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Preparation of wood adhesives based on tannins and glycerol esters (triacetate)

Anelise Lima de Abreu Dessimoni, Leydiane de Oliveira Pereira, Tattiane Gomes Costa, Maria Lucia Bianchi, Taís Regina Lima Abreu Veiga, Maria Fernanda Vieira Rocha

Universidade Federal de Lavras, Departamento de Química. Caixa Postal 3037. CEP 37200-000, Lavras - MG, Brasil

Address For Correspondence:
Anelise Lima de Abreu Dessimoni , Universidade Federal de Lavras (UFLA), Departamento de Química. Campus Universitário - Caixa Postal 3037. CEP 37200-000, Lavras, Minas Gerais, Brazil.
Tel: 5538-999826364; E-mail: mfvrocha@yahoo.com.br

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ABSTRACT

Background: The use of products obtained from gluing of wood can, directly, contributes to the conservation of forest resources, from the point of view of its full use. However, the synthetic resins used in the bonding are obtained by petroleum derivatives, whose price has grown steadily in recent years as a result of the reduction of fossil resources. An alternative would be the use of compounds derived from renewable sources, such as tannins, instead of phenol. Furthermore, driven by energy policies that encourage the use of renewable sources, we are in the midst of a biodiesel production surge. One of the co-products of biodiesel production is glycerin, which corresponding itself to 10% of the total mass of the obtained oil. Glycerin, or more specifically the glycerol, may be converted to glycerol triacetate. Thus, the objective herein was to prepare environmentally friendly adhesives, using glycerol triacetate and tannins. For preparation of the wood adhesives, glycerol triacetate and H_2SO_4 were mixed at 80°C for one hour. After this procedure, the tannin was added and the material subjected to the curing process. Adhesives A and B were produced with 25 and 40% tannin, respectively. The analysis of the adhesives differed only in solids content and viscosity. The shear strength and rupture percentage values indicate that the prepared adhesives have great potential and can be used commercially in the future.

INTRODUCTION

The growing concern with the environment coupled with the reduction of fossil resources has provided the search for development of ecologically sustainable and economical materials (JAHANSHAHI, *et al*., 2016; GOULART *et al*., 2012).

The gluing of the raw material, wood, in any form (panels, waste, and others), has contributed indirectly to the conservation of natural forest, since it allows the production of by-products with equal quality to those produced with solid wood.

The adhesive or resin (binding agent) have great importance on the final quality of different types of panels (PIZZI&MITTAL, 2003), since the structural balance of the product is checked through the adhesive bond between the wood elements, their distribution and orientation in the structure of the compound (ALBINO& MORI; MENDES, 2012).

The four main types of adhesives currently used in the composite panel industry wood based are: urea-formaldehyde (UF), melamine formaldehyde (MF), phenol-formaldehyde (PF) and resorcinol formaldehyde

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(RF), being that the adhesives PF (Figure 1) and UF are the most used (ZHANG *et al*., 2013; GOULART *et al*., 2012).

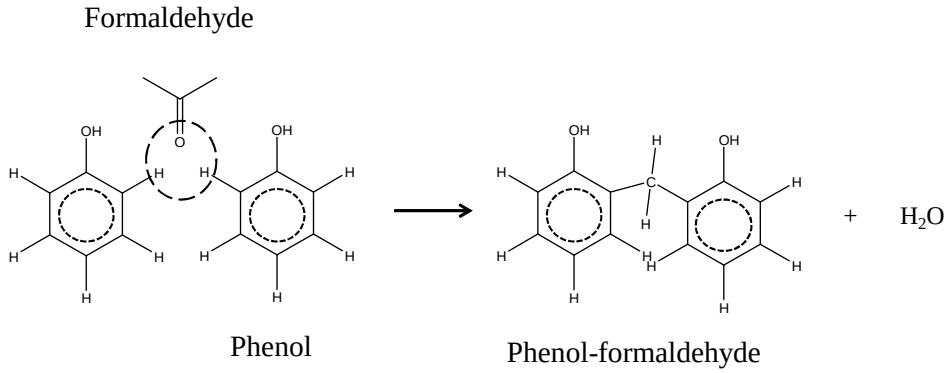

Fig. 1: Formation of phenol-formaldehyde (CARDONA; KU; CHOUZENOUX, 2011)

The synthetic resins are made with petroleum products, whose price has grown steadily in recent years. Due to the high value of the raw material used in the manufacture of adhesives, these account for much of the final cost of the panels (ALBINO *et al*., 2012; LI *et al*., 2016).

