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Development of hybrid composite materials with a polymeric matrix reinforced with vegetable fibers and kaolin from the Rio Negro basin

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Abstract: Composites with natural fibers are evaluated as a viable sustainability alternative to conventional materials, combining low-cost characteristics with consumer products. In Brazil, a considerable amount of lignocellulosic waste is discarded in nature, polluting the environment. Tucumã fruit (*Astrocaryum aculeatum*) generates about 60 tons/month of solid waste only in the city of Manaus (Amazonas State). In addition, the Amazon region has enormous deposits of clay silicate materials, such as kaolins, in the Rio Negro basin area that can be used as fillers in polymeric composite materials. This work investigates a new composite material (ETK) made of epoxy resin (ER), tucumã endocarp powder (TEP), and kaolin (K), without coupling agents, being a composite with a lower environmental impact design. The ETK samples were prepared by cold molding with 25 different compositions. Characterizations were performed by SEM and FTIR. Mechanical properties were determined through tensile, compressive, three-point flexural, and impact tests. FTIR and SEM results showed an interaction between ER, TEP, and K. Incorporation of TEP and K reduced the mechanical properties of ETKs. Composites resulting from RE + TEP (10% to 40%) + kaolin (2% and 4%) have significant potential for use in industrial consumer products.

1. Introduction

Clays are abundant materials in nature, and due to the combination of low costs and environmental impact involved in obtaining them, the study and development of applications of their nanoparticles have been widely spread. The state of Amazonas, the largest in Brazil, is rich in clay mineral deposits, especially the Solimões (Upper

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Miocene period) and Içá (Pleistocene period) geological formations, with a predominance of kaolinite (kaolin) deposits [1].

Tucumã (*Astrocaryum aculeatum*) is a fruit native to the Amazon, and its pulp is consumed in several foods in the cuisine of Manaus-Am. It has a high content of lipids, energy, and vitamin A, with a medium content of Beta-carotene. Its endocarp is used in local crafts, and 92% is discarded in the trash without any reuse, yielding about 30 tons of woody endocarp monthly [2].

Composites with thermoplastic polymer and tucumã endocarp powder were developed with the addition of 10%, 20%, 30%, 40%, and 50% by weight in recycled polypropylene matrix without coupling agents with applications in the form of floors and coatings [3].

This work presents the development and analysis of the composite produced with epoxy resin, tucumã endocarp powder, and clay mineral kaolin from the State of Amazonas in Brazil. The clay mineral proportions considered in the composite understudy will be below 10%; precisely, 2%, 4%, 6%, and 8%, combined with 10%, 20%, 30%, and 40% of tucumã endocarp in epoxy resin polymer matrix, characterizing itself as a new unpublished composite material, whose industrial application must be evaluated.

2. Methodology

Obtaining the tucumã endocarp powder**:** The samples were obtained at the Manaus Moderna fair with an average diameter of 34.28±4.84 mm and an average mass of 22.08±2.63 g. Then the pits were manually broken with a hammer (master, Tramontina, Brazil) to obtain the pits into smaller pieces. After that, the broken pits were ground in a knife mill (Marconi brand) with a 200-mesh sieve opening, and the powder obtained was dried at 60°C for 4h. Kaolin (Kaolin): The kaolin for this study (Kaolin-AM, white) was collected in the city of Careiro-AM, geographic coordinates (3°49'10.0"S 60°21'40.4"W). Kaolin was obtained by dry sieving using sieves up to 200 mesh. Epoxy Resin: epoxy resin (2001, Redelease), and hardener (3154, Redelease) was used. The -anti-blister additive (Siladit 53, Redelease) was also used. To prepare the samples, Molds: metallic molds were initially made (ASTM A36 steel) with a cavity to obtain samples for the traction, bending, compression, and impact tests. Preparation of specimens: The specimens were made considering variations with and without clay and also with and without tucumã endocarp powder, making up 25 types of samples, a Taguchi design with 25 compositions with % by mass of kaolin (2 %, 4%, 6%, and 8%) and powder (10%, 20%, 30%, and 40%). Mechanical tests**:** The tensile test was performed according to the ASTM D638-14 reference standard. The bending test was performed following ASTM D790-03. Moreover, the compression test was carried out using the ASTM D695-2a reference standard. All tests were performed using a universal testing machine (5984, Instron, USA), with a load cell of 150 kN, and a speed of 10 mm min^{-1}. Izod impact testing was performed according to the standard (ASTM D256-04) using a plastic pendulum impact testing machine (IT504, Tinius Olsen, USA). Particle diameter: Kaolin and tucumã endocarp powder were analyzed for particle size (Mastersizer 2000, Malvern Instruments, UK) according to ASTM D4464-14. Fourier transform infrared spectroscopy (FTIR): An equipment was used (IRAffinity-1S, Shimazdu, Japan). The spectra were obtained in 4000 to 500 cm^{-1} in an attenuated total reflectance module (ATR). Scanning Electron

