

CONDENSED TANNINS OF THE SPECIES *PINUS TAEDA*: EXTRACTION,
CHARACTERIZATION AND POTENTIAL FORMULATION OF WOOD BIOADHESIVE

TANINOS CONDENSADOS DA ESPÉCIE *PINUS TAEDA*: EXTRAÇÃO, CARACTERIZAÇÃO E
POTENCIAL FORMULAÇÃO DE BIOADESIVO DE MADEIRA

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Abstract

The species *Pinus taeda* was evaluated as a source of condensed tannins for the potential formulation of phenolic adhesives from the extraction of the wood cortex. Extraction yield, percentage of tannins and non-tannins, and reactivity to the formaldehyde by the Stiasny number were analyzed in the responses of the extraction processes with extractive agents sodium sulfite (Na_2SO_3), sodium hydroxide (NaOH), and urea $[(\text{NH}_2)_2\text{CO}]$ in the percentages of 2, 4, 6, 8, and 10 in relation to the weight of the bark of this species. The extracts were analyzed using the techniques of IR - Infrared Spectroscopy, SEM - Scanning Electron Microscopy, DRX - X-ray Diffractometry, and EDS - Energy-Dispersive X-ray Spectrometry. In another step, the formation time of the commercial tannin gel and of the *P. taeda* were compared in relation to formaldehyde. The results show that the specie have condensed tannins, and sustain that they are catechins. These catechins form polymers identified by SEM in less time in relation to the formaldehyde in the formation of the gel, suggesting that the tannins can be extracted from the species as a potentially new commercial source that lumber companies can use to manufacture phenolic resins.

Keywords: Extractives, Gel time, Tannin-formaldehyde, Catechins, Polymer.

Resumo

A espécie *Pinus taeda* foi avaliada como fonte de taninos condensados para a potencial formulação de adesivos fenólicos a partir da extração do córtex da madeira. Rendimento de extração, porcentagem de taninos e não-taninos e reatividade ao formaldeído pelo número de Stiasny foram analisados nas respostas dos processos de extração com agentes extrativos sulfito de sódio (Na_2SO_3), hidróxido de sódio (NaOH) e ureia $[(\text{NH}_2)_2\text{CO}]$ nas porcentagens de 2, 4, 6, 8 e 10 em relação ao peso da casca desta espécie. Os extratos foram analisados por meio das técnicas de IV - Espectroscopia de Infravermelho, MEV - Microscopia Eletrônica de Varredura, DRX - Difratometria de Raio-X e EDS - Espectrometria de Energia Dispersiva de Raio-X. Em outra etapa, foram comparados os tempos de formação do gel de tanino comercial e do *P. taeda* em relação ao formaldeído. Os resultados mostram que a espécie possui taninos condensados, sustentando que são

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catequinas. Essas catequinas identificadas por MEV formam polímeros em menor tempo em relação ao formaldeído na elaboração do gel, sugerindo que os taninos podem ser extraídos da espécie como uma fonte comercial potencialmente nova e que as madeiras podem usar para fabricar resinas fenólicas.

Palavras-chaves: Extrativos, Tempo de gel, Tanino-formaldeído, Catequinas, Polímero.

1. INTRODUCTION

Some chemical compounds are known as primary metabolites, acting in the processes of photosynthesis and respiration, while others are biosynthesized as secondary metabolites, and can provide protection against pathogens, attract pollinators, and various other equally important functions for the survival of living organisms (LV et al., 2016; SANCHO-KNAPIK et al., 2017).

Among the secondary metabolites, also known as specialized metabolites, is an important group called phenolics (LV et al., 2016). These phenolics contain a phenol grouping, giving origin to a heterogeneous class of flavonoids (LI et al., 2020), such as the condensed tannins (LOKESHWARI, 2016; PIMENTEL et al., 2017).

Many of these tannins are found in woody materials, like the bark of several tree species, including the genus *Pinus* that has over 100 variations. In southern Brazil, in due to a good adaptation to high altitudes and cold climates, the *Pinus* covered 30% of planted forest or 1.56 million hectares, favoring the supply of timber companies to the detriment of native vegetation, such as the Brazilian pine (AGUIAR et al., 2014; EMBRAPA, 2016).

The species *taeda*, one of the variations of *Pinus*, is often preferred for its rapid growth (CARDOSO et al., 2013), and it is widely used by timber companies that have set up their factories in the region of Santa Catarina to lower production and transport costs (AGUIAR et al., 2014).