A collage using natural adhesives such as tannins and lignin, has received special attention, because besides being a renewable font, its use reduces the emission of carcinogenic gases deriving from the collage with phenol formaldehyde (MANSOURI *et al*., 2011;CARDONA *et al*., 2011; . JAHANSHAH *et al*., 2016).

For being formed of polymer structures, the condensed tannins, alone, is a mixture of prepolymers ready for polycondensation with the binding agent (CARNEIRO *et al*., 2001).

According Maminski *et al*. (2011), in the literature, there are reports on the use of polyesters as curing agents of coatings, being that esters of glycerol are used to obtain polyglycerols, which in turn are used in polyester synthesis utilized in the preparation of adhesives.

Glycerol is a sub product of biodiesel manufacture, formed by 10% of the total mass of produced biodiesel. With the production of this biofuel on a large scale, there will be increasing supply of glycerol, amounts that have no established market, generating a large environmentally abilities (AYOUB& ABDULLAH, 2012).

Recently, much research has been directed to the use of excess glycerol, aimed at producing higher value-added materials (ISMAIL *et al*., 2010).

For Ferreira *et al*., (2011), a good alternative to glycerol surplus produced in the biodiesel production chain is the esterification of it.

Thus, the objective this study was repurpose the glycerol, from the preparation of the wood adhesive using tannins and glycerol ester (triacetate). These objectives are not aimed at only add value to a residue of the biodiesel production chain, but also solve the problems found in the toxicity of formaldehyde resins used in bonding of wood panels.

MATERIAL AND METHODS

2.1. Raw material:

The raw material used in this study is the black wattle tannin that it was given by TANAC, obtained in powder form, and commercially available glycerol (Merck).

2.2. Preparation of the adhesives:

Different combinations were made in this study to facilitate mixing between the glycerol and the tannin and the chosen proportions are shown in Table 1. It was added 1 mL of sulfuric acid for each 100 g mixture.

To prepare the mixture, the glycerol triacetate and sulfuric acid were mixed at 80 ° C for 1 hour. After this period, the tannin was carefully added to the mixture and it was stirred slowly at 60 ° C for 50 min. The adhesive was left for 12 hours for the "cure" at room temperature and then was left in a oven at 80 ° C for 4 hours.

Table 1: Mass composition of each adhesive

Adhesive	Glycerol triacetate (TAG)	Tannin
A	75	25
B	60	40

2.3. Characterization of the adhesives:

2.3.1. Elemental analysis (CHNS-O):

Approximately 3 mg of tannin and each prepared adhesive was analyzed for levels of the elements C, H, N and S in a FLASH EA device, series 1112. The oxygen content was obtained by difference.

2.3.2. Spectroscopy in the infrared region (FTIR):

The analysis of tannin and adhesives prepared by spectroscopy in the infrared Fourier transform spectroscopy (FTIR) was performed on the equipment ShimadzuIRAffinity-1, serie FTS 3000, in the spectral range 400-4000 cm^{-1} and a resolution of 4 cm^{-1}. The samples were prepared as KBr pellets (3 mg of sample to 97 mg of KBr).

2.3.3. Thermogravimetric analysis (TGA and DTA):

The Thermogravimetric analysis of tannin and prepared adhesives were held in a thermomechanical analyzer Shimadzu DTG-60AH. Approximately 5 mg of each sample were used, these being heated to 10°C $min^{-1}$from 30°C until 900°C, under atmospheric air at a flow of 30mL min^{-1}.