Microscopy (SEM): The morphologies of tucumã powder ridge and composite fractures were observed by SEM (JSM-IT500HR, JEOL, Japan).

3. Results and Discussions

3.1. Fourier transform infrared spectroscopy (FTIR)

Figure 1 shows the results of the FTIR test for the epoxy resin, tucumã, kaolin, and the resulting composite. There are absorptions in the middle part of the spectrum for the epoxy resin, which is constituted by epoxy groups and hydrocarbons, observing vibrational regions of C-H elongation between 2870 cm^{-1} and 2960 cm^{-1}, with hydroxyl groups vibrating at 3200 cm^{-1} and epoxy functional groups are around 910 cm^{-1}, similar to [4]. The tucumã powder presents vibrations of molecular groups around 3500 cm^{-1}, referring to O-H stretching due to the existing humidity. In the region of 2750 cm^{-1}, 0-H binding bands are observed. The addition of tucumã powder tends to reduce the presence of benzene rings in the molecular structure, thus explaining the potential loss of mechanical properties, which is corroborated by the increase in peaks in the region 1500 cm^{-1} to 1600 cm^{-1} of the aromatic groups, also mentioned in [5]

Kaolin presents in the region of 3620 cm-1 to 3680 cm^{-1} O-H stretching due to the presence of humidity, in 1120 cm^{-1} longitudinal stretching of Si-O, between 1000 cm^{-1} to 1030 cm^{-1} Si-O stretching in the function of the presence of quartz, O-H bending at 911 cm^{-1} of internal hydroxyls, Si-O bending at 753 cm^{-1}, Si-O perpendicular stretching at 755 cm^{-1}, Si-O-Si bending at 677 cm^{-1}, Al-O-Si folding at 556 cm^{-1} and Si-O folding at 427 cm^{-1}, similar to that indicated in [6]. The spectrum of the composite, in turn, presents the combined characteristics of the epoxy resin + tucumã powder +kaolin in the regions between 820 cm^{-1} to 1200 cm^{-1}, 1400 cm^{-1} to 1600 cm^{-1}, and 3580 cm^{-1} to 3800 cm^{-1}, concluding that there is an interaction between the elements in the formation of the composite.

3.2. Particle Diameter

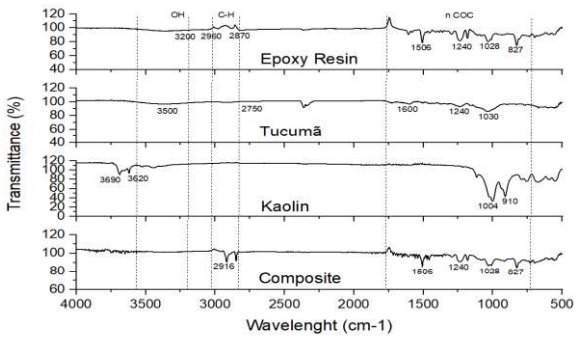


Fig. 1. FTIR spectrum for the epoxy resin, tucumã endocarp powder, amazon kaolin, and the resulting combined composite.

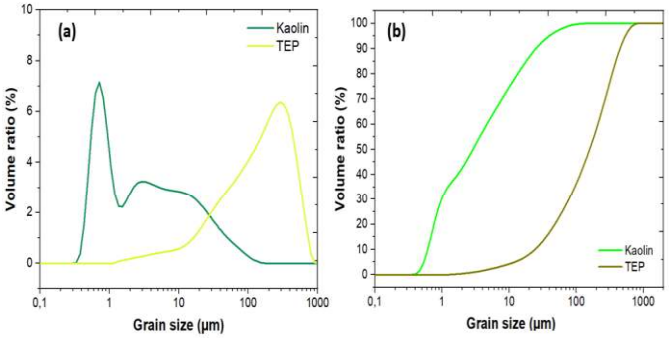


Fig. 2. Individual granulometric distribution (a) and accumulated (b) kaolin and tucumã powder volume.

