removal of residual sodium silicate results in better fiber—matrix interactions through a greater interfacial area relative to the greater roughness contained in the waste.

As shown in Fig. 10, alkaline treatments increased the roughness, which was attributed in essence to the partial removal of chemical compounds such as extractives, lignin and hemicelluloses [40]. The in-use performance of a composite is inherent to the properties of its matrix and reinforcement phases, in which the interaction between the two is crucial to obtaining better quality composites.

On the basis of the literature previously mentioned, the presence of substances such as extractives and parts of sodium silicate adhesive used in the production of cardboard tubes can result in composites with low mechanical strength owing to the presence of these substances on the surface of the waste, inhibiting the polymerization of vegetable polyurethane. The SEM images show that the partial removal of these substances after alkaline treatment is satisfactory for better adhesion of the fibers to the polymeric matrix through the principles of adhesion, with a proportional increase in the mechanical properties.

Verified via X-ray diffractogram (Fig. 11), a decrease in the intensity of the bands was noted for the waste subjected to alkaline treatments, highlighting the effects of surface treatments on the properties of the waste.

Cardboard tube waste before and after alkaline treatment with NaOH and Ca(OH)₂ solutions presented crystallographic planes typical of the crystalline structure of cellulose, namely, 110, 200 and 004 [41]. The intensities of the crystallographic planes 110 and 200 (amorphous and crystalline regions, respectively) were lower for the wastes that were not subjected to surface treatments than for those that were treated with NaOH solution. This result is consistent since these wastes contain more amorphous components, such as lignin and extractives. The greater intensity for waste treated with alkaline NaOH solution demonstrates that some components present in the waste were removed.

The crystallinity indices of the samples were calculated via Eq. (1) on the basis of the relative intensities of the amorphous and crystalline portions. The crystallinity index was 53 % for untreated waste and waste



Fig. 11. X-ray diffraction (XRD) curves of unmodified and modified cardboard tube waste samples.

superficially treated with NaOH solution and 60 % for waste treated with Ca(OH)_2 solution.

The presence of sodium silicate adhesive in the waste before and after surface treatment was confirmed by the other peaks, which were attributed to compounds traditionally used in the production of this adhesive. For example, peak 104 refers to calcite (JCPDS#47–1743), whereas peak 200 at 44° 2 θ is attributed to the presence of a cubic structure of MgO and can be attributed to the clean phase of the periclase MgO [42]. In addition, magnesium silicate (talc) can be detected in cardboard tube waste when the diffractogram obtained from the literature is compared with the –202 crystallographic plane at 37° 2 θ , which refers to kaolinite [43], and the presence of CaCO₃ through crystallographic plane 222.

3.3. Characterization of composites

3.3.1. ATR-FTIR analysis

By analyzing the FTIR spectra of the resin and composites (Fig. 12), we identified the presence of important chemical bonds, such as covalent and secondary bonds and hydrogen bonds, between the green polyurethane matrix and the fibers obtained from the cardboard tube waste.

As shown in Fig. 12, a greater relative intensity is noted for the peak at 3328 cm⁻¹, which is typical of the hydroxyl groups present in cellulose. The greater intensity of this peak for composites produced with fibers treated with Ca(OH)₂ is justified by greater removal of chemical constituents from the cell wall of the fibers and exposure of cellulose fibrils in contact with the polymer matrix. Furthermore, this peak is also characteristic of the stretching vibration of the N—H bonds in the ure-thane groups present in polyurethane [41]. This change in intensity at 3328 cm⁻¹ was also observed by Hadjadj et al. [44], who reported a greater intensity with increasing fiber content in polyurethane matrix composites reinforced with cellulosic fibers; that is, a greater number of urethane bonds formed.