2.3.4. Analysis Differential scanning calorimetry (DSC):

The tannin and adhesives were subjected to DSC analysis, carried out in a thermomechanical analyzer SHIMADZU DSC-60A. Approximately 5 mg of each sample were used, these being heated to 10°C $min^{-1}$from 30°C until 500°C, under atmospheric air at a flow of 30 mL min^{-1}.

The kinetic parameters were obtained from the DSC curve. T (onset) and ΔH were determined by the program Ta-60 ws collection monitor. Initially it drew a base line from which was determined the initial temperature and final temperature of the exothermic curing process. The integration of the area of the exothermic peak represents the total heat (ΔH) involved in there action.

For each sample were used three heating rates 10, 15 and 20 °Cmin^{-1}, and were evaluate the following kinetic parameters: activation energy, enthalpy and curing temperature of the adhesive. The activation energy (Ea) was determined using the Barrett method (1967) and calculated by the equation proposed by Kissinger (1957):

$$\ln (ø/Tp^2) = \ln (A_oR/T) – Ea/ RTp$$

Where ø is the heating rate; Tp **i**s the absolute peak temperature (Ton set) in each heating rate, A_o is the pre-exponential factor Arrhenius, R is the universal gas constant (8, 3145 J mol^{-1} K^{-1}) and Ea the energy reaction activation.

In this method, the logarithm of heating rate (ø) of the absolute peak temperature (Tp) squared is plotted as a function of the inverse absolute peak temperature (Tp).

2.3.5. Solids content and pH determination:

The determination of solids content was performed by the gravimetric method. One gram of the adhesive was dried in an oven at 103 ± 3 °C. After this period, the material remained in a desiccator for 15 minutes. Then we proceeded again the weighing. The solids percentage was calculated from the difference between initial and final weight divided by the initial mass. The pH determination of the tannin, triacetate and adhesives were made by direct reading on pH meter or potentiometer.

2.3.6. Viscosity Determination:

The viscosity was determined by the equipment Physic MCR 301 (Anton Paar), using the Rheoplus / 32 V3.31 program. The determination was performed at room temperature and the thickness of the adhesive used was 1mm.

2.3.7. Mechanical analysis:

The shear strength resistance analysis was performed according to ASTM D 2339-98 (ASTM, 2000), for bonded joints. These joints were made using two superposed slats *Pinus* spp.

The adhesives synthesized in this work were used with a weight of 250 gm^{-2}. In order to evenly distribute the adhesive over the entire area, it was manually applied with a spatula on one of the slats. In order to improve contact between the plates, facilitating the transfer and penetration of the adhesive into the wood, the slats are placed on one another and brought for the assembly for 2 minutes after application of the adhesive.

For the polymerization of the adhesive the joints were subjected to the hydraulic press with 10 Kgf cm^{-2} pressure at 170^{o}C for 10 minutes. It used the same pressure, temperature and time for all synthesized adhesives.

RESULTS AND DISCUSSION

3.1. Characterization of the prepared adhesives

3.1.1. Elemental analysis (CHNS-O)

The elemental analysis (Table 2) allows quantifying, relative to the initial molecule (tannin), changes in the ratios C:O, and then evaluate the formation of the adhesive prepared.

Table 2: Elemental analysis (CHNS-O) of the tannin, triacetate and adhesives.

Material	%N	%C	%H	%S	%O
Adhesive A	1,0	44,4	6,2	0,4	48,2
Adhesive B	1,1	43,5	5,9	0,2	49,3
Tannin	1,1	48,7	5,3	0,1	44,9
Triacetate	0,0	47,9	6,1	0,0	46,0

It is observed in Table 2 that the carbon percentage in the adhesive are lower than the values found in tannins and triacetate and the amounts of oxygen are higher, which is explained by the fact that adhesives are formed by a higher percentage of triacetate (75% and 60%). At the glycerol ester the ratio C: O is lower, which explains the increase in oxygen content in the prepared adhesive. In addition, the adhesive is formed by condensation of two tannin molecules and a molecule triacetate and final adhesive also shows the ratio C: O lower for the tannin (Figure 2).