Figure 2 shows that the granulometric curve of tucumã powder presents an approximately normal distribution, while kaolin presents a bimodal distribution with a shift to the left. There are significant peaks in the particle size range of 0.6 µm to 290 µm for kaolin and tucumã powder, respectively, with a volume ratio of 6.7 to 6.4. The peak volume ratio was higher for kaolin, and the particle size was finer than tucumã powder. The granulometric distribution curves by accumulated volume are also shown in Figure 2. For kaolin, the effective diameter (d10) is

0.61 µm, where 10% of the particles have a smaller diameter [7], and for tucumã powder, it is 24.5 µm. It can be observed that for kaolin 43% of the particles are below 2 µm and 87% are below 20 µm, while for tucumã powder 8% are below 20 µm, 37% are below 100 µm, and 8% below 330 µm. The very fine-grained powder has a degraded appearance, so it was preferred to work with the granulation shown above.

3.3. Characterization of ER, kaolin and ETKS by SEM

Figure 3 shows the SEM images. The surface of the TEP (Figure 3a) appears to be rough, prismatic, and irregular, similar to what was seen in [3]. Kaolin (Figure 3b) contains its characteristic pseudo-hexagonal structure in the form of lamellar layers, as evidenced in [8]. The 100% ER (ETK1) (Figure 3e) has a structure in the form of overlapping layers due to the cold molding process by gravity. The ER + 2% Kaolin (ETK2) composite (Figure 3c) has small particles of kaolin grains dispersed in the ER matrix. The ER + TEP + Kaolin composites (ETK8 and ETK22) (Figures 3d and 3f) present more evident regions of rupture, with a dispersion of Kaolin and TEP grains in the RE structure, where the granular shapes of the added charges, characterizing the intermolecular interaction resulting from these elements added to ER. Microbubbles are formed in the samples (Figures 3c, 3d, 3e, 3f) even with an anti-bubble additive as recommended by the ER manufacturer, which also contributes to a reduction in the mechanical strength properties of the resulting composites.

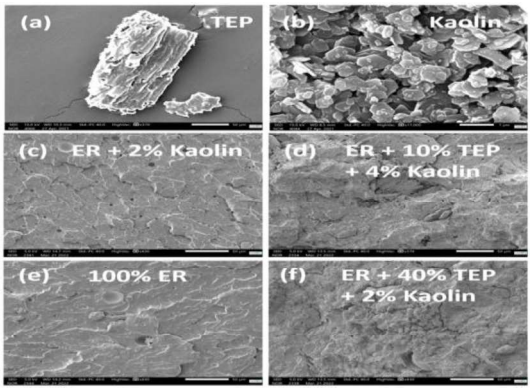


Fig. 3. SEM Images: (a) TEP, (b) Kaolin, (c) ER + 2% Kaolin (ETK2), (d) ER + 10% TEP + 4% Kaolin (ETK8), (e) 100% ER (ETK1) and (f) ER + 40% TEP + 2% Kaolin (ETK22), being (a) and (b) in its natural state, (c), (d), (e), (f) in the region of the fracture of the traction test.

3.4. Mechanical properties of ETKS

Figure 4 presents the results of the mechanical tests. In the tensile test (Figure 4a), the composites according to samples ETK6, ETK11, ETK16, and ETK2, with ER + TEP without Kaolin, showed stability around 38 MPa even with the TEP increment varying from 10% to 40% by weight, a result about 100% higher than that presented in previous studies with recycled PP + TEP thermoplastic resin [3]. Kaolin increment of 2%, 4%, 6% and 8% by weight in the composition, samples ETK2, ETK3, ETK4, and ETK5, shows a significant decrease in tensile strength. Bending test (Figure 4b) shows a decrease of 60MPa in the ER 100% composition, sample ETK1, to 40 MPa on average in the condition without kaolin, with only ER + TEP, samples ETK6, ETK11, ETK16, and ETK21, a reduction of 33%. The Kaolin increment of 2%, 4%, 6% and 8% in bonded shows an average decrease of up to 50% in flexural strength for ER + TEP + Kaolin composites, as evidenced in the ETK14 sample. The best performance is in the ETK7 sample with 47 Mpa. For the compression test (Figure 4c), compositions without kaolin, with ER + TEP, presents better

performance, as can be seen in samples ETK6, ETK11, ETK16, and ETK21, with emphasis on ETK16 (composition ER + 30% TEP), which presents the best performance around 120 Mpa. As for the Izod impact test (Figure 4d), the compositions without TEP and Kaolin showed an average reduction of 50% in strength, and the addition of TEP does not improve this impact resistance property. The best performance is in samples ETK6 (ER + 10% TEP) and ETK11 (ER + 20% TEP) between 18 J.m and 20 J.m.