For the composites, the peak at 3328 cm^{-1} was wider than that for the resin, with a greater intensity at approximately 3500 cm^{-1} ; that is, as this peak is related to the N—H stretching bands, it is concluded that for the composites, not all N—H groups were linked by hydrogen bonds [41]. This phenomenon was more prominent in composites reinforced with fibers modified with Ca(OH)₂, in which this chemical modification provided greater intensity in the removal of compounds from waste.

The spectra (Fig. 12) also show the presence of other important chemical groups, such as the peak at 2914 cm^{-1} due to asymmetric hydrophobic CH₂, which is more intense for untreated waste because of the higher concentration of hydrophobic impurities; the peak at 1717 cm^{-1} is attributed to the C=O stretching vibration, C–N stretching vibration and N–H bending vibration at 1519 cm^{-1} . In addition, the stretching vibration of the N-CO-O group at 1203 cm^{-1} , which is present in all the composites and in the resin, indicates the occurrence of polymerization in vegetable polyurethane. These same peaks were also verified by Hadjadj et al. [44] and were attributed to the polymerization of polyurethane.

The intense peak at 1717 cm⁻¹ shows that the composites presented a lower intensity than did the pure resin. This specific peak is very important because it refers to the carbonyl group formed by the reaction between the hydroxyl group and MDI (prepolymer). Thus, owing to the presence of fibers from the cardboard tubes, fewer of these groups formed. This shows that although the fibers have hydroxyl groups in Construction and Building Materials 462 (2025) 139902

their composition, there was a reduction in carbonyl groups, which was mainly attributed to the presence of other chemical groups in the fibers that possibly inhibited the formation of chemical bonds between the MDI and the hydroxyl groups of the fibers. As initial mixing occurred between the prepolymer and the polyol before the fibers were inserted to form the composites, the supply of prepolymer for the formation of covalent bonds with the inserted fibers was possibly limited.

3.3.2. Raman spectroscopy

Fig. 13 shows the Raman spectra of the resin and composites. For the polyurethane matrix (resin), there were no intense peaks in the analyzed spectral range. On the other hand, the treatments with added fibers show intense peaks, especially at 65 cm^{-1} and in the region between 1000 cm^{-1} and 2000 cm^{-1} . Similar behavior was reported by Tijing et al. [45], who added carbon nanotubes to polyurethane matrices. According to the authors, the increased intensity of the peaks in the composites is indicative of good reinforcement—matrix interactions.

Concerning the Raman spectral bands, low frequencies $(200-8 \text{ cm}^{-1})$ are more suitable for explaining the amorphous and crystalline behavior of materials, especially lignocellulosic materials [46]. Therefore, the intense peak at 65 cm⁻¹ observed in the composite treatments can be attributed to an increase in the amorphous region, which indicates the formation of a reinforcement-matrix complex. Thus, the greater intensity of this peak in the treatments with treated cardboard tube waste indicates greater interaction with the matrix, especially in the NaOH treatment. Agarwal [46] emphasized the difficulty in performing low-frequency Raman spectroscopy due to scattering and fluorescence problems, as well as the contribution of Rayleigh scattering, which masks the low-frequency Raman scattering of the samples. This explains the nonfeasibility of the isolated evaluation of the cardboard tube waste samples.

Other peaks were observed at 642 cm^{-1} , attributed to aromatic ring vibrations (p-substituted benzene); aromatic C-H out-of-plane deformation; 1181 cm^{-1} , related to C-O stretching vibrations of secondary alcohols; 1439 cm^{-1} , related to C-O stretching vibrations of p-substituted benzene; 1615 cm^{-1} , which can be attributed to aromatic C-C stretching vibrations; C O stretching vibrations of amides; and skeletal vibrations of C-C double bonds in aromatic rings [47].

3.3.3. XRD

Owing to the low fiber content used for reinforcement in the composites, no visible band corresponding to cellulose I was observed in the X-ray diffractogram (Fig. 14). This behavior was also reported by Lei et al. [41].



The resin and composites only showed a more intense crystalline



Fig. 12. ATR-FTIR spectra of the resin and composites.

