EVALUATION OF MECHANICAL PROPERTIES OF COMPOSITE OF PINHÃO WITH POLYURETHANE DERIVED FROM CASTOR OIL

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Abstract: Polymer matrix composites reinforced with pine nut shell that can be used in various application such as aerospace industry, automotive industry, electronics, and construction industry. The polyurethane derived from castor oil is a matrix that can be used to fabricate green composites, because it is derived from renewable resource, biodegradable and solvent free. The Paraná pine nut is a sub product of Paraná pine, cheap and there is a plenty of it because is a food residue. The aim of this study was to produce Paraná pine nut composites with polyurethane derived from castor oil. These composites were obtained by hot-pressing method. The mechanical proprieties were analyzed using three-point flexion test, density test and swelling test. The results indicate that these materials have mechanical resistance to be used as wooden partition panels.

Keywords: Castor oil, Paraná pine nut, composites.

1. INTRODUCTION

Composites materials are the result of at least two materials combined to form another one that usually reveal the best qualities of those materials or constituents, plus exhibit another property that neither materials possessed, like strength, stiffness, weight, acoustical insulation and others [1]. The composites materials have two basics phases called matrix and reinforcement. The first one is continuous, and its purpose is to prop the fibers, protect against environmental effects, and transfer the stress between the fibers when one fractures [2]. The second is scattered and surrounded by the matrix, giving the main resistance to composites materials [3]. There are various applications field to use polymeric composites such as aerospace industry, automotive industry, electronics, construction industry and others [4].

Medium density fiberboard is composed of wood fibers blended with resin and put under heat and pressure producing a panel. Among its applications, is very used by the furniture industry as furnishings, shelving, laminate flooring, decorative molding, office dividers, walls and ceilings, sliding doors, kitchen worktops, and others products [5].

The most used adhesive used to bind the wood fiber is urea-formaldehyde (UF) because its versatility and fairly low cost [6]. The formaldehyde is a volatile organic compound (VOC), toxic substance when inhaled by human beings causing “eyes, nose and throat irritation, headaches, loss of coordination, nausea, damage to liver, kidney and central nervous system” [7] besides, these substance are carcinogenic and mutagenic [8]. The “sick building syndrome” (SBS) and “building related illness” (BRI) are other two problems that involve the VOC’s indoor exposure [9].

The wood used to produce MDF panels in Brazil comes from dedicated forest. It is also known that the Brazilian wood industry utilize about 30-60% of the material, producing a lot of waste during the process and causing environmental problems [10-11]. It must also consider the entire manufacturing process like the wood harvest, the dryers that can be heated by combustion of the wood residue, burning oil or natural gas. These dryers will release toxic gases to the atmosphere. The presses used are heated by the stream generated by boilers [12].

An alternative to replace these polymers used to bond composites materials and reduce the environmental problems with wood harvest is to use the polyurethane derived from castor oil, PU. Because it comes from a renewable resource, it’s the oil extracted from the seeds of *Ricinus communis* plant and is a biodegradable material [13-15].

Pinion, seed from *Araucária angustifolia* tree, also known as Paraná pine tree, is a widely consumed food in southern Brazil [16]. The pinion shell, seed residue, is discarded most often in the trash [17]. Little is the knowledge of waste recovery, this practice can help to preserve the species and contribute to the biodiversity as well as being sustainable [18].

The aim of this study was to produce Paraná pine shell composites with polyurethane derived from castor oil with different rates of polyurethane and analyze the mechanical proprieties using tree-point flexion test, also its physics proprieties by both density and absorption test and swelling thickness. The SEM it is used to verify the fracture point of the composites.

2. MATERIALS AND METHODS

2.1 Materials

The Paraná pinion shell was a donation from Embrapa Florestas. These shells were put into a stove at 100ºC by 24 hour. After that, they were mashed by a kinetic mixer and were not undergone chemical treatment. The polyurethane was a donation from Cequil – Central de Industria e desenvolvimento de Polímeros Ltda, from Araraquara, São Paulo, Brazil. According to the manufacturer orientations, the weight proportion of polyol/prepolymer is 1:1.

The samples were manufactured by mixing the mashed Paraná pinion shell with the adhesive derived from castor oil, with homogenizer MH-100, series 6069 from MH equipment, with 50% and 40% of adhesive. The mix were placed into a metal mold, and put into a heat press, MA 098/AR15 from Marconi Equipment, under 9t of pressure, temperature of 70º C, for 20 minutes. Then, the samples were prepared for three-point flexion test, density test and swelling test.

2.2 Methods

The density test were made according to the standard EN323:2002, where the density is the result of the ratio of weight and volume of the sample.

The absorption test (A) and the thickness swelling (G) were calculated according the standard EN 317:2002, in percentage. The samples were immersed in water for 2 hours and 24 hours. The amount of absorbed water was calculated according Eq. (1):

$$A(\%) = \frac{m_2 - m_1}{m_2} \times 100 \tag{1}$$

Where m_1 is the weight (g) before the test and m_2 is the measured weight (g) after the test.