The bark of this species that is left over from the processing of raw material is under-utilized in boilers or abandoned in the environment. With the purpose of adding commercial value to this material, the aim of this work is to extract condensed tannins, which are phenolic in nature, to formulate natural resins that can replace the phenol derived from petroleum, possibly resulting in a technological potential for the wood industry. Hoong et al (2011) assert that these polyphenolic resources of natural base have an enormous potential market for the wood-based industries worldwide, because, actually the Europe use of tannins as a substitute for phenol in wood adhesive formulations.

2. MATERIALS AND METHODS

2.1 Bark of *Pinus taeda*

Samples of 5-year-old plants were collected in the state of Santa Catarina, southern Brazil. Voucher specimens of the species were deposited at the Herbarium - UTFPR filed under HPB 315.

The collected samples were weighed in a semi-analytical scale (Knwaagen KN 2200/2). To eliminate moisture, the material was conditioned in a drying oven (Novatécnica NT516) for 5 days at temperatures of 50 °C, and stirred every 6 hours.

After drying, the samples were weighed, ground in a knife mill (Solab SL32), and sieved in 60-mesh sieve shakers (Bertel).



2.2 Tannin extraction

For the extractions, the ground bark samples (10 g) and the percentages of each extractor agent, in relation to the weight of the sample, were placed in Erlenmeyer bottles (Table 1) and autoclaved (Vertical CS) at 120 °C for 3 hours. The amount of distilled water for solubilization was 1:15 (w/v).

Table 1. Parameters evaluated in the tannin extractions from the bark of *Pinus taeda*.

Treatment	% Extractive agent	Extractive agent
S2%	2%	Na ₂ SO ₃
S4%	4%	Na ₂ SO ₃
S6%	6%	Na ₂ SO ₃
S8%	8%	Na ₂ SO ₃
S10%	10%	Na ₂ SO ₃
H2%	2%	NaOH
H4%	4%	NaOH
H6%	6%	NaOH
H8%	8%	NaOH
H10%	10%	NaOH
U2%	2%	(NH ₂) ₂ CO
U4%	4%	(NH ₂) ₂ CO
U6%	6%	(NH ₂) ₂ CO
U8%	8%	(NH ₂) ₂ CO
U10%	10%	(NH ₂) ₂ CO

The treatments were triplicated and the results (extraction yield, yield of polyphenols condensed using the Stiasny, and percentages of tannins and non-tannins) were evaluated using the Tukey test - Statistica 7.0 software - and principal component analysis (PCA) with Pirouette statistical software. All the statistical analyses were carried out with a significance level of P <0.05.

2.3 Characterization of extracts

Extraction yield (EY) is efficiency of extraction and it was defined as the amount of extract recovered in mass compared with the initial amount of dry bark (ASPÉ; FERNÁNDEZ, 2011). The extraction yield was calculated by Equation (1).

$$EY (\%) = \frac{w_d}{w_i} \cdot 100\% \quad (1)$$

EY corresponds to extraction yield (%), w_d , weight dried extract (g), w_i , inicial weight of the dried extract bark *Pinus taeda* (g).

Stiasny number (SN) reflects the presence of polyphenols that react to the formaldehyde, determined by the adapted methodology (YAZAKI; HILLIS, 1998). Solution of extract (50 mL) was put in a round bottom flask and formaldehyde 37% (10 ml) and HCl 10 mol L⁻¹ (5 mL) were added. The mixture was heated under reflux for 30 min. The precipitate was dried at 105 °C until constant weight. The reactivity was calculated with the Equation (2).



$$SN (\%) = \frac{\text{tannin mass after HCl-formaldehyde reaction}}{\text{mass of initial extract}} \cdot 100 \quad (2)$$

Tannins (T) and non-tannins (NT) were calculated using Equations (3) and (4) (VIEIRA et al., 2014).

$$T = \frac{(SN \cdot EY)}{100} \quad (3)$$

$$NT = EY - T \quad (4)$$

Since, T corresponds to the tannins content (%), SN Stiasny number (%), EY extraction yield (%) e NT non tannins content (%).

The samples H2%, H4%, H6%, H8%, H10%, S10% and U10% were evaluated to compare the results of the different extractions, and the samples H10% before and after the reaction with formaldehyde were compared to verify the surface of the adhesive. All samples were ground and mixed with spectroscopic grade KBr. For the readings, we used a spectrophotometer (Perkin Elmer-Frontier) in transmittance mode in the range of 4000 to 400 cm^{-1} with 2 cm^{-1} resolution, accumulation of 32 scans and normalization with baseline correction.

The superficial structure was analyzed using scanning electron microscopy (Hitachi TM 3000) in the samples (H10%, S10% and U10%) before and after reaction with formaldehyde.