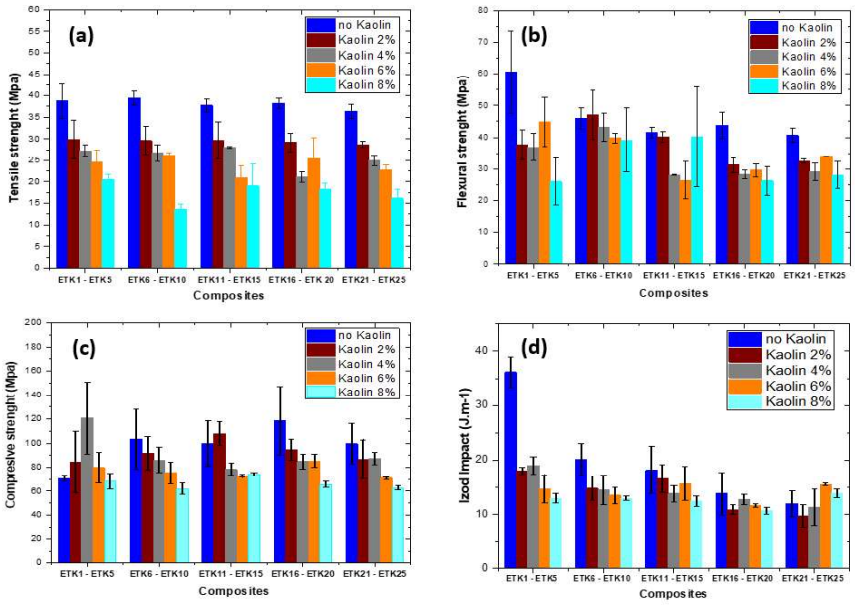


Fig. 4. Results of the mechanical properties: (a) traction, (b) bending, (c) compression and (d) Izod impact of the samples of the 25 combinations developed in the present study.

The study of the ER interaction reinforced with TEP and Kaolin (ETK2 to ETK25) being carried out for the first time, there being no similar study in scientific works already published, shows an interesting potential for use, as they are materials (TEP and Kaolin) abundantly provided by nature and are sustainable because there is replacement without damaging the environment. Composites with ER combined with TEP (ETK6, ETK11, ETK16, and ETK21) without kaolin, generally present better mechanical characteristics when compared to compositions with ER + TEP + kaolin, with the addition of kaolin leading to a loss of mechanical properties. Despite these losses, composites resulting from RE + TEP (10% to 40%) + Kaolin (2% and 4%), ETK7 to ETK10 - ETK12 to ETK15 - ETK17 to ETK10 - ETK22 to ETK25, have significant potential for use in industrial consumer products in general.

4. Conclusions

The results show that composites with epoxy resin + Tucumã powder present superior mechanical characteristics than composites with epoxy resin + kaolin, and epoxy resin + tucumã powder + kaolin. Tensile, flexural, compression, and Izod impact tests were carried out to discover the best combination with the best mechanical characteristics. In this sense, in addition to the compounds of epoxy resin + tucumã powder, the compounds of epoxy resin + tucumã powder (10% to 40% by weight) + kaolin (2% to 4% by weight) stand out as promising composites for industrial applications, especially in the construction industry in wall mosaic tiles and flooring. As the composites were made without coupling agents, future work can be carried out considering this possibility.

Declaration of Competing Interest

The authors declare no conflict of interest.

Credit author statement

AC Kieling, JCM Neto, GG Pino, MD Santos: Conceptualisation; Methodology; Formal Analysis; Writing – original draft. **SD Júnior, YOS Moreira**: Resources. **TH Panzera, MGS Valenzuela, FRV Diáz**: Supervision; Writing – review.

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