Fig. 13. Raman spectra of the resin and composites.



Fig. 14. X-ray diffraction (XRD) curves of the resin and composites.

region at approximately 18° , with several other low-intensity bands up to approximately 100° , indicating some degree of crystallinity. The characteristic band observed with the greatest intensity and the others are attributed to the scattering of polyurethane chains with regular interplanar spacing [48].

Compared with the evaluated composites, the resin presented the highest relative intensity in the crystalline phase at approximately 18°. This finding corroborates the FTIR/ATR results for composites in which the presence of treated and untreated fibers influences the formation of carbonyl groups [41]. Furthermore, the use of fibers in the composites resulted in a decrease in O—H bonds and N—H groups in the polymer chains.

Another relevant fact concerns the intensity of the other lower intensity peaks. As observed in the FTIR/ATR analysis, an intense peak attributed to the hydroxyl group was verified for the composites containing treated and untreated fibers, highlighting the possible role of the fibers as crosslinking agents in the polymerization of vegetable polyurethane. This means that instead of the prepolymer bonding to the hydroxyls present in the vegetable polyol, part of it bonded to those that constitute the fibers, thus resulting in the breaking of the regularity of the molecular chains of the vegetable polyurethane and consequently its mobility, causing difficulty in organizing molecular chains to form the crystalline region [41].

3.3.4. Density and void content

Fig. 15 presents the results of the physical properties of the apparent density and void content for the materials under study.

The void content increased significantly with the addition of waste to the composites, with significant differences being observed between the composites and the resin. In contrast, in the pure polyurethane polymer, there were 13 % voids, and in the composites produced with wastes modified with NaOH, there were 23 % voids, an increase of 73 %. This increase is attributed mainly to the composite production method, which results in a random distribution of the fibers and therefore results in poor dispersion, in addition to the hydrophilic nature of the fibers, which tend to agglomerate, resulting in an increase in voids. A lower void content is noted for the composites reinforced with fibers modified with Ca(OH)₂. As previously discussed for the other properties evaluated, this observation is due to the greater intensity of the surface modification, which made the wastes more hydrophobic and consequently promoted better fiber—matrix interactions.

The intrinsic porosity of composites significantly affects their usage properties. Composites that are more porous than pure polyurethane are rationally satisfactory for the thermal comfort of a building, since the larger the voids are, the greater the amount of oxygen trapped in them,



Fig. 15. Void content and density of the resin and composites. Averages followed by the same letter indicate no significant difference according to the LSD test (p > 0.05).

which has a low thermal conductivity. On the other hand, greater porosity of the composite can result in points of weakness for the loaded composite, as pores are regions without the presence of polymers and fibers that act to prevent the propagation of cracks.

The composites obtained with fibers modified with Ca(OH)₂ resulted in significantly higher apparent density. As the density of the composites is proportional to the content of fibers used and their respective density and the density of the matrix, owing to the use of fibers, there was less release of CO₂ gas during the polymerization of green polyurethane, resulting in higher density composites.

3.3.5. Water absorption analysis

For the water absorption test (Fig. 16), higher levels of this property are reported for the composites than for the resin. This physical property is governed, for example, by the moisture content and chemical composition of the reinforcing material, porosity in the composites and dispersion of the fibers in the matrix [49]. Water absorption is directly related to the mechanical integrity of the composites, since the greater the degree of water absorption is, the greater the swelling of the fibers and consequent detachment of the fiber—matrix interface.

The resin presented the lowest water absorption content (Fig. 16),



Fig. 16. Water absorption properties of the resin and composites. Averages followed by the same letter indicate no significant difference according to the LSD test (p > 0.05).

which was due to the absence of fiber addition. On the basis of the FTIR/ ATR spectra, both the alkaline-treated fibers and those without surface treatment presented intense peaks related to O-H groups, which are responsible for the water absorption of the composites. There was no significant difference in the physical properties of the composites. Although fibers modified with alkaline NaOH had the highest content of holocellulose, the greater number of hydroxylic sites available to bond with water did not result in greater water absorption. This may have occurred mainly because of a better interaction of the fibers with the polymeric matrix, causing the hydrophilic fibers to be covered by the hydrophobic polyurethane matrix.