For the x-ray diffractometry, we analyzed the samples of *Pinus taeda* bark and the samples extracted with H10%, S10% and U10% using a diffractometer (XRD-7000-Shimadzu) in copper (Cu) tubes, K- α radiation ($\lambda = 1.5406 \text{ \AA}$), 30 kV voltage and a scanning range of 5000 - 70000 in θ 2 mode.

The energy dispersive x-ray spectroscopy (EDS) analysis was conducted on samples H10%, S10% and U10% using a digital scanning electron microscope (EVO MA10 - Zeiss) to verify the presence of metal or crystallinity.

Formaldehyde 37% (10% and 20%) in relation to the weight of tannin was added to samples (1 g) of solutions of commercial tannins and *P. taeda* tannins at 45%. Gel time tests were conducted at 100 °C. The samples were weighed in a glass test tube, and then placed in a boiling water bath. The Kolle handle was manually moved rapidly upward and downward, and the gel time was measure using a stopwatch (NAVARRETE et al., 2011).

3. RESULTS AND DISCUSSION

Given the abundance of *Pinus taeda* in Brazil, studies related to this species have been conducted for various industrial applications, such as wood adhesives. This activity is linked to compounds such as phenolic acids and flavonoids (including condensed tannins) that are known to be present in plants (SANCHO-KNAPIK et al., 2017).

3.1 Tannin extraction

Figure 1 shows the principal component analysis (PCA) for the three extractives and Table 2 shows the average results of extraction yield (EY), Stiasny number (SN), tannins (T), non-tannins



(NT) and standard error (α). Mean values followed by the same letter in the same column do not statistically differ among themselves according to the Tukey test at a 5% level of probability.

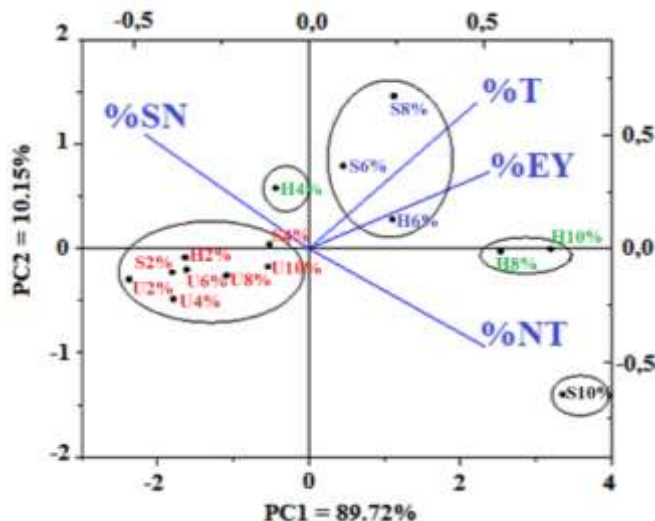


Figure 1. Principal Component Analysis (PCA) for the three extractives (U: $(\text{NH}_2)_2\text{CO}$, S: Na_2SO_3 e H: NaOH) evaluating extraction yield (EY), Stiasny number (SN), tannins (T) and non-tannins (NT).

For the PCA of the extractions, two components explained 99.87% of the variability of the data, distinctly showing five sample groups. The samples S6, S8%, and H6% formed the first group (Quadrant I), which had high percentages of tannins (%T) and extraction yield (%EY). The second group (Quadrant II), formed by H4% showed a high percentage of the Stiasny index (%SN). The third group (Quadrant III), formed by all the percentages of extractive urea, H2%, S2%, and S4% had the lowest percentages of tannins, extraction yield, and non-tannins. The fourth group (Quadrant IV), with sample S10% and the group formed by the samples H8% and H10%, had the highest percentages of non-tannins (%NT), respectively.

Table 2. Tukey test for the average results of extraction yield (EY), Stiasny number (SN), tannins (T), non-tannins (NT), and standard error (α).

T*	EY (%)	σ	SN (%)	σ	T (%)	σ	NT (%)	σ
H2%	23.7 ^{hij}	0.1	96.2 ^{ab}	2.1	22.8 ^{de}	0.5	0.9 ^d	0.5
H4%	29.9 ^{ef}	2.3	94.7 ^{ab}	2.2	28.3 ^{bcd}	2.5	1.5 ^{cd}	0.6
H6%	35.0 ^{cd}	0.9	89.6 ^{abc}	1.7	31.4 ^{abc}	1.4	3.6 ^{abcd}	0.5
H8%	39.8 ^{ab}	1.6	85.4 ^{abc}	1.6	34.0 ^{ab}	1.1	5.8 ^{abc}	0.7
H10%	42.5 ^a	0.9	84.1 ^{bc}	3.4	35.7 ^a	0.8	6.7 ^{ab}	1.5
S2%	22.7 ^{ij}	1.5	96.3 ^{ab}	1.6	21.8 ^{de}	1.2	0.8 ^d	0.4
S4%	28.2 ^{fg}	0.8	93.2 ^{ab}	5.2	26.3 ^{cde}	1.6	1.9 ^{cd}	1.4
S6%	33.8 ^{de}	1.9	92.9 ^{ab}	3.0	31.5 ^{abc}	2.1	2.3 ^{bcd}	1.0
S8%	38.1 ^{bc}	1.7	93.2 ^{ab}	0.9	35.9 ^a	1.9	2.5 ^{bcd}	0.2



