

Development of a bio-based adhesive from *Protium heptaphyllum* resin

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Abstract

In this work, a bio-based adhesive is prepared from *Protium heptaphyllum* resin. The resin is first characterized by ¹H and ¹³C nuclear magnetic resonance spectroscopy and the bioadhesive is then prepared using a simple mixture of the resin with linseed oil, catalyzed by cobalt octanoate, to induce crosslinking. The precursors and bioadhesive obtained are characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). The NMR analysis shows the presence of groups of triterpenes, such as α - and β -amyrins, and diols, such as brein and maniladiol. Thermogravimetric analysis reveals that the resin has less thermal stability than the bioadhesive. Mechanical tests indicate that the bioadhesive has greater adhesion strength compared to the commercial adhesive, reaching an average stress at break of 7.66 and 0.113 MPa for the wood and carbon steel substrates, respectively. In conclusion, the bioadhesive can be used for the production of composites.

Keywords: adhesive, *Protium heptaphyllum*, reticulation reaction, linseed oil.

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1. Introduction

Adhesives are polymeric materials capable of interacting, both chemically and physically, with a substrate in such a way that the stresses are transferred between both components^[1]. Commercially available adhesives, such as polychloroprene, polyvinyl, cyanoacrylate and vinyl acetate, are generally produced from non-renewable sources. Furthermore, some of the most used petroleum-based adhesives contain dangerous chemicals, e.g., formaldehyde, which have a negative impact on the environment and human health^[2].

In order to produce more environmentally friendly materials, significant research has been focused on using renewable resources to obtain adhesives. The adhesives prepared from the modification of linseed oil^[3], soy protein^[4,5], castor oil plant^[6,7] lignin and chitosan^[8-10] are good examples of this approach. The employment of these raw materials is possible as a result of their active sites, such as hydroxyl groups and unsaturated bonds. These groups can react, in the presence of a catalyst, with crosslinking agents that have chemical groups compatible with the substrate (wood, metals or plastics).

Natural resins are extractive substances secreted by plants as a protective mechanism to injury. Most natural resins are composed of terpenes, which are macromolecules derived

from isoprene (2-methyl-1,3-butadiene). These compounds present active sites (double bonds and hydroxyl groups) that are prone to chemical attack and can be exploited for the development of adhesives.

In the Amazon region of Brazil, there are many species of trees that secrete natural resins with the potential for the development of adhesives. Among these natural resins, *Protium heptaphyllum* is highlighted for having an established market due to its application in the cosmetics industry. This resin is mostly composed of α - and β -terpenes^[11] and is used in folk medicine as an anti-inflammatory, analgesic, stimulant, cough remedy and for clearing airways^[12]. Another important application of this resin is in the caulking of wooden boats, a classical craftwork realized by riverains.

The use of natural resins in their crude form for the preparation of adhesives results in poor mechanical resistance, due to their relatively small molecular weight and absence of interchain bonds. In this context, crosslinking with vegetable oils has been a strategy used for improving the mechanical performance of adhesives. Addis et al.^[13] performed a chemical modification of linseed oil from various crosslinking agents and tested it as an adhesive in three types of wood. They evaluated the curing time, the type of crosslinking agent

and the rate of adhesive impregnation and reported that the material is a promising bioadhesive for wood.

Although *Protium heptaphyllum* resin has long been used by riverains for craftwork, its scientific investigation is very limited. Only the work of Vieira et al.^[11] reports the application of *Protium heptaphyllum* resin as an adhesive. The authors demonstrated that the pure resin can be used for the adhesion of wood; however, they verified that it has low mechanical resistance and becomes brittle after curing, which decreases its adhesion strength on the substrate surface.

In this work, a bioadhesive is prepared from the crosslinking of *Protium heptaphyllum* resin and linseed oil and catalyzed by cobalt octanoate (12Co). Linseed oil is selected because of its high content of double bonds, which is important for the formation of a consistent chemical network in the cured material. In addition, linseed oil acts as a plasticizer, which resolves the problem of brittleness described by Vieira et al.^[11]. The resin and bioadhesive are initially characterized and their chemical composition, thermal stability and main thermal transitions determined. Subsequently, the adhesion force of the bioadhesive is evaluated through shear stress assays in specimens of wood and carbon steel. A commercial adhesive from polychloroprene is used for comparison. On this basis, the aim of this study is to develop a bioadhesive suitable for the production of composites.

2. Materials and Methods

2.1 Materials

Protium heptaphyllum resin was acquired from a local market in Macapá, Brazil. The material was received as a dark gray solid, with some vegetable residues of branches and leaves dispersed among the solids. Linseed oil (Corfix, Porto Alegre) was acquired from a local market in Porto Alegre, Brazil, and received as a clear, crude and unpolymerized light yellow oil. The 12Co 12% catalyst was supplied by Miracema Nuodex (Guarulhos, Brazil). Chloroform P.A. 99.98% and deuterated chloroform (CDCl₃) were purchased from Sigma Aldrich®.