3.1.2. Spectroscopy in the Infrared Region (FTIR):

The production of adhesives from the condensation of tannins with glycerol ester (triacetate) can be observed by characteristic bands of the tannin and triacetate persistent in the adhesive spectrum (Figure 2).

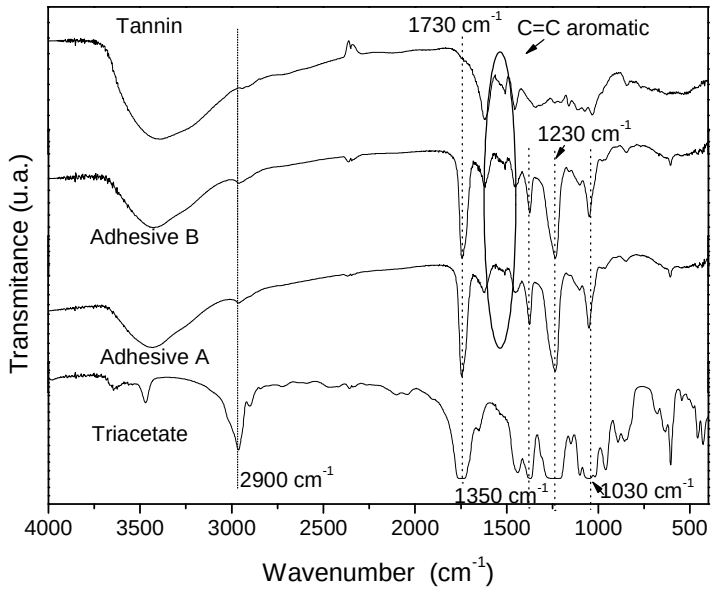

Fig. 2: Infrared spectrum of the tannin and the triacetate of the adhesives A and B

According Ismail *et al*. (2010), the bands at 1730 and 1230 cm^{-1}, present in the spectrum of the adhesives and triacetate, are ester group characteristics.

The bands at 1620 and 1450 cm^{-1} corresponds to C = C aromatic present in both spectra, except at the spectrum triacetate (RAMIRES&FROLLINI, 2012).

The band at 1350 cm^{-1} appears in the spectra of triacetate and adhesives, and is linked to C-C bonds in the same (RAMIRES& FROLLINI, 2012).

At 1030 cm^{-1} is observed bands related to the binding of the C-O of primary alcohols with intensity much higher in the spectrum of adhesives (ZHANG *et al*., 2013).

According Li *et al*. (2016), the band observed in both spectra near 2900 cm^{-1} is related to the axial deformation -C-H. The band in the region of 3330–3400 cm^{-1} can be assigned to the stretching vibration of hydroxyl phenolic, observed in both spectra, except at the spectrum triacetate.

Based on IR spectrum, a possible structure for the prepared adhesives is proposed in Figure 3.

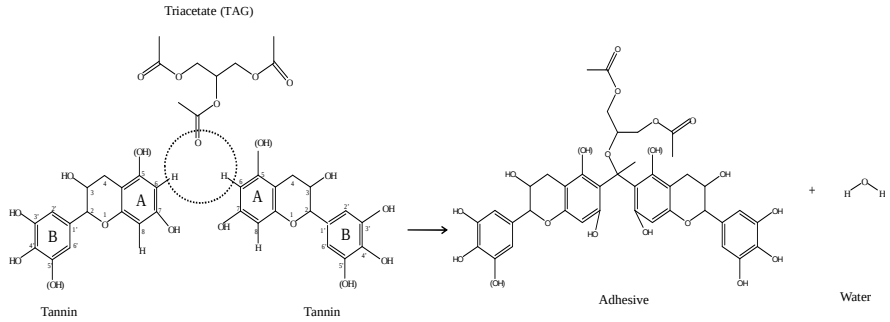

Fig. 3: Scheme of the adhesive formed from the base of glycerol triacetate and tannins

The esterification of glycerol increases its compatibility with the tannins and is due to strong nucleophilic character of carbonyls present in the triacetate, that this reacts with the tannins on C6 or C8 carbon of the ring A. According to Carneiro *et al*. (2011) are the C6 positions and / or C8 free of flavonoid units which constitute the reactive sites in the tannin.