S10%	39.6 ^{ab}	1.7	79.0 ^c	14.3	31.5 ^{abc}	7.0	8.1 ^a	5.3
U2%	20.4 ^j	0.4	97.9 ^a	0.6	20.0 ^e	0.5	0.4 ^d	0.1
U4%	22.1 ^{ij}	1.8	95.3 ^{ab}	2.5	21.0 ^e	1.9	1.0 ^d	0.5
U6%	23.5 ^{hij}	0.1	95.7 ^{ab}	1.5	22.5 ^{de}	0.5	1.0 ^d	0.3
U8%	25.3 ^{ghi}	0.7	93.8 ^{ab}	0.8	23.7 ^{de}	0.5	1.5 ^{cd}	0.2
U10%	27.5 ^{fgh}	0.6	92.5 ^{ab}	1.9	25.5 ^{cde}	0.1	2.0 ^{bcd}	0.5

* Treatment.

The extraction yield increases for the treatments when the percentage of extractives increases. The highest percentage of extraction occurred with the H10% treatment. NaOH is a strong base and, therefore, has greater penetration in the cellulose walls, damaging them and extracting other compounds, like greases, waxes, sugars and lignins. The tannins are acid since the hydrogen of the hydroxyls is weakly bound to oxygen due to the stability of the benzene ring, favoring an acid-base neutralization reaction and enhancing the extraction of tannin-sodium (ASPÉ; FERNÁNDEZ, 2011). The extractive S10% does not statistically differ from H10%, although it has lower quantities of extraction. The extractive (NH₂)₂CO has the lowest percentage of extraction.

Similar values for S2% (EY: 22.8%), were found in studies in which the mixture Na₂SO₃ (2%) and Na₂CO₃ (0.5%) was used as an extractive for *Acacia mangium* (EY: 23%) (HOONG et al., 2011). The extraction yield of several species of *Pinus*, *P. caribaea* var. *bahamensis*, *P. caribaea* var. *caribaea*, *P. caribaea* var. *hondurensis*, and *P. oocarpa*, using the mixture Na₂SO₃ (2% and 5%) and Na₂CO₃ (2% and 5%) as an extractive obtained an average extraction yield of 21.08%, 17.62%, 19.84%, and 23.51%, respectively (FERREIRA et al., 2009).

The Stiasny number reflects the polyphenols that react with the formaldehyde in solution (PIZZI, 1994) and indicates the purity of the extracts (PING et al., 2011). High values, above 65% are needed to use resins (YAZAKI; COLLINS, 1994). In this work, the values found exceeded 79%, and resembled the values found in studies of *Cassia fistula* (70%) (LAI; LIEW, 2012), *P. pinaster* (68.7%) (YAZAKI; COLLINS, 1994), *Acacia mangium* (83.8 at 91.5%) (HOONG et al., 2011), and *P. pinea* (78.3 at 83.1%) (GÖNÜLTAS; BALABAN-UCAR, 2012). In other studies mean values of the Stiasny numbers were obtained for the species *P. caribaea* var. *bahamensis* (86.83%), *P. caribaea* var. *caribaea* (71.83%), *P. caribaea* var. *hondurensis* (74.54%), and *P. oocarpa* (90.71%) (FERREIRA et al., 2009).

The percentages of extracted tannins also had increasing coefficients when the extractive reagents increased, with the exception of S10%. The increase of Na₂SO₃ did not favor higher amounts of extracted tannins. The higher percentages of (NH₂)₂CO were equal to the lower extractives of H2%, H4%, S2%, and S4%, and the higher portion of extracted tannins remained constant with H10% and was statistically equal to H8% and S8%, according to the Tukey Test. The non-tannin is represented by gum, sugar, grease, and other compounds that make up the tannins in the bark of the species (BIANCHI et al., 2015). The extractives S10%, H10%, H8%, and H6% have statistically similar indexes, and S10% has the highest yield. Values above (T: 20.06 to 35.77%; NT: 0.42 to 8.14%) were determined in this study in relation to other species, such as *P. caribaea* var. *bahamensis* (T: 18.39%; NT: 2.70%), *P. caribaea* var. *caribaea* (T: 13.19%; NT: 4.40%), *P. caribaea* var. *hondurensis* (T: 15.38%; NT: 4.46%), and *P. oocarpa* (T: 21.51%; NT: 1.99%) (FERREIRA et al., 2009). In *Cassia fistula* the amount of tannins (20%) was determined (LAI; LIEW, 2012).