2.2 Methods

2.2.1 Purification of *Protium heptaphyllum* resin

The resin was first crushed with a hammer and vegetable residues (branches and leaves) were manually removed. The resin was then purified through solid/liquid Soxhlet

extraction with chloroform at 70 °C for 8 h. Finally, the extract was concentrated in an oven at 105 °C for 24 h, resulting in a red-orange translucent solid (Figure 1) with a mass yield of 92%.

2.2.2 Adhesive formulation and preparation of specimens for mechanical tests

The bioadhesive was produced from the crosslinking of the *Protium heptaphyllum* resin and linseed oil in the presence of the 12Co catalyst. 12Co is considered the most efficient catalyst among transition metals and it can induce a crosslinking reaction of linseed oil at 82 °C^[14]. The bioadhesive preparation involved the simple mixing of the components at 100 °C in a mass ratio of 80:20 (resin/linseed) with 0.5% of 12Co. In a typical procedure, 16 g of the purified *Protium heptaphyllum* resin were weighed in a porcelain crucible and heated to 100 °C until complete liquefaction was achieved. Subsequently, linseed oil (4 g) and 0.5% of 12Co (0.01 g) were added and the mixture was homogenized for 5 min. This mixture was allowed to cure for 72 h in an oven at 60 °C. After curing, samples of the adhesive were collected for FTIR, TGA and DSC characterization.

2.2.3 Characterization of precursor materials and bioadhesive

¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopies were performed to identify the main compounds present in the purified *Protium heptaphyllum* resin. Samples were dissolved in deuterated chloroform at 60 mg/mL and analyzed at 50 °C using a Bruker® spectrometer, Avance III, 300 MHz.

The thermal stability of the purified resin, linseed oil and adhesive was evaluated using TGA. The analysis was performed using a TGA Q50 V20.13 Build 39 under a N₂ flow rate of 100 mL/min from room temperature to 840 °C at a heating rate of 20 °C/min. An alumina pan was used and the approximate sample mass was 15 mg.

DSC was performed on the purified resin, linseed oil and adhesive using a TA Instrument calorimeter with a N₂ cooling module. Samples of ~5 mg were analyzed from 0 to 200 °C at a heating rate of 10 °C/min and in a N₂ flow rate of 50 mL/min.

FTIR spectroscopy was employed to evaluate the main functional groups of the *Protium heptaphyllum* resin and linseed oil. The spectra were collected with a Perkin-Elmer Frontier spectrometer in transmittance mode using the KBr pellet method in the range of 4000–650 cm⁻¹. For the bioadhesive of *Protium heptaphyllum*, the analysis was

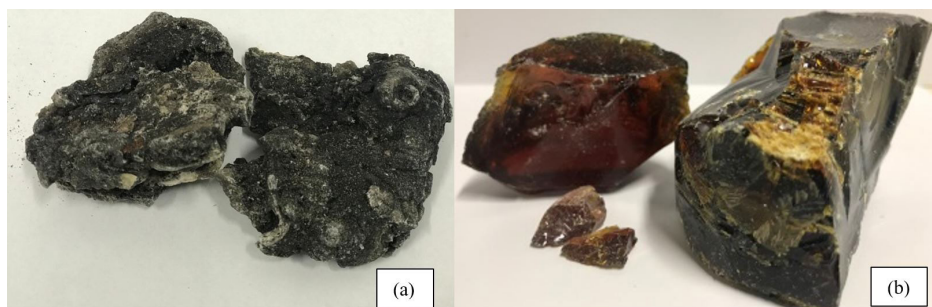


Figure 1. *Protium heptaphyllum* resin (a) before and (b) after purification.

performed in total attenuated reflection using a wavenumber range from 4000 to 700 cm^{-1} , 16 scans and a 4 cm^{-1} resolution.

2.2.4 Mechanical shear testing

To determine the adhesion force, the bioadhesive was prepared in a similar manner as described in section 2.2.2. The mixture (crude resin, linseed oil and catalyst) was impregnated in specimens of wood or carbon steel that were placed in an oven with air recirculation (DELEO, model ABAR-FC) at 60 °C for 72 h for curing.

The carbon steel specimens were based on the ASTM D1002-10^[15] standard, with dimensions of 100 mm×25 mm and thickness of 1.5 mm. The bioadhesive was impregnated on the specimen with a grammage of 144 g/m^2 , in a bonding area of 12.5×25 mm^2 . After the contact of both specimen sides, they were attached with double metal clips.

For wooden specimens, the modified ASTM D906^[16] standard was employed. Laminated *eucalyptus* wood with dimensions of 100 mm×25 mm and a thickness of 4 mm was used. The bioadhesive was applied on the substrate with a grammage of 154 g/m^2 in a bonding area of 30×25 mm^2 . The specimens were again attached with double clips.

The tests were carried out using a universal machine EMIC, model 23-5D. The specimens were attached by two flat plate claw screws and tensioned. For the metal substrate, a shear rate of 1.27 mm/min was used, according to ASTM D1002-10^[15], while for the wooden specimens, a shear rate of 10 mm/min was used, according to ASTM D906^[16]. The test with a commercial polychloroprene adhesive was made using the same procedure, except for the curing time, which was 72 h.