The higher water content absorbed by composites made with a green polyurethane matrix reinforced with cardboard tube waste was also verified by other studies in the literature. Calegari et al. [50] reported a significant increase in water sorption in composites in relation to green polyurethane polymers. The insertion of scrap paper into the composites increased water sorption by 1700 %, and this increase was mainly associated with the characteristics of the waste and the porosity inherent to the composite. Lei et al. [41] noted an increase in the water absorption content of composites containing paper waste compared with that of composites containing pure polyurethane. According to the authors, the presence of O-H groups in paper waste was responsible for attracting water molecules through hydrogen bonds, whereas the polyurethane matrix showed hydrophobic behavior. Another evidence pointed out by the authors for increased water absorption is the presence of a hollow lumen in the anatomical structure of lignocellulosic materials, causing the lumen to behave like a capillary tube absorbing water.

3.3.6. Tensile mechanical properties

Fig. 17 shows the typical tensile stress \times strain curves obtained from the tensile tests for the resin and composites. The mechanical performance of a material is related to its ability to resist stress and deformation [51]. The resin exhibited ductile behavior typical of polymeric materials, with low tensile stress and high specific deformation, as also noted by Calegari et al. [50]. The compositions with fibers significantly increased the tensile strength of the composites, with a large increase in stiffness, although the ultimate strain decreased.

On the basis of the specific stress \times strain curves for the resin and composites, we can obtain important mechanical properties (Table 3).

The tensile stress was significantly greater for the composites than for the resin. The composites produced with unmodified and Ca (OH)₂-treated fibers presented the highest average values for this property. The role of fibers in the mechanical performance of composites is notable. Compared with that of pure polyurethane, the tensile stress of



Fig. 17. Tensile strength vs. strain of the resin and composites.

composites produced with unmodified fibers increased by 213 %.

The surface modification of fibers with NaOH did not significantly optimize the mechanical performance of the composites, which was lower than that of composites produced with fibers without surface modification and modified with Ca(OH)2. The decrease in mechanical strength due to pretreatment with NaOH can be attributed to the fact that the cardboard waste used comes from recycled Kraft paper and has therefore already been treated with NaOH. Therefore, an increase in the number of cycles of exposure to alkaline treatment should change the structure of the fibers, decreasing their mechanical strength. The decrease in the ultimate tensile strength of the composite with fibers treated with NaOH is related to an increase in the volume of the paper, which is explained by the decrease in the compressibility of the fibers and the bonding area between them, as well as by removing lowmolecular-weight carbohydrates, such as hemicelluloses, which contribute to the bonding between fibers [52]. These morphological changes in the fibers due to alkaline treatment are related to the modification in the crystalline structure of the cellulose (from cellulose I to cellulose II), with a consequent decrease in mechanical strength [53].

Jonoobi et al. [54] reported a decrease in the mechanical properties of wood panels when the fibers were treated with NaOH. According to the authors, the alkaline treatment removes a series of hydroxyl groups on the fiber surface, which may have resulted in a lower number of fiber bonds with the resin. Therefore, this may explain the inferior mechanical performance presented by this treatment in relation to the pretreatment with Ca(OH)₂, as well as the greater incidence of voids in the composite. However, a 76 % increase in the tensile stress was achieved for the composites with fibers modified with NaOH compared with those with resin. This optimization of the mechanical performance was achieved because of better interactions between the constituent phases of the composites, as shown in the SEM electron micrographs (Fig. 18).