3.1.3. Thermogravimetric analysis (TGA and DTA):

The figure 4 shows the thermogravimetric curve (TGA and DTA) of the tannin and adhesives A and B.

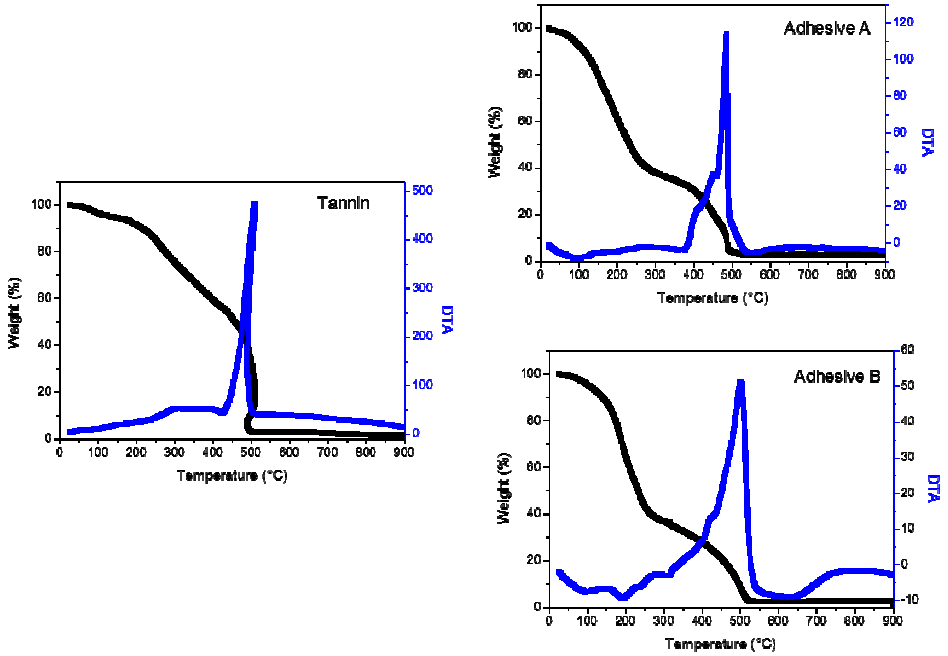

Fig. 4: Thermogravimetric analysis of the tannin and adhesives A and B (TGA and DTA)

The TG and DTA curves shown in Figure 4 exhibit a very similar profile with two mass losses. According Ramires & Frollini (2012), it is because the tannin degradation begins at approximately 230 ° C and decomposition of the aromatic rings near 485 ° C. It is observed in the TG curves of the adhesive the beginning of the mass loss at temperatures below 200 ° C. This loss of mass at a temperature below 200 ° C is related to the stage of condensation of the prepolymer, which occurs during formation of the adhesive which is accompanied by the release of water (ZHANG *et al*., 2013).

3.1.4. Analysis Differential scanning calorimetry (DSC):

The tannin degradation begins at approximately 230 ° C, which can be observed by exothermic peak in the DSC curve of Figure 5. The endothermic peak near 435 ° C also present in tannin DSC is due to vaporization of the volatiles derived from the decomposition aromatic ring (RAMIRES& FROLLINI, 2012).