Statistical analyzes were performed using the free PAST software, version 2.17c. Variance (ANOVA) and Tukey's test were used at the 95% significance level.

2.2.5 Optical microscopy

The micrographs of the fracture area in the specimens were observed using a digital optical microscope model U1000X with a magnification of 1000×.

3. Results and Discussions

3.1 Characterization of precursor materials and bioadhesive

The ¹H and ¹³C NMR spectra of the *Protium heptaphyllum* resin are shown in Figures 2 and 3, respectively. Since techniques for separating the components of the *Protium heptaphyllum* resin were not used, the spectra are only discussed qualitatively, with the primary purpose of identifying functional groups and structures. For this, the chemical shifts of the compounds found in the *Protium heptaphyllum* resin depicted in the literature are used.

In the region between 0.8 and 2.0 ppm for the ¹H NMR and 0 to 56 ppm for the ¹³C NMR spectra, a set of chemical shifts characteristic of carbon chains is noted; however, it is not possible to identify these compounds. In addition, no chemical deformations above 140 ppm were observed, which is typical of triterpenoids with alkene groups, such

as β -amirnone, α -amirnone and lupenone^[17]. The peaks at β -79.07 ppm and α -77.03 ppm in the ¹³C NMR spectrum are related to carbons in position C3 linked to hydroxyls (C-OH), which is confirmed by the double doublet at 3.25 ppm in the ¹H NMR spectrum, which is characteristic of protons attached to carbons adjacent to hydroxyl groups. In addition, in the ¹³C NMR spectrum, the peaks at 144.6 ppm (C13) and 121.26 ppm (C12) are characteristic of β -amyrin. The peaks at 139 ppm (C13) and 124 ppm (C12) are from α -amyrin^[17,18]. The peaks at 67.4 ppm and 66.4 ppm in the ¹³C NMR spectrum are attributed to carbinolic carbons, at position C16, and the double doublet at 4.2 ppm in the ¹H NMR spectrum is characteristic of diols, such as brein and maniladiol^[17,19].

The TGA curves and their respective derivatives (DTG) of the purified *Protium heptaphyllum* resin, linseed oil and bioadhesive are shown in Figure 4. Table 1 presents the values of the thermal stability at 5% mass loss ($T_{5\%}$), and the mass loss (Δm_i) and peak temperature (T_{max} , which is the temperature of the maximum rate of decomposition obtained from the DTG curves) of each thermal event observed for the curves.

Figure 4 shows four thermal events for the resin and adhesive, while for the linseed oil, the degradation occurs in a single step. The first thermal event appears between 106 and 201 °C and is attributed to the loss of volatile components. It is noted that the resin ($\Delta m_1 = 9.18\%$) presents a higher variation in mass loss than the adhesive ($\Delta m_1 = 4.10\%$), which may be due to the thermal processes of heating at 100 °C until liquefaction and curing at 60 °C used for preparing the adhesive. The second thermal event is observed between 201 and 435 °C and is related to the loss of the main components (amyrins and diols) of the *Protium heptaphyllum* resin, as reported by Silva Junior et al.^[20] and Vieira Junior et al.^[17]. Silva Junior et al.^[20] showed that the isomers α - and β -amyrins, the major components of *Protium heptaphyllum* resin are degraded in the range of 210 to 380 °C. Vieira Junior et al.^[17] obtained similar results for the *Protium heptaphyllum* resin. In this step, the remaining mass of the resin ($\Delta m_2 = 90.65\%$) is lost, while for the bioadhesive, a broadening of the peak ($\Delta m_2 = 89.48\%$) is observed. From analyzing the T_{max} of the both peaks, it is observed that the resin has the highest value; however, this does not mean that it has a greater thermal stability, since the peak broadening is displaced for a higher temperature

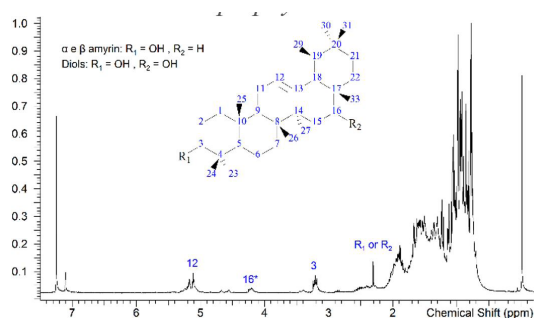


Figure 2. ¹H NMR spectrum of *Protium heptaphyllum* resin.