The presence of bubbles in the resin (Fig. 18a) is related to the very nature of polyurethane since CO_2 gas is released during polymerization, thus resulting in the formation of bubbles on the surface of the material. As shown in Fig. 18b, there was no detachment of the fibers in the matrix for the composites with fibers without surface modification. In contrast, the composites made with NaOH-treated fibers showed fiber agglomeration and a gap between the constituent phases (Fig. 18c), a characteristic not found for the composite made with Ca(OH)₂-treated fibers. The presence of crazing also stands out, illustrating the point of failure of the material.

The limit of proportionality for the resin and composites followed the same trend as that of the tensile stress. Owing to the ductile nature of polyurethane, a low limit of proportionality was observed (Table 3), with a smaller section in the elastic region and a larger section in the plastic region (Fig. 17). With the insertion of fibers, there was a reduction in ductile behavior, resulting in intermediate behavior between the ductility of the polymeric matrix and the fragility of the fibrous reinforcement. This behavior was reflected in the E values, with composites produced with NaOH-treated fibers presenting mean values statistically equal to those of the resin. On the other hand, the composites with Ca (OH)2-treated fibers and unmodified fibers presented the highest average values. The stiffness of composites reflects not only their mechanical response to external loads but also their thermal insulation performance. Similarly, a greater rigidity of the composite results in lower sound properties [51]; the same is true for thermal properties, in which more elastic materials have a greater capacity to isolate heat flow [55]

The composition of NaOH-treated fibers did not change the strain at break of the composites, with values statistically equal to those of the resin samples. On the other hand, composites produced with unmodified fibers and Ca(OH)₂-treated fibers significantly reduced the strain at break, with the latter presenting the lowest average value of strain at break. The reduction in strain at break is due to the brittle nature of the lignocellulosic fibers used as reinforcements in the composites. Owing to their ability to interact best with the green polyurethane of Ca(OH)₂-

Table 3

Values reported for tensile properties.

Composition	Tensile stress (MPa)	Limit of proportionality (MPa)	E (MPa)	Strain at break (%)	Toughness (N.mm/mm ³)
Resin	$\textbf{4.59} \pm \textbf{0.48} \text{ a}$	$0.78\pm0.25~a$	$5.29\pm0.34~\text{a}$	$90.06\pm10.97c$	$0.0013 \pm 0.0002 \; a$
Without treatment	$14.38\pm1.27c$	$9.10\pm1.22~d$	$82.38\pm12.41~\mathrm{b}$	$54.61 \pm 10.44 \text{ b}$	$0.0047 \pm 0.0009 c$
NaOH treatment	$8.10\pm0.40~b$	$3.12\pm0.16~\mathrm{b}$	$20.14\pm3.27~\mathrm{a}$	$89.13 \pm \mathbf{2.36c}$	$0.0027 \pm 0.0005 \ b$
Ca(OH) ₂ treatment	$13.18\pm0.49c$	$7.69\pm0.43c$	$61.36\pm11.20~b$	$33.05\pm0.71~\text{a}$	$0.0046 \pm 0.0004c$

Averages followed by the same letter indicate no significant difference according to the LSD test (p > 0.05).



Fig. 18. SEM micrographs of the resin and composites. (a) Resin; (b) composite with unmodified fibers; (c) composite with NaOH-treated fibers; (d) composite with Ca(OH)₂-treated fibers.

treated fibers, these fibers absorb stress from the matrix and fail abruptly without great strain.

The strains at break are explained by the toughness of the composites. The samples modified with Ca(OH)₂ and the unmodified fibers presented statistically equal mean values for toughness, thus indicating that the energy absorption of these composites was greater than that of the other composites. This is an extremely important mechanical property because it reflects the ability of a composite to resist fracture; that is, it reflects the amount of tensile stress necessary for the propagation of a thin preexisting crack [56]. As it is a ductile matrix, the transfer of effort to the fibers reduces the matrix tension, and the matrix becomes unable to deform freely because of the restrictions imposed by the fibers. Although the lignocellulosic fibers used in the present study cannot undergo as much plastic deformation before fracture as metallic and polymeric fibers and can provide greater energy absorption at rupture, they can increase the toughness of the composites, making them useful for use in practical situations since, in addition to needing to be strong, composites also need to be tough.