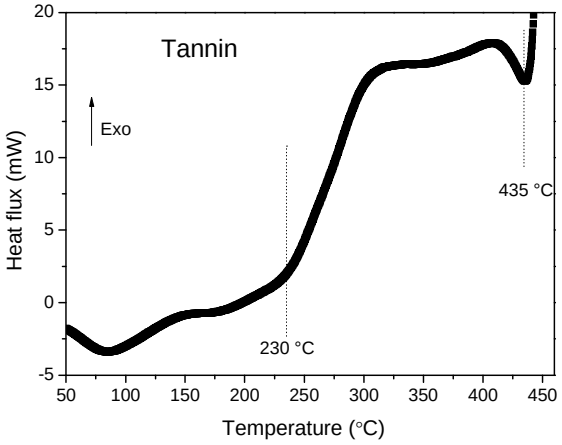

Fig. 5: Analysis of exploratory calorimetry of the tannin

According to Mori *et al*. (2002), the reactivity of the adhesive can be studied by differential scanning calorimetry (DSC) allows to determine the kinetic parameters of the polymerisation reaction during the curing of the adhesive. Looking at the Figure 6 and 7, it is observed that the adhesives produced with tannin base have several broad peaks at cure temperature (Table 3). The same was observed in the study of Mori *et al*. (2002) to analyze the cure of the adhesives from tannin from the bark of three species of *Eucalyptus* by differential scanning calorimetry. In this same study, Mori found that the commercial adhesive black wattle tannin has two curing peaks, 126 and 216 ° C.

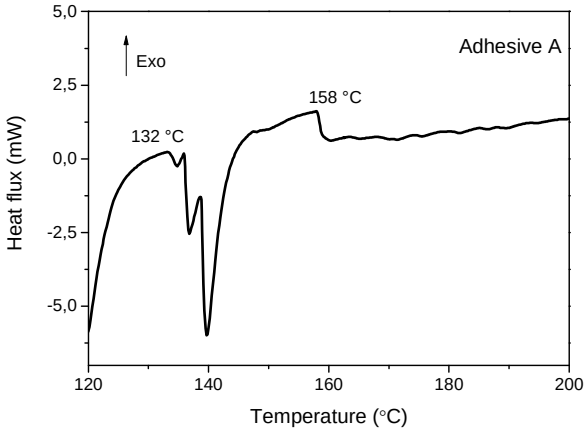

Fig. 6: Scanning calorimetry analysis of adhesive A

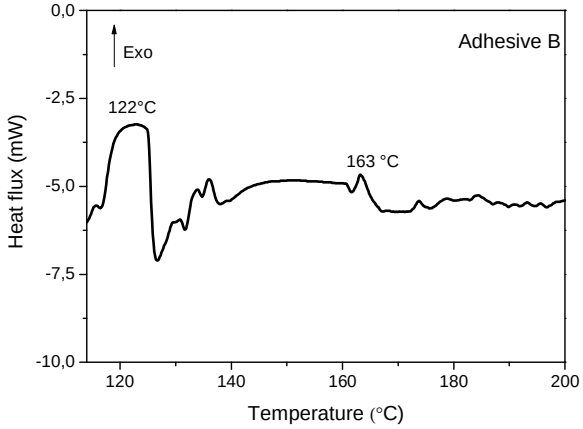

Fig. 7: Scanning calorimetry analysis of adhesive B

The kinetic parameters obtained from the DSC curves of the adhesives prepared in this study are presented in Table 3.

Table 3: Kinetic parameters of curing adhesives A and B, Ea: activation energy, ΔH: enthalpy, T: temperature

Kinetic parameters/ Adhesives	Ea (kJ mol^{-1})**	ΔH (Jg^{-1})*	T peak (°C)*
Adhesive A	18,07	41,59	132,76 158,61
Adhesive B	17,49	28,79	122,86 163,24

* Average of three heating rates (10, 15 and 20 ° C).
** Referring to curves obtained with a heating rate of 10 ° C min^{-1}

The values determined for the kinetic parameters are lower than the values found by Mori *et al*. (2002), who found value 28.3 $kJmol^{-1}$ for commercial adhesive based on tannin of black wattle (*Acacia molissima*). Lower activation energy values ensure lower energy consumption and less time during working conditions, allowing choosing the best adhesive based on its formulation.