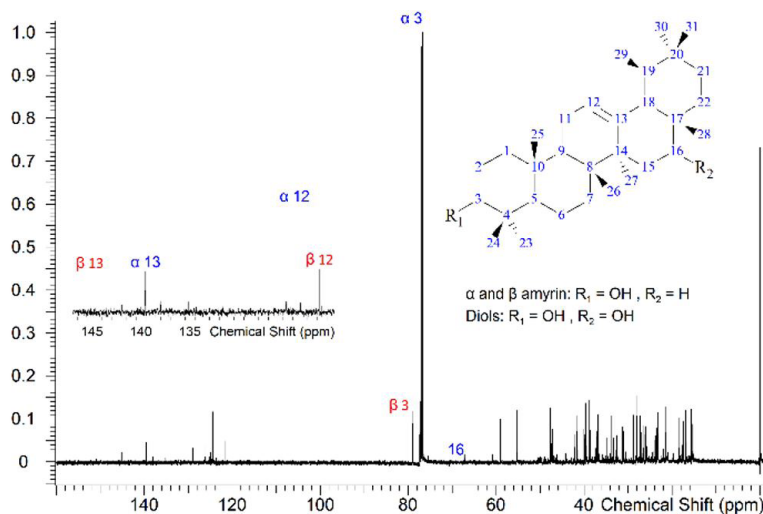


Figure 3. ^{13}C NMR spectrum of *Protium heptaphyllum* resin.

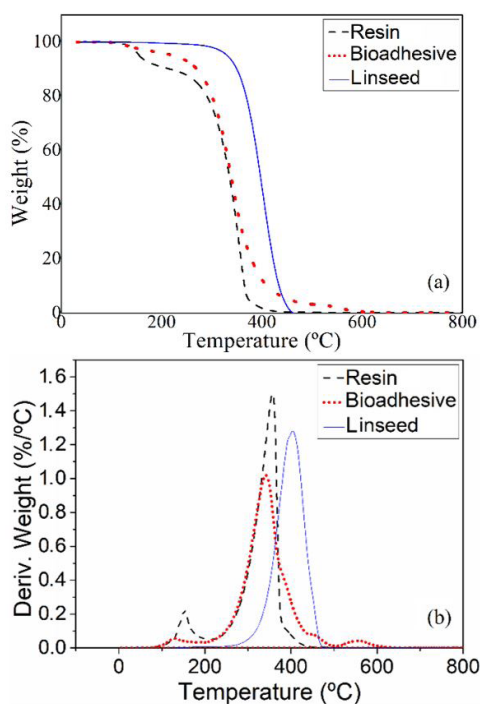


Figure 4. TGA (a) and DTG (b) curves for resin, adhesive and linseed oil.

and third and fourth additional peaks are identified for the bioadhesive.

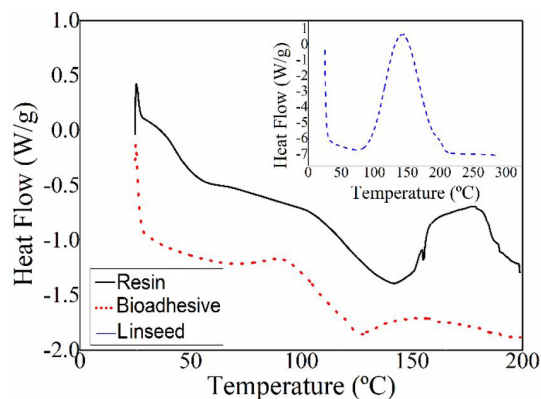
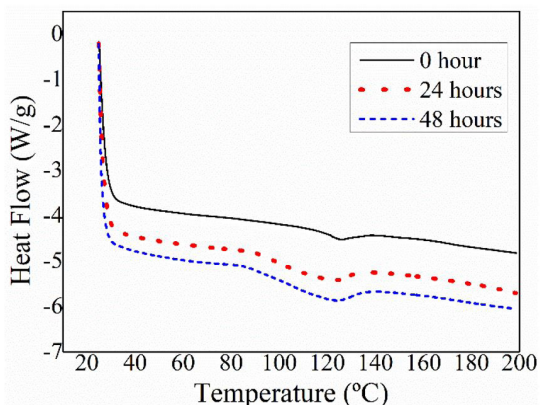
The third (shoulder) and fourth thermal events were observed only for the bioadhesive. They occurred in the temperature range of 435 to 498 °C for the third peak ($\Delta m_2 = 3.36\%$) and from 498 to 607 °C for the fourth peak ($\Delta m_2 = 2.84\%$). These peaks may be the decomposition from macromolecules or oligomers formed from the crosslinking of the *Protium heptaphyllum* resin with linseed oil, since they have T_{\max} higher than the crude resin and linseed oil.

The DSC results of the *Protium heptaphyllum* resin, linseed oil and bioadhesive are shown in Figure 5. Linseed oil showed an exothermic peak between 75 and 200 °C, with a maximum close to 150 °C. Lazzari and Chiantore^[21] demonstrated that this exothermic peak, in the range of 100 to 200 °C, is a result of the formation of peroxides that react with conjugated double bonds characteristic of oils that have undergone some type of treatment or prepolymerization. Thus, it is inferred that the commercial linseed oil used to prepare the bioadhesive had already been oxidized to some level, probably due to exposure to the environment. The oxidation of triglycerides, using transition metals, such as cobalt, as catalysts, occurs from the hydrogen abstraction of methylene groups present in the unsaturation. The cobalt catalyst provides both the formation of hydroperoxides and their decomposition due to the formation of stable ions. The combination of these radicals initiates the crosslinking reaction^[22]. Other possible termination reactions described by Charamzová et al.^[23] suggest that alkoxide groups, formed from hydroxyl groups (major components of *Protium heptaphyllum* resin), can be combined with radicals from unsaturations.