In order to use tannin to replace phenol-formaldehyde resins, it is important to analyze the ratio of higher tannin % and lower non-tannin % since the sugars, gums or waxes contaminate the reticulation or cure of the resin when applied to glue wood, possibly resulting in cracks if the cure is provided quickly or slowly, and has high viscosity (PIZZI, 1994). These final aspects of gluing wooden plates are important details and each species from which the tannin is extracted can have a unique specification.

3.2 Characterization and comparison before and after adding the formaldehyde

The best performance for the reagents was observed in the group of sodium hydroxide. For this extractive, we conducted an infrared spectrum for each percentage of the extractor (H2%, H4%, H6%, H8%, H10%), compared with the treatments of urea (U10%) and sodium sulfite (S10%) that presented the highest indices of that group (Figure 2).

Hydrolysable and condensed tannins have different IR spectra because of their molecular structure. Condensed tannins have a strong characteristic band at 1288-1282 cm^{-1} (C-O vibration of asymmetric pyran ring), while the hydrolysable tannins (gallotannins and ellagitannins) feature bands at 1731-1704 cm^{-1} (stretching vibration of the carbonyl group) and 1325-1317 cm^{-1} (symmetric stretch of the C-O bond of the ester function) (FALCÃO; ARAÚJO, 2013).

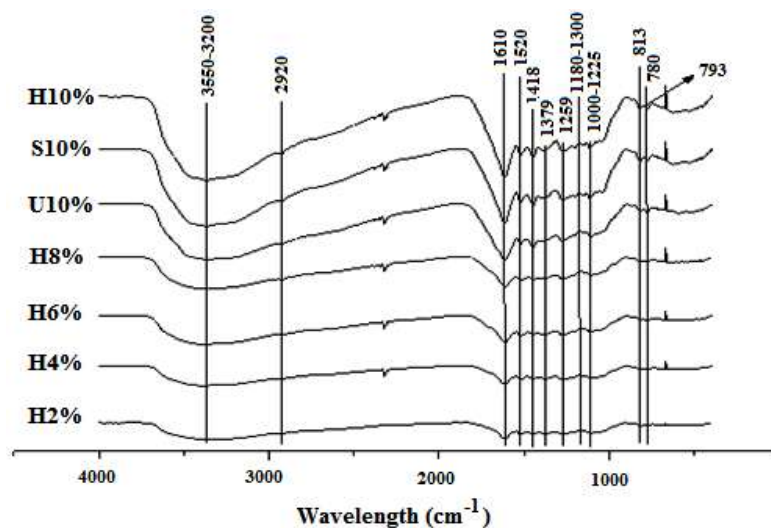


Figure 2. IR spectrum for the extractions with Na_2SO_3 (S10%), NaOH (H2%, H4%, H6%, H8%, and H10%), and $(\text{NH}_2)_2\text{CO}$ (U10%).

Deformations at 3318 cm^{-1} to $-\text{OH}$ were found in condensed tannins from grape bagasse (PING et al., 2012), and for *P. pinaster* (CHUPIN et al., 2013) this same deformation was identified at 3300 cm^{-1} . The $-\text{OH}$ grouping linked to the aromatic ring produces other bands at 1300 and 1180 cm^{-1} due to vibrations of the $-\text{C}-\text{O}$ link of the phenol (ARASARETNAM; VENUJAH, 2017).

Small bands at 2980 and 2850 cm^{-1} are formed by the stretch vibration of the aliphatic hydrogen atoms of the bonds $-\text{CH}$ (ARASARETNAM; VENUJAH, 2017; PING et al., 2012). The vibrations in the C-C bonds of the aromatic ring have bands at 1610 cm^{-1} , 1520 cm^{-1} , and 1444 cm^{-1} (PING et al., 2012; SAAD et al., 2014).

The C=C-C stretching vibrations of the C aromatic ring appear in the regions 1580-1615 cm^{-1} and 1450-1510 cm^{-1} and angular deformities in the region of 1000-1225 cm^{-1} (FERNANDEZ;

AGOSIN, 2007). Bands between $1540\text{-}1520\text{ cm}^{-1}$ are responsible for the stretching of the aromatic ring and the (+)-catechins and (+)-gallotanins can be distinguished because the catechins have 2 ligands -OH (1520 cm^{-1}) and the gallotannins have 3 ligands -OH (1535 cm^{-1}) (FOO, 1981). Therefore, the tannins obtained in this work are possibly catechins, because in the spectrum (Figure 2), the band is at 1520 cm^{-1} . The band at 1520 cm^{-1} was also observed in tannins of *Rhizophora apiculata* mangrove, indicating the predominance of procyanidins that are composed of catechin-type monomers. A double peak featuring galocatechin type prodelfinidin is observed only with the minimum amount of 60% of these monomers in the extraction (OO et al., 2009).