The thickness swelling was calculated using Eq. (2):

$$G\ (\%) = \frac{A_2 - A_1}{A_2} \times 100 \qquad (2)$$

Where A_1 is the thickness before the swelling (mm) and A_2 is the thickness measured after the test (mm).

The three-point flexure test was realized according the standard ASTM D790-03, with 5 samples on a universal test machine, EMIC DL10000. It was used load of 20 KN and speed of 5 mm/min.

To evaluate the failure zone of the composite after the flexure test it was used de Zeiss equipment, model EVO MA15.

3. RESULTS AND DISCUSSION

3.1 Density

The results of the test of density is shown on the Table 1:

Table 1: Results of density test.

Sample	Density [kg/m³]
40% PU	1222.57±21.30[b]
50% PU	1161.70±46.65[a]

The composites density decreased 5%, from 1222.57 to 1161.70, with an increase of PU. This is related with the homogeneity of the composite particles and the quantity of the pinion shell. Azevedo [19] tested the density of PU derived from castor oil and resulted in 1.09 g/cm³. The density of pinion shell is 441.65 Kg/m³. Despite the density values of 40% and 50% PU are within the standard deviation, according to the Tukey test these values are considered different with 95% confidence level.

Kelly et al. [20] characterized high-density polyethylene (HDPE) composites of coconut and banana fibers and pinion shell in the proportion of 5%, 10% for pinion shell and obtained 0.36% and 0.37% of density in its composites.

3.2 Water Absorption test and Thickness Swelling

The results of the water absorption test and thickness swelling are shown on the Table 2:

Table 2: Results of water absorption test and thickness swelling in 2 hours and 24 hours.

Sample	2h Absorption [%]	24h Absorption [%]	2h Swelling [%]	24h Swelling [%]
40%	1.521±0.002	5.207%±0.006	1.114%±0.006	4.123%±0.012
50%	0.710±0.003	4.104%±0.012	1.389%±0.006	3.337%±0.011

The water absorption decreased with the PU amount. To 2 hours, the absorption decreased 0.810% according to resin increase. Whereas this difference is 1.103% to 24 hour. We may conclude that the PU concentration impacts on water absorption, probably because there are better interaction between matrix and particles. So, the greater is the PU amount, the larger the area that involve the particle will be and its coverage will be better.

Another parameter influenced by adhesive proportion and fibers coverage is the swelling. Since the PU is hygroscopic both the absorption and the thickness swelling will occurs in the particle. The good particle coverage happens when there are little thickness swelling. The thickness for the 2 hours samples is bigger for 50% PU, but over time it is observed a decrease in the swelling rate. So we may conclude that the water initially penetrate fast into the open pores and after that the process is slower.

Marinho *et* al. [21] studied composites with polyurethane derived from castor oil and bamboo particles with 10%, 15% e 20% of PU, obtaining absorption of 68.3%, 33.7% and 22.9% respectively, and swelling between 16.3% to 12.3% for PU variety, whom explained that the increased PU provides lower swelling index, and the PU hygroscopic proprieties.

Campos *et* al. [22] research the physical proprieties of MDF of eucalyptus and PU derived from castor oil with 8% to 12% proportion observing for absorption test values between 35.54% and 27.96%. As to swelling test, the values were 16%, 13% and 10% for 8%, 10% and 12% PU proportion. Once more, we observe the influence of the resin quantity on the absorption and swelling of composites.

3.3 Three-point Flexion test

The results of three-point flexion test are shown on the Table 3:

Table 3: Results of three-point flexion test.

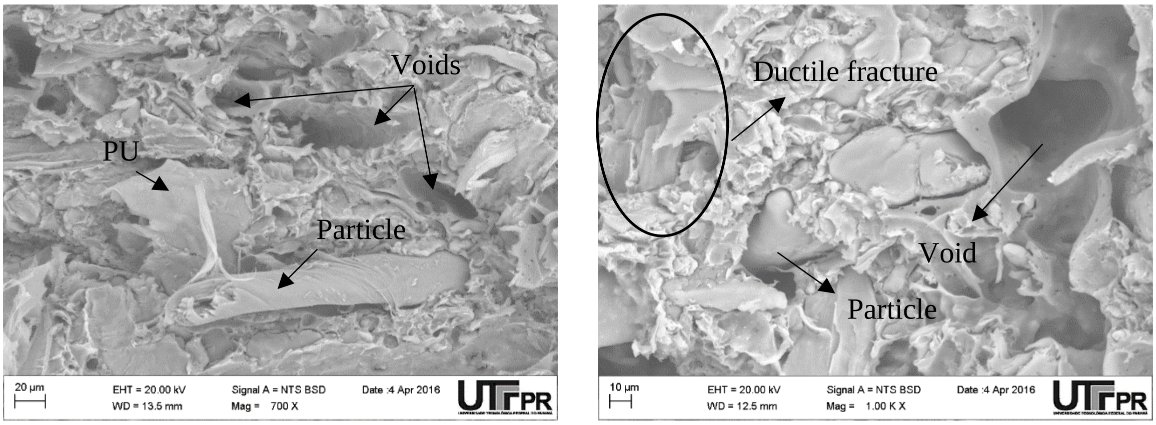
Flexion test		40% PU	50% PU
Tension	[MPa]	18.59±2,04	17.30±2.68
Minimum Tension	[MPa]	15.68	13.70
Maximum Tension	[MPa]	21.04	20.55