The resin presented two endothermic events, compatible with the results reported by Vieira Junior et al.^[17] for *Protium heptaphyllum* resin. The first one appears close to 52 °C, with an enthalpy of 3.3 J/g, and is associated with the softening of the material. The second one arises in the range of 100 to 160 °C and is more intense, with an enthalpy of 24.89 J/g. This is attributed to the loss of volatile materials, such as water or solvent, which are likely to be residues from the purification process. For the adhesive, the DSC curve exhibited two exothermic events, with the first one occurring in the range of 63 to 126 °C, with an enthalpy of 15.32 J/g, and the second one in the range of 126 to 190 °C with an enthalpy of 7.50 J/g. Both events may indicate a two-step curing of the adhesive, in which in the first step occurs via the oxidation of the linseed oil or reactions of OH groups from resin with unsaturated groups of linseed oil, while the second step occurs with crosslinking between the linseed

Table 1. Main thermal events in the samples.

Samples	$T_{5\%}$ (°C)	Thermal events								Ash (%)
		1°		2°		3°		4°		
		Δm wt. %	T_{max} (°C)	Δm wt. %	T_{max} (°C)	Δm wt. %	T_{max} (°C)	Δm wt. %	T_{max} (°C)	
Resin	155	9.28	152	90.65	357	-	-	-	-	0.07
Linseed	331	100	404	-	-	-	-	-	-	0.00
Bioadhesive	222	4.10	129	89.48	341	3.36	457	2.84	556	0.22

**Figure 5.** DSC curves for samples of *Protium heptaphyllum* resin, linseed oil and bioadhesive.**Figure 6.** DSC curves for bioadhesive samples at 0, 24 and 48 h.

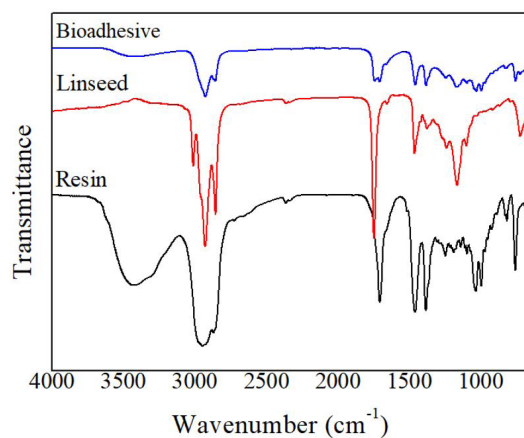
oil chains or between the linseed oil and components of the *Protium heptaphyllum* resin (amyryns and diols).

To assess whether the exothermic event observed for the bioadhesive in Figure 5 is from curing, thermograms from DSC were evaluated at 0, 24 and 48 h of curing. The results are exhibited in Figure 6. In general, the curves also showed two exothermic events and an evolution in the energy released was observed. The first event (70 to 125 °C) released 5.22 J/g at 0 h and 8.60 J/g at 48 h. Similarly, the second exothermic event (125 to 190°C) increased from 4.80 J/g at 0 h to 8.61 J/g at 48 h. Thus, the fact that this energy increases with the elapsed curing time of the bioadhesive is an indication that chemical bonds are formed (crosslinking), since this behavior is characteristic of a curing process.

From comparing the resin and bioadhesive spectra, Figure 7, the main difference is the decrease in the intensity of the bands at 3430 and 3100 cm^{-1} , corresponding to the OH groups of the resin components (amyryns, brein and maniladiol) and the =C-H groups of the linseed oil, respectively. The reduction of the OH band is possibly a consequence of the reaction of OH with double bonds through an oxidation mechanism^[23]. The =C-H band is indicative of the crosslinking of the resin with linseed oil, since the bioadhesive does not show this band. Such processes can be correlated with the DSC results, in which a double-step curing was observed.

3.2 Adhesion strength in wood and steel

The adhesion strength of the bioadhesive was evaluated through shear stress assays in carbon steel and wood substrates. In addition, a commercial adhesive (polychloroprene) was used

**Figure 7.** FTIR spectra for resin, adhesive and linseed oil.

for reference. Figure 8 shows the results of the mechanical shear stress tests and Table 2 the ANOVA of the values obtained. Comparing the bioadhesive and polychloroprene, it is observed that the adhesion strength of the first one is 3 times the second one for the wooden substrate, and 2 times for the metallic substrate. In terms of performance between substrates, the difference was significantly higher, being the shear stress of the wooden substrate 67 times of the metallic substrate for the bioadhesive, and 47 times for the polychloroprene. This result is related to the greater affinity of the resin with the wood material, which has surface groups that facilitate physical interactions and a roughness that favors mechanical anchoring. Besides, the penetration of the

Table 2. ANOVA results for substrates.

Substrate	Factor	Sum of squares	DF	Mean square	F	P-value
Metal	Between groups	13018	1	13	14.89	0.00272
	Within groups	10489	12			
Wood	Between groups	85.6104	1	85.6104	109.4	4.702.10⁻⁷
	Within groups	8.60465	11	0.78224		

DF= degrees of freedom; F= value from the F distribution; P-value= probability of significance.