3.1.5. Content of total solids and pH determination:

In Table 4 are the solids content values for adhesives A and B.

Table 4: Solid content values for adhesives A and B

Sample	Solid content (%)
Adhesive A	31,87
Adhesive B	19,82

The solid content found for the adhesive A is higher than that found for the adhesive B, however; both values are lower than the values suggested by Almeida *et al*. (2010). For these same authors, the solid content of adhesive must be greater than 40%. According Iwakiri (2005), low solids content can cause problems relating to penetration of adhesive, producing the glue line "hungry".

At the Table 5, it is observed that the prepared adhesives have pH close to 3, ideal for producing the best glue line, because according Carneiro *et al*. (2001), in general, it is observed that the adhesive prepared with a pH below 3 react faster and therefore produce worse results.

Table 5: The pH values for the tannin, adhesives and triacetate

Sample	pH
Tannin	5,2
Adhesive A	3,1
Adhesive B	3,3
Triacetate	6,2

The acidity of the prepared adhesives is explained by the formation reaction of the same (Figure 2), which occurs by condensation of the triacetate molecules and tannin, condensation occurs during the release of water which reacts with acetic acid to form triacetate.

3.1.6. Rheological study / viscosity determination:

The flow behavior of the adhesives A and B are shown in Figures 8 and 9, respectively.

The adhesives A and B exhibited increased of the shear rates proportional to the shear stress, while the adhesive B has the same shear rate at higher voltages, which is explained by its high viscosity.

From the graphics of the rheological study (Figure 8 and 9), the viscosities for adhesives A and B are 240 and 2388 cps, respectively.

According with the viscosity values shown in Table 6, the adhesive provides lower viscosity to the synthetic resin UF, PF, RF, and the adhesive B, higher values to UF and PF resins.

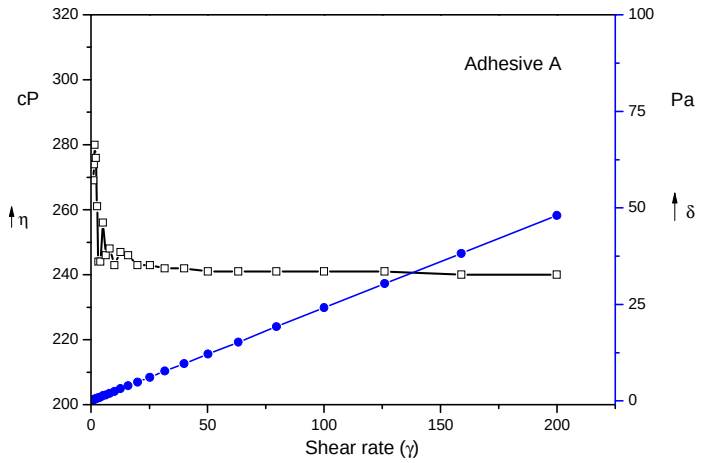

Fig. 8: Graphic of the rheological study of the adhesive A

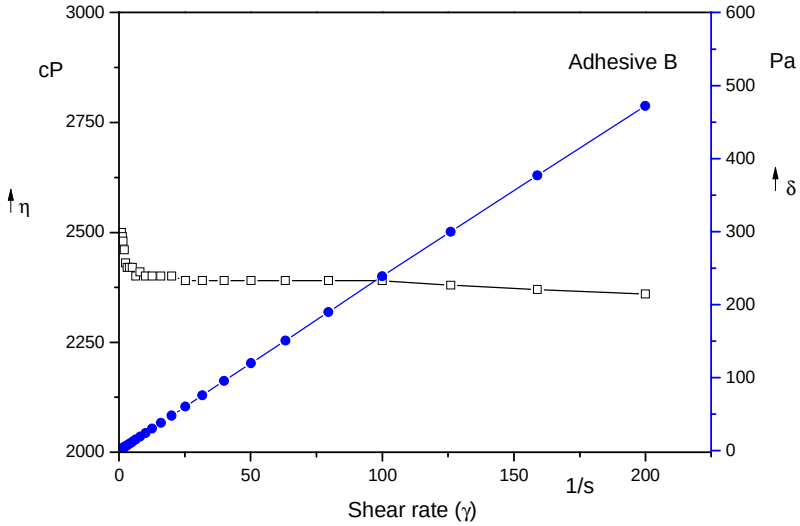

Fig. 9: Graphic of the rheological study of the adhesive B

Table 6: Viscosity values for the synthetic resins and tannin-formaldehyde adhesive