Bands at $1390\text{-}1330\text{ cm}^{-1}$ for phenols are responsible for the angular deformation of O-H and at $1260\text{-}1180\text{ cm}^{-1}$ for the axial deformation of C-O (ARASARETNAM; VENUJAH, 2017). C-O stretching of the pyran ring observed in the flavonoids was assigned to the band 1274 cm^{-1} (FERNANDEZ; AGOSIN, 2007). In the spectrum (Figure 2) these bands appear at 1259 cm^{-1} for the C-O and 1379 cm^{-1} for O-H . Studies highlight these bands at 1370 cm^{-1} (CHUPIN et al., 2013).

A band of $700\text{-}900\text{ cm}^{-1}$ corresponds to an absorption of H adjacent or isolated of aromatic. This angular deformation outside the plane of adjacent C-H of the aromatic rings bind with each other, producing bands between $900\text{-}675\text{ cm}^{-1}$ (FERNANDEZ; AGOSIN, 2007). These bands are also influenced by the hydroxylation of the B ring of the tannins. This hydroxylation presents bands between $780\text{-}730\text{ cm}^{-1}$ distinguishing the catechins ($780\text{-}770\text{ cm}^{-1}$) from the galocatechins (730 cm^{-1}) (FOO, 1981; OO et al., 2009). In the spectrum (Fig 2), bands are observed in the region of 730 cm^{-1} , corroborating with the previous observation, indicating that the obtained tannins can be catechin type.

Studies report that the cis structures can be identified by a band between $800\text{-}795\text{ cm}^{-1}$ (FOO, 1981). A band at 793 cm^{-1} is observed in this work, which may infer that the catechin is related to the cis configuration.

The comparison of the tannins before and after adding the formaldehyde revealed the presence of the -CH_2 bond of the methylene bridges between the tannins in the formation of the condensed prepolymer, and the wavelength was evaluated at 1700 cm^{-1} to 1000 cm^{-1} (Figure 3).

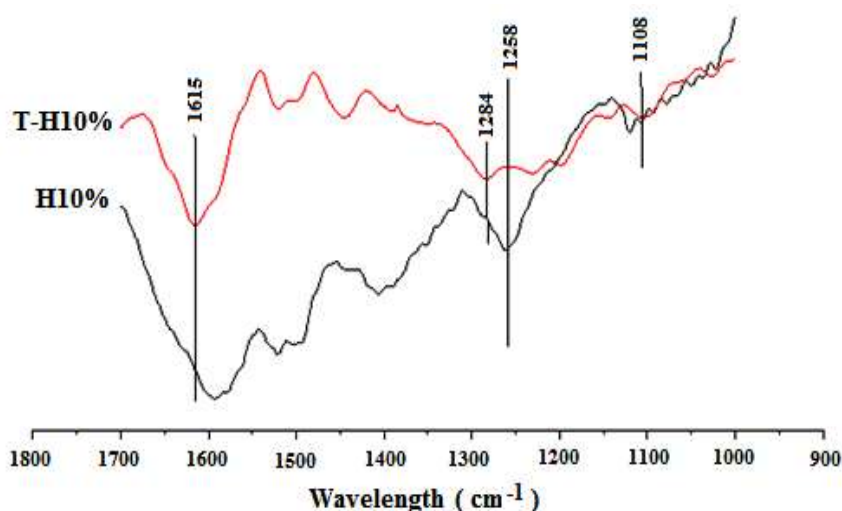


Figure 3. IR spectra by comparing the tannin of the extraction in H10% before and after the reaction with formaldehyde (T-H10%).

The tannins derived from the catechins in the reaction with formaldehyde, a band at 1250 cm^{-1} disappears, and remains with a shoulder at 1280 cm^{-1} . Bands at $1020\text{-}1140\text{ cm}^{-1}$ appear in a broader peak, close to 1110 cm^{-1} (SOTO et al., 2005). In the spectrum (Figure 3), the peak at 1258 cm^{-1} disappears for the formed prepolymer (T-H10%) and a broad peak at 1106 cm^{-1} is observed in the place of smaller bands of the H10%. The peak of 1611 cm^{-1} indicates a high number of interflavonoid bonds in C4-C8 in relation to the methylenic binds (KIM; KIM, 2003).