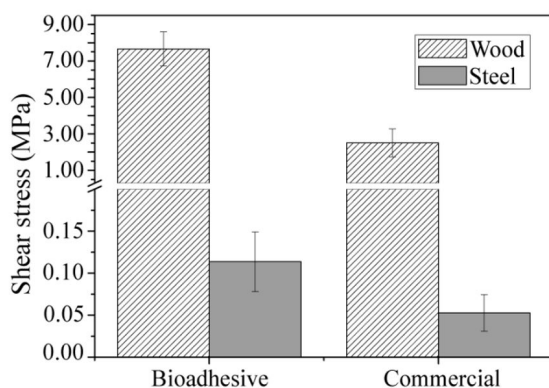


Figure 8. Comparative results of shear stress of samples evaluated on steel and wood substrates.

adhesive into the pores of the substrate (absorption effect) provides greater resistance, and this effect appears for the wood but is absent for the metallic substrate^[24]. The values of tensile shear stress are much higher than those obtained by Vieira et al.^[11], who employed crude *Protium heptaphyllum* resin as an adhesive and reached only 0.14 MPa of shear stress using wood as a substrate. This better performance is mainly attributed to the crosslinking with linseed oil. In addition, the linseed oil acts as an internal lubricant, providing gains in deformation and eliminating the problem of brittleness reported by Vieira et al.^[11]. Compared with the polychloroprene adhesive, the bioadhesive of *Protium heptaphyllum* was superior, as evidenced by the higher average values of shear stress for both substrates that were statistically different ($p < 0.05$) according to ANOVA (Table 2). The difference in performance was more visible for the wood substrate, since the bioadhesive was three times higher than the polychloroprene.

Figure 9 shows micrographs of the fractured area of samples from adhesion strength tests for both substrates. According to Wei et al.^[25], there are three different failures that can occur in adhesives: adhesive failure, cohesive failure and mixing failure. In this work, different failures were observed in the tested substrates. For the metallic substrate, there were areas where the adhesive completely detached from the substrate (delimited area), characterizing adhesive failure and parts where the contact area still had adhesive, showing a cohesive fracture. The mechanical interlocking, adsorption, and chemical bonding are the three primary mechanisms that control the adhesion^[26]. Besides, the roughness of the metallic surface is another decisive factor for the interaction^[27]. Therefore, one reason that may have contributed to the adhesive having presented

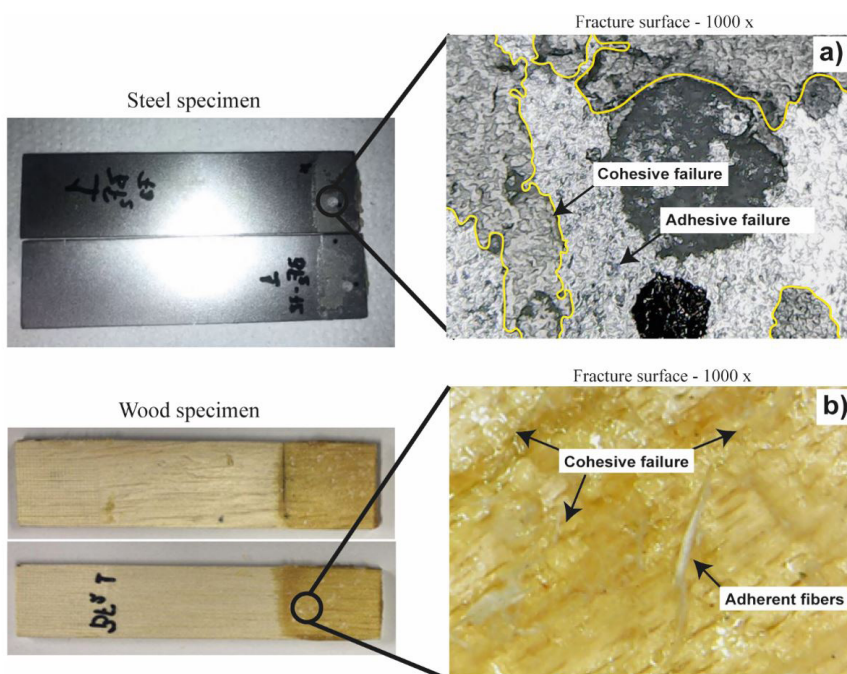


Figure 9. Micrography of the fractured surface area of the adhesion strength specimen tests of the *Protium heptaphyllum* adhesive, realized in carbon steel (a) and wood as substrates (b).

adhesive failure is the fact that the substrate has undergone no kind of pre-treatment to increase adhesion. For the wood adherent, cohesive failure is perceived in regions of the bonding area with part of the adherent fibers (Figure 9b), which for ASTM D5573-99^[28] standard can be defined as Light-Fiber-Tear failure (LFT failure). In both cases, the occurrence of cohesion failures may be related to a slight reticulation of the bioadhesive^[29], which did not form a consistent interlacing among the molecules that are required to hinder an early cohesion fracture during the shearing of the bioadhesive. On the other hand, it indicates that the *Protium heptaphyllum* adhesive has a fixation to the substrate stronger than the internal resistance (cohesion), which is required for adherence behavior^[25].