Adhesive	Viscosity (cP) 25° C	Reference
Phenol - formaldehyde (PF)	574	Goulart *et al*., 2012
Urea - formaldehyde (UF)	380	Tostes *et al*., 2004
Resorcinol formaldehyde (RF)	5500	Albino; Mori; Mendes, 2012
Tannin formaldehyde (TF)	Higher than 6000	Carneiro *et al*., 2001.

The high viscosity presented by the adhesive B is due to higher tannin content in its composition, which is expected because, according to Mori *et al*. (2012), the use of tannin in the production of adhesives increases the viscosity thereof. What is consistent with data of Carneiro *et al*. (2001), who also found high viscosity values prepared as tannin adhesives and formaldehyde (Table 6).

The viscosity value of the adhesive is a determining factor for a good collage, as very viscous adhesives have greater difficulty in spreading, in contrast the less viscous adhesives that can come to form a glue line "hungry" (GOULART *et al*. 2012).

3.1.7. Mechanical analysis:

The Table 7 shows the strength values found for adhesives A and B.

Table 7: Mean values for shear strength and percent of wood failure

Adhesive	Shear strength (Mpa)	CV (%)	Wood failure (%)
A	1,79	27,52	5
B	1,49	16,13	5

Where: CV = coefficient of variation

The low shear strength values observed in adhesives prepared in this study (A and B) is due to the tannin composition thereof. In studies reported by Carneiro *et al*. (2001), all tannic adhesives were less resistant than phenolic adhesives.

Albino *et al*. (2010) evaluating the anatomy of bonded joints with *Eucalyptus grandis* wood observed shear strength values between 3.81 and 5.73, using as adhesive resorcinol - formaldehyde (Cascophen- RS-216) with the addition of hardener (FM) on a one for five part adhesive. These values were higher than found in the study, which occurs due to the resorcinol formaldehyde adhesive is a thermo-hardening strong.

The average calculated for the joints of paricá (*Schizolobium parahyba* Var. *amazonicum*) analyzed by Urbinati (2013) is 2.80 MPa, using the phenol-formaldehyde extended in 22.5% of wheat flour.

It is observed also in Table 7, that both adhesives showed low percentage of wood failure values. For Urbinati (2013), the failure percentage in the wood of the indication of the resistance of the wood in relation to the glue line resistance. The most suitable is that the wood's resistance equals the resistance of the glue line.

Table 8: Bonding requirements in the standard EN 314-2 (CEN, 1993)

Shear strength (MPa)	Wood failure (%)
$0,20 \leq fv < 0,42$	≥ 80
$0,42 \leq fc < 0,62$	≥ 60
$0,62 \leq fc < 1,04$	≥ 40
$1,04 \leq fv$	No requirement

Conclusion:

The infrared spectra showed characteristic bands of the tannin and from triacetate persistent on the spectrum prepared of the adhesives.

The prepared adhesives showed relatively low values of activation energy, which ensures lower power consumption and less time spent in the healing process and bonding.

The content of total solids, the viscosity and shear stress are dependent on the amount of tannins present in the adhesive. The values of shear strength and percent of break, that show that the adhesives are able to use, it is observed that a low solids content in the adhesive B was offset by the high viscosity thereof, not producing the glue line "hungry" caused by low solids contents, or "thick", caused by the high viscosity thereof.

The adhesive prepared in this study has great potential since they do not have in their composition, formaldehyde, which is considered carcinogenic and therefore poses risks to human health.

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