3.3.7. Impact strength

The influence of different surface modifications of cardboard tube waste on impact strength is presented in Fig. 19. The impact strength was significantly greater for the composites than for the resin, with the composites produced with unmodified fibers showing the highest average value of this mechanical property.

The increase in the impact strength of the composites in relation to that of the pure polymer (resin) is due to the fibers that improve the



Fig. 19. Impact strength of the resin and composites produced with unmodified and surface-modified cardboard tube waste fibers.

main energy absorption mechanisms, thus resulting in more energy for rupture [57]. Like the behavior of the composite in terms of tensile strength, the increase in impact strength due to the presence of fibers is also due to the barriers provided to the propagation of cracks during the test. In short, the presence of the volumetric fraction of fibers in the

composites prevents the growth and propagation of cracks in the polymer matrix. Regarding the significant differences for the composites (Fig. 19), the greater impact strength reported for the composites with unmodified cardboard tube waste fibers can be attributed to the greater strength of the untreated fibers. Surface treatments remove the substances contained in the cell wall of the fibers, which consequently reduces the useful area of the fibers and, therefore, the mechanical strength is reduced. Therefore, during crack growth and propagation, the lower mechanical strength observed for the modified fibers can result in fiber failure due to their fragility [58].

The results reported in this study are slightly lower than those reported by Faria et al. [59], who obtained average impact strength values ranging between 218 and 247 J/m in composites produced with a polyurethane matrix reinforced with coconut fibers. The lower impact strength is justified since the authors used reinforcement levels between 30 % and 60 % (vol%). This greater volumetric fraction of fibers acts as a barrier to the growth of cracks, thus hindering their propagation through the matrix. Furthermore, it increases deformability as a greater volume of fiber is inserted into the composites [60].

3.3.8. Thermal insulation

The thermal conductivity of a material is related to its thermal insulation capacity and is directly related to the well-being of the users of a building. Among the materials traditionally used for this purpose, bricks, wooden panels and foamed polymers, such as polyurethane, stand out [61]. For the thermal conductivity values (K) of the materials evaluated (Fig. 20), the EPS foam presented the lowest average value, which differed significantly from those of the cardboard residue, resin and composites evaluated.

EPS foam was used in this research as a material to verify the equipment calibration, as it is a very commonly used thermal insulation material. The thermal conductivity reported in this research for cardboard waste was 0.0651 W/(m-K); therefore, within the range of values verified by Čekon et al. [62], the thermal conductivity of different types of cardboard ranging from 0.05 to 0.12 W/(m-K) was recorded.

The addition of cardboard tube waste significantly reduced the thermal conductivity of the composites (Fig. 20); that is, the waste made the composites better thermal insulators. This characteristic of the composites is evidenced by the increase in void content (Fig. 15). The greater porosity of the composites is due to the presence of voids containing air, which has a low K value (0.0262 W/(m·K)) [63], increasing



Fig. 20. Thermal conductivity (K) of the EPS foam, cardboard, resin and composites. Averages followed by the same letter indicate no significant difference according to the LSD test (p > 0.05).

the thermal conductivity due to the presence of air in the pores of the composite. The trend observed in the present work extends to other studies whose authors characterized composites made with green polyurethane and lignocellulosic fibers. Faria et al. [13] reported K values ranging from 0.0214 to 0.0283 W/(m·K) for composites produced with surface-treated coconut fibers, and K values of 0.0440 W/(m·K) were reported by Malchiodi et al. [64]. The thermal properties of the composites are related to the matrix and reinforcement phases. Reinforcement is attributed to the geometric parameters intrinsic to the fibers, such as their dimensions, density and pore size [65], and its content significantly influences the thermal conductivity of the composite.