4. Conclusions

A bioadhesive was prepared from the crosslinking of *Protium heptaphyllum* resin with linseed oil using cobalt octanoate as a catalyst.

Through ¹H and ¹³C NMR spectroscopy analyzes it was confirmed the main chemical structures of the *Protium heptaphyllum* resin. From the thermal analyzes it was identified a curing process, which was additionally noted in the FTIR spectra. The mechanical assays results demonstrated that the bioadhesive prepared has greater mechanical properties than the commercial material (polychloroprene) used as reference. It is highlighted that the adhesion strength of the bioadhesive was three times that of the commercial adhesive used as reference for the wood substrate.

Finally, taking in to account the good results obtained for the wood substrate, we consider that the bioadhesive prepared from the *Protium heptaphyllum* adhesive has potential to be applied in the production of wood-based composites.

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6. References

- Conner, A. H., & Bhuyan, M. S. H. (2017). Wood: adhesives. *Reference Module in Materials Science and Materials Engineering*, 1-17. <https://doi.org/10.1016/b978-0-12-803581-8.01932-9>.
- Norström, E., Fogelström, L., Nordqvist, P., Khabbaz, F., & Malmström, E. (2015). Xylan - a green binder for wood adhesives. *European Polymer Journal*, 67, 483-493. <http://dx.doi.org/10.1016/j.eurpolymj.2015.02.021>.
- Sahoo, S. K., Khandelwal, V., & Manik, G. (2019). Synthesis and characterization of low viscous and highly acrylated epoxidized methyl ester based green adhesives derived from linseed oil. *International Journal of Adhesion and Adhesives*, 89, 174-177. <http://dx.doi.org/10.1016/j.ijadhadh.2019.01.007>.
- Mo, J., Wang, F., Xu, Z., Feng, C., Fang, Y., Tang, X., & Shen, X. (2019). Characterization and performance of soybean protein modified by tyrosinase. *International Journal of Adhesion and Adhesives*, 92, 111-118. <http://dx.doi.org/10.1016/j.ijadhadh.2019.04.013>.
- Pang, H., Zhao, S., Wang, Z., Zhang, W., Zhang, S., & Li, J. (2020). Development of soy protein-based adhesive with high water resistance and bonding strength by waterborne epoxy crosslinking strategy. *International Journal of Adhesion and Adhesives*, 100, 102600. <http://dx.doi.org/10.1016/j.ijadhadh.2020.102600>.
- Moghadam, P. N., Yarmohamadi, M., Hasanzadeh, M., & Nuri, S. (2016). Preparation of polyurethane wood adhesives by polyols formulated with polyester polyols based on castor oil. *International Journal of Adhesion and Adhesives*, 68, 273-282. <http://dx.doi.org/10.1016/j.ijadhadh.2016.04.004>.
- Oliveira, P. R., May, M., Panzera, T. H., Scarpa, F., & Hiermaier, S. (2020). Reinforced biobased adhesive for eco-friendly sandwich panels. *International Journal of Adhesion and Adhesives*, 98, 102550. <http://dx.doi.org/10.1016/j.ijadhadh.2020.102550>.
- Ji, X., Li, B., Yuan, B., & Guo, M. (2017). Preparation and characterizations of a chitosan-based medium-density fiberboard adhesive with high bonding strength and water resistance. *Carbohydrate Polymers*, 176, 273-280. <http://dx.doi.org/10.1016/j.carbpol.2017.08.100>. PMID:28927608.
- Ji, X., & Guo, M. (2018). Preparation and properties of a chitosan-lignin wood adhesive. *International Journal of Adhesion and Adhesives*, 82, 8-13. <http://dx.doi.org/10.1016/j.ijadhadh.2017.12.005>.
- Vargas Villanueva, J. G., Sarmiento Huertas, P. A., Galan, F. S., Esteban Rueda, R. J., Briceño Triana, J. C., & Casas Rodriguez, J. P. (2019). Bio-adhesion evaluation of a chitosan-based bone bio-adhesive. *International Journal of Adhesion and Adhesives*, 92, 80-88. <http://dx.doi.org/10.1016/j.ijadhadh.2019.04.009>.
- Vieira, R. K., Vieira, A. K., Kim, J. T., & Netravali, A. N. (2014). Characterization of Amazonic White Pitch (*Protium heptaphyllum*) for potential use as 'green' adhesive. *Journal of Adhesion Science and Technology*, 28(10), 963-974. <http://dx.doi.org/10.1080/01694243.2014.880220>.
- Bandeira, P. N., Deusdênia, O., Pessoa, L., Teresa, M., Trevisan, S., & Gomes, L. (2002). Secondary metabolites of *Protium heptaphyllum* march. *Química Nova*, 25(6b), 1078-1080. <http://dx.doi.org/10.1590/S0100-40422002000700006>.
- Addis, C. C., Koh, R. S., & Gordon, M. B. (2020). Preparation and characterization of a bio-based polymeric wood adhesive derived from linseed oil. *International Journal of Adhesion and Adhesives*, 102, 102655. <http://dx.doi.org/10.1016/j.ijadhadh.2020.102655>.
- Juita, Długogorski, B. Z., Kennedy, E. M., & Mackie, J. C. (2011). Oxidation reactions and spontaneous ignition of linseed oil. *Proceedings of the Combustion Institute*, 33(2), 2625-2632. <http://dx.doi.org/10.1016/j.proci.2010.06.096>.
- American Society for Testing and Materials (2019). *ASTM D 1002-10: Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading (Metal-To-Metal)*. West Conshohocken: ASTM.
- American Society for Testing and Materials (2017). *ASTM D 906: Standard Test Method for Strength Properties of Adhesives in Plywood Type Construction in Shear by Tension Loading*. West Conshohocken: ASTM.
- Vieira, G. M., Jr., Souza, C. M., & Chaves, M. H. (2005). The *Protium heptaphyllum* resin: isolation, structural characterization and evaluation of thermal properties. *Química Nova*, 28(2), 183-187. <http://dx.doi.org/10.1590/S0100-40422005000200003>.
- Vásquez, L. H., Palazon, J., & Navarro-Ocaña, A. (2012). *The pentacyclic triterpenes e a, β-amyrins: a review of sources and biological activities*. In: L. H. Vázquez (Ed.), *Phytochemicals: a global perspective of their role in nutrition and health* (pp. 487-502). United States: IntechOpen.