It can be seen that the composite flexion resistance increase with the particles increment providing greater stiffness, resulting in a better distribution of its stresses. The tension for 40% PU was 18.59 MPa and 17.30 MPa for 50% PU, resulting in a strength increase of 12.6% between the proportions. The minimum tension and the maximum tension also increased with the PU proportion decrease, with 12.6% for 40% PU and 2.3% for 50% PU respectively. The break strength was 3.6% for 50% PU and 2.80% for 40%PU.

Those values are higher than those provided by Milanese *et* al. [23] with untreated sisal composites with adhesive of polyurethane derived from castor oil that resulted in 1.6 MPa, and for thermal treated sisal with PU, 3.7 MPa and thermally treated sisal with phenolic resin, 11.2 MPa. For sawdust composites with of polyurethane derived from castor oil made by Bronkow *et* al. [24] the flexion test resulted in 20.62 MPa, value very similar to this research. These values variations are probably due to the fact that those reinforcement are different from those used in its research.

3.4 SEM

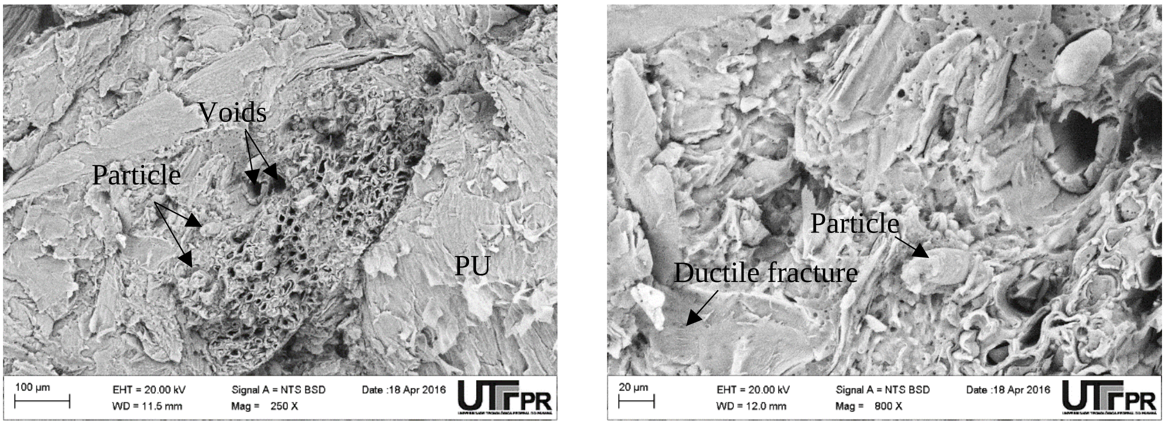
The figures Fig. 1 and Fig. 2 shows SEM micrographs of flexure tensile fracture surface of 50% and 40% PU respectively. Fig. 1a and Fig. 2a are possible to distinguish the particle of pinion shell and the PU, also the presence of ductile fracture. It can also be seen voids in the surface, this happened probably because the particles unglued themselves.



(a) (b)

Figure 1: SEM Micrography of 50% PU sample surface (a) particle and adhesive (b) amount of voids on the surface.

In the Fig. 1b and Fig. 2b ones observe the good interaction between particle-resin interfaces, where the resin covers the particle. Because of that it is difficult to distinguish PU and particle, this indicate good mixture homogeneity, adhesion and wettability, as well as small particles presence. It is also possible to observe the presence of bubbles in the composite with 40% PU whereas the 50% PU it none was identified. The bubbles presence are inherent of PU obtaining process, which may increase with humidity presence in the pinion shell particles.



(a) (b)

Figure 2: SEM Micrography in 40% PU samples (a) particle surface (b) interaction between particle and adhesive.

Jesus [25] showed SEM of sugar cane bagasse reinforcement composite also found the breakdown of cellulose fiber by pullout mechanism and the good adhesion between the fibers by coating. Suarez *et* al. [26] showed an effective adhesion between matrix and fiber in its composites for 98% polypropylene and the presence of fiber breakage and fiber pullout for its composites with 95% of polypropylene and MAPP sawdust. The cracks and the presence of holes can be seen in 90% polypropylene composites. Macedo *et* al. [27] showed the adhesion by SEM of coconut bark dust composites with 80%of PHB. In its paper work it is possible to see some holes, where some fibers detached themselves of the composite.

4. CONCLUSIONS

Materials with renewable resources and have less environmental impacts are quite sought by the companies to improve the competitiveness in business market. The aim of this paper was analyze the mechanical and physics proprieties of composite of pinion shell with polyurethane derived from castor oil. The results presented in this paper indicate that this composite can replace the materials used in the furniture and construction industry due to its hygroscopic characteristics, low water absorption and thickness swelling.

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