Chen et al. [66] predicted mathematical models and reported that the thermal conductivity tends to increase for composites as a function of filler content. Thermal conductivity levels ranging from 0.2 to 0.6 W/(m K) were reported for composites with filler contents of 0 and 20 %, respectively. Even a fiber content of only 10 % in waste results in a large volume of fibers due to their low density. As previously discussed, fiber agglomeration was verified at various points in the composites via electron micrographs obtained via SEM. These agglomerations occurred mainly because of alkaline treatments, which made the fibers more reactive and allowed them to react with each other when in contact. However, the greater reactivity of the fibers meant that there were points in their absence, increasing the porosity and thermal insulation of the composites.

On the basis of K values ranging from 0.06 to 0.08 W/(m·K), composites containing cardboard tube waste are classified as thermally insulating materials because K values are lower than 0.1 W/(m·K), according to DIN 4108–10 [67]. According to this standard, materials with K values lower than 0.03 W/(m·K) are excellent thermal insulators; those between 0.03 and 0.05 W/(m·K) are classified as moderate, and those above 0.07 W/(m·K) are less efficient.

In turn, the K values for the composites evaluated in this work are slightly higher than those of traditional materials, such as thermal insulators, glass wool (0.0400 W/(m·K)) and fiber insulating boards (0.0480 W/(m·K)) [63]. This gives the evaluated product broad horizons for insulating applications, with the advantage of establishing a correct destination for cardboard tube waste.

4. Conclusions

This study focused on the need to provide an appropriate destination for cardboard tube waste, considering the production of composites with polyurethane resin. To remove substances such as total extractives, insoluble lignin and traces of adhesives contained in cardboard waste, surface treatments with $Ca(OH)_2$ and NaOH were carried out.

Compared with the results of the tests on the pure resin samples, the mechanical properties of the composites significantly increased; for example, the composites produced with waste treated with $Ca(OH)_2$ presented increases of 187 % in tensile strength, 1060 % in modulus of elasticity, 254 % in toughness, and 60 % in impact strength. We highlight that the numerical results of these mechanical properties were greater in the composites treated with $Ca(OH)_2$, the statistical analysis revealed that there were no significant differences. On the other hand, the treatment of waste with NaOH was less effective since the mechanical properties of the composites (without treatment and treatment with Ca $(OH)_2$).

With respect to the thermal insulation properties, in relation to the pure polyurethane resin samples, the composites exhibited lower thermal conductivity because of the increased number of voids in the matrix. For the composites treated with Ca(OH)₂, this decrease was approximately 30.4 %. However, based on the statistical analysis, there was no significant difference in the thermal conductivity results of the composites produced with untreated and treated waste. In turn, the

composites produced were compatible with other materials traditionally used for thermal insulation, such as glass wool and fiber insulating boards.

Finally, the use of cardboard tube waste as reinforcement in a green polyurethane matrix promotes the reduction of polymer consumption, in addition to the valorization of the waste into another material with greater added value through the principles of circular economy, with a consequent reduction in the cost of the composite. Undoubtedly, the generated product has environmental advantages, as it is a biodegradable matrix reinforced with cardboard waste and is more environmentally friendly than traditional composites produced with synthetic materials.

Author contributions

Douglas Lamounier Faria; Laércio Mesquita Junior and Rafael Carvalho do Lago: Conceptualization, Investigation, Data Curation and Writing – original draft. Julio Soriano; Mário Guimarães Júnior; Natal Junio Pires; Augusto Cesar da Silva Bezerra; Juliano Elvis de Oliveira; Thiago de Paula Protásio; Maria Alice Martins and Leticia Catta Preta da Silva: Conceptualization; Methodology; Validation; Writing - original draft. Lourival Marin Mendes; José Benedito Guimarães Junior; Anand Ramesh Sanadi and Gustavo Henrique Denzin Tonoli: Funding acquisition, Supervision, Resources, Project administration.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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