Scanning electron microscopy (SEM) analyses were carried out for the samples H10%, S10% and U10% (before and after the reaction with formaldehyde) with 2000x magnification (Figure 4).

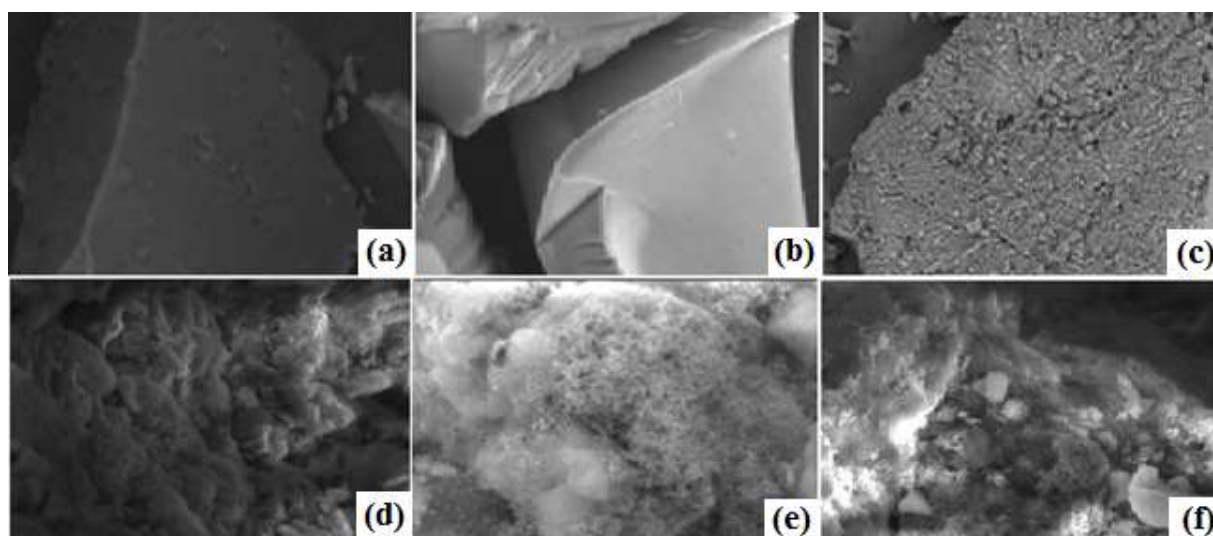


Figure 4. Scanning electron microscopy (SEM) for the extractives (2000x magnification): Without the addition of formaldehyde: (a) H10%, (b) S10% and (c) U10%, and with the addition of formaldehyde (d) H10%, (e) S10% and (f) U10%.

The extracts H10% (Figure 4 a) and S10% (Figure 4 b) had a superficial uniformity, with a smooth and pour-free appearance, which was not observed in the sample U10% (Figure 4 c).

When brought into reaction with formaldehyde, Figure 4 (d), (e) and (f), pores are formed in the three extractives. A similar result was found in studies with resins of tannin-aniline-formaldehyde (MULANI et al., 2014).

The diffractograms of DRX (Figure 5) show the sample of *P. taeda* bark and the extracts H10%, S10% and U10% without the addition of formaldehyde.

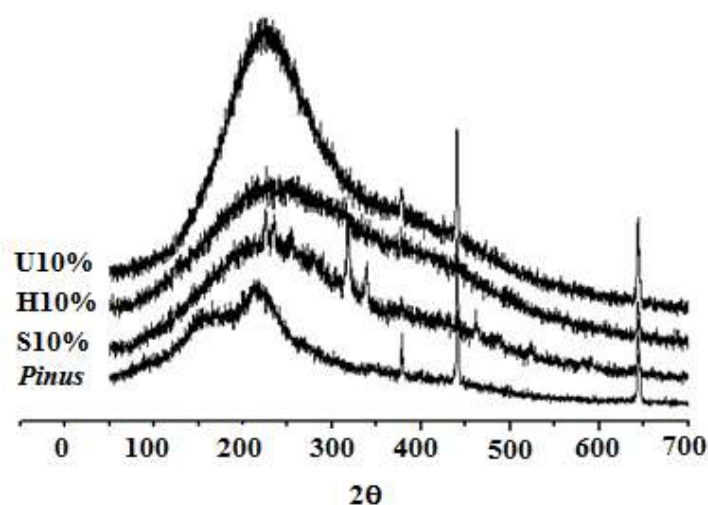


Figure 5. DRX of tannins for the sample of *P. taeda* bark and for the extracts NaOH (H10%), Na₂SO₃ (S10%) and (NH₂)₂CO (U10%) without the addition of formaldehyde.