19. Maia, J. G., & Zoghbi, M. G. B. (1998). *Óleos essenciais da Amazônia: inventário da flora aromática*. In: L. G. J. Farias & C. M. L. Costa. *Tópicos especiais de produtos naturais* (pp. 147-162). Brasil: POEMA.
20. da Silva Júnior, W. F., Pinheiro, J. G. O., Moreira, C. D. L. F. A., Rüdiger, A. L., Barbosa, E. G., Lima, E. S., da Veiga Júnior, V. F., da Silva Júnior, A. A., Aragão, C. F. S., & de Lima, Á. A. N. (2017). Thermal behavior and thermal degradation kinetic parameters of triterpene a, b amyryl. *Journal of Thermal Analysis and Calorimetry*, 127(2), 1757-1766. <http://dx.doi.org/10.1007/s10973-016-6046-x>.
21. Lazzari, M., & Chiantore, O. (1999). Drying and oxidative degradation of linseed oil. *Polymer Degradation & Stability*, 65(2), 303-313. [http://dx.doi.org/10.1016/S0141-3910\(99\)00020-8](http://dx.doi.org/10.1016/S0141-3910(99)00020-8).
22. Lima, G. E. S., Nunes, E. V., Dantas, R. C., Simone, C. A., Meneghetti, M. R., & Meneghetti, S. M. P. (2018). Catalytic behaviors of coil and MnII compounds bearing α -Diimine ligands for oxidative polymerization or drying oils. *Journal of the Brazilian Chemical Society*, 29(2), 412-418. <http://dx.doi.org/10.21577/0103-5053.20170155>.
23. Charamzová, I., Vinklársek, J., Kalenda, P., & Honzicek, J. (2018). Application of oxovanadium complex stabilized by N,N,N-chelating ligand in air-drying paints. *Coatings*, 8(6), 204. <http://dx.doi.org/10.3390/coatings8060204>.
24. Gardner, D. J., Blumentritt, M., Wang, L., & Yildirim, N. (2015). *Adhesion theories in wood adhesive bonding*. In K. L. Mittal (Ed.), *Progress in adhesion and adhesives* (pp. 125-168). United States: Scrivener Publishing. <http://dx.doi.org/10.1002/9781119162346.ch5>.
25. Wei, H., Xia, J., Zhou, W., Zhou, L., Hussain, G., Li, Q., & Ostrikov, K. (2020). Adhesion and cohesion of epoxy-based industrial composite coatings. *Composites. Part B, Engineering*, 193, 108035. <http://dx.doi.org/10.1016/j.compositesb.2020.108035>.
26. Baldan, A. (2012). Adhesion phenomena in bonded joints. *International Journal of Adhesion and Adhesives*, 38, 95-116. <http://dx.doi.org/10.1016/j.ijadhadh.2012.04.007>.
27. Chen, P., Wang, Y., Li, J., Wang, H., & Zhang, L. (2018). Adhesion and erosion properties of epoxy resin composite coatings reinforced with fly ash cenospheres and short glass fibers. *Progress in Organic Coatings*, 125, 489-499. <http://dx.doi.org/10.1016/j.porgcoat.2018.09.029>.
28. American Society for Testing and Materials – ASTM. (2019). *ASTM D5573-99: standard practice for classifying failure modes in fiber-reinforced-plastic (FPR)*. West Conshohocken: ASTM.
29. Silva, L. F. M., Ochsner, A., & Adams, R. D. (2011). *Handbook of adhesion technology*. Berlin: Springer. <http://dx.doi.org/10.1007/978-3-642-01169-6>.

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