The X-ray diffractograms show that the tannins are amorphous, that is, they are non-crystalline solids that lack a regular and systematic atomic arrangement over atomic distances, and the low intensity peaks in the 44.00° and 64.34° region may be associated with lignin, as was also noted in the pure sample of *P. taeda*. When extracting hydrolysable tannins from the *Caesalpinia coriaria*, the results revealed an amorphous characteristic for the tannins, suggesting a complexation between tannins and other substances (LOKESHWARI, 2016). Works with bark of the specie *Pinus densiflora* also identified amorphous material due to lignin (HAN et al., 2018).

The energy dispersive x-ray spectrometry (EDS) was carried out to try to evaluate any remnants in the extracts (Table 3).

Table 3. Analysis of SEM-EDS for tannins extracted with the extractives H10%, S10% and U10%.

T*	R**	C (%)	O (%)	Cl (%)	Na (%)	Al (%)	S (%)	N (%)
H10%	1	47.69	36.04	0.00	16.27	0.00	0.00	0.00
	2	45.92	36.98	0.00	17.10	0.00	0.00	0.00
	3	49.29	37.57	0.00	13.15	0.00	0.00	0.00
S10%	1	43.39	35.59	0.52	11.06	0.62	8.81	0.00
	2	47.79	36.54	0.00	9.28	0.46	5.94	0.00
	3	38.74	37.24	0.00	14.64	0.35	9.02	0.00
U10%	1	64.11	33.21	1.70	0.00	0.98	0.00	0.00
	2	50.79	36.10	0.32	0.00	0.00	0.00	12.80
	3	50.59	34.84	0.27	0.00	0.27	0.00	14.04

* Treatment; **Region.

Sample analyses using SEM-EDS identified the presence of residues of the reactants in the extraction process, as well as contaminants of aluminum foil used for packing the samples, and chlorides related to the possible impurity of reagents.

The tannins obtained from the extractives had percentages of carbon and oxygen from the tannin molecule. For NaOH 10%, there was sodium, a residual, that remains after the extraction process. Similarly, the sample of the extraction with Na₂SO₃ showed remnant percentages of sodium and sulfur. Moreover, nitrogen was observed in the samples of extractions with (NH₂)₂CO.

Gel time is the speed at which an adhesive turns from liquid to solid. This speed depends on the chemical mechanisms (reactivity) and it is related to the lifetime of the adhesive (GHAHRI; PIZZI, 2018). Table 4 shows the average gel time of the commercial tannin of the black acacia species (pH: 6.27) and the comparison of the tannin of the species *P. taeda* (pH: 7.12) with treatments of 10% and 20% of formaldehyde in solutions of 45% total solids. The mean values followed by the same letter do not differ statistically among themselves according to the Tukey test at a 5% level of probability.

Table 4. Tukey test for the average gel time of the commercial tannin (10% and 20%, the studied tannin (10% and 20%), and standard error (σ).

Tannins	%	Gel Time (s)	σ
Commercial	10	190.00 ^a	11.13
	20	171.66 ^a	16.50
Studied	10	50.66 ^b	4.51
	20	50.66 ^b	11.59

In the comparative addition of the formaldehyde, no statistic difference was found using the Tukey test between the 10% and 20% commercial tannin or the 10% and 20% tannin of *P. taeda*. This analysis reveals that adding larger amounts of formaldehyde to the solution does not favor the quick intercrossing of the bonds in the reaction medium, which can lead to a waste of material, environmental contamination, and increased production costs.

The gel time of the *P. taeda* tannin was shorter in relation to the commercial tannin of the black acacia, and the difference is an important factor in the gluing process, regulating less time in industrial operations. This variation also depends on the structure of the tannin molecule. Molecules that contain the resorcinol group (commercial tannin of the black acacia species) have only one hydroxyl in the A ring, and the phloroglucinol group (tannin of the *P. oocarpa* species) have two hydroxyls, and this hydroxyl variation determines the greater reactivity of tannin in relation to the formaldehyde (VIEIRA et al., 2014).

4. FINAL CONSIDERATIONS

Based on the extraction results of the tannins of *P. taeda* bark, and the phytochemical analyses, the tannins found in the studied plant matter are condensed, and, based on the IR spectra, we can infer that they are catechins. These catechins form polymers observed in the MEV characterization in a shorter time than formaldehyde in the formation of the gel time in comparison to the commercial tanning currently used on a large scale. Therefore, we conclude that it is possible



and feasible to use and exploit the bark of *P. taeda* to extract tannins, and that this bark serves as a potentially new commercial source for lumber companies in the production of phenolic resins.

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