Use of Tannin from *Pinus oocarpa* Bark for Manufacture of Plywood

Érika da S. Ferreira
Departamento de Engenharia e Tecnologia Florestal,
Universidade Federal do Paraná
Curitiba, Paraná, BR

Roberto C. C. Lelis
Departamento de Produtos Florestais,
Universidade Federal Rural do Rio de Janeiro
Seropédica, Rio de janeiro, BR

Edva de O. Brito
Departamento de Produtos Florestais,
Universidade Federal Rural do Rio de Janeiro
Seropédica, Rio de Janeiro, BR

Setsuo Iwakiri
Departamento de Engenharia e Tecnologia Florestal,
Universidade Federal do Paraná
Curitiba, Paraná, BR

Abstract

Tannin is a polyphenol obtained for several renewables resources, it has been largely distributed among superior plants. On the bark of some species, the concentration of tannin could be 40%, what permitted its commercial exploration. The concentration of tannin on *Pinus oocarpa* bark is between 25 - 30% and it has higher reactive. The objective of this work was to evaluate the phenol-formaldehyde adhesive, it modified with 10% tannin from *Pinus oocarpa* bark and the pure tannin adhesive for manufacture of plywood panels. Plywood panels were produced with three plies of sumaúma *(Ceiba pentandra* L. Gaertn) specie, 27,0 mm of thickness and amount of adhesive applied of 380 g/m² (double line). The panels were pressed with 140ºC of temperature, specific pressure of 10 kgf/cm², pressing time of 10 minutes and using 100 x 10 x 10 formulation (resin, wheat flower, and water). The quality of plywood panels was evaluated by the static bending (modulus of rupture - MOR and modulus of elasticity - MOE) and the bonding line shear test of the adhesive. The addition of 10% tannin extract were not modified MOR, however decrease the values obtained to MOE. The bonding line shear test showed that the additions of 10% tannin extract to the pure tannin resin were decreased the resistance in all tests, dry and wet - boil. The results also showed that it is

possible to produce plywood with pure resin from tannin of the *Pinus oocarpa* bark, however, the panels presented low resistance to humidity, proper for interior use.

Key words: Tannin, bark, *Pinus oocarpa*, adhesive, plywood

Introduction

The synthetic adhesives urea-formaldehyde and phenol-formaldehyde are the main adhesives used in the wood bonding and their by-products. One of the advantages of the phenol adhesives elapses from its resistance to the action of the humidity being in that way recommended for bonding of exposed products to the environment (Sellers et al., 1995).

In the developing countries, the cost of the synthetic resin is very loud in relation to the total cost of the panels. That is due to the fact that almost all of the raw materials for production of adhesives are made to base of derived products of petroleum. Like this, it becomes new researches in order to know alternative raw materials for production of adhesives. In that effort, it is in first plan the obtained resins of natural raw materials as the tannins (Sellers, 2001).

The tannins are poliphenols obtained of several renewable sources, as for instance, of the bark of black acacia (*Acacia mearnsii* de. Wild), *Pinus radiata* and of the wood of the quebracho (*Schinopsis* sp). In the bark of some species, the concentration can arrive even to 40%, allowing like this commercial exploration (Pizzi, 1983).

The development of adhesives to the base of natural poliphenols (tannins) it began in the decade of fifty with the researches of Dalton (1950, 1953) and Plomley et al. (1957). The main interest was to substitute the synthetic phenols, obtained of the petroleum, for natural phenols with structures similar to the adhesives ones.

The crisis of the petroleum in the decade of seventy impelled new researches on the job of the tannin in the substitution of synthetic resins (Pizzi & Mittal, 1994). Nowadays, the poliphenols (tannins) they are used at several countries of the world in the bonding of wood products, like Germany, England, New Zealand and Australia (Roffael & Dix, 1994).

Plywoods can be it produced in a great variety of types and quality, depending on the used raw material and application can be used in several uses, as building site industry, furnitures, shipbuilding, constructions for agriculture, industrial constructions and packings.

With the tannin-formaldehyde adhesives panels can be manufactured with high technological properties (Roffael & Dix, 1994). Through the use of the tannin, it can be obtained a water resistant bonding and making possible the use of the panels in exterior areas.

In Brazil, in the last years, it is growing the interest for the development of natural adhesives based on tannins, mainly of eucalyptus bark and wood, being thought about use of the residues generated by the sawmill industry (Mori, 2000; Tostes, 2003).

This work had as general objective to test adhesive based on tannins of *Pinus oocarpa* bark, as well as phenol-formaldehyde adhesive modified with tannin of *Pinus oocarpa* bark in the bonding of plywood.

Material and Methods

Collection of the Bark for Extraction of the Tannin

The barks were collected in povoaments of *Pinus oocarpa*, with 11 years, in Fazenda Monte Alegre, of DURATEX, located in Agudos, São Paulo. Five trees with medium diameter to the height of the chest of 21,8 cm it was selected at random. The trees were marked and their barks removed with aid of a large knife, tends as pattern the retreat of the barks of medium diameter to the height of the chest to the base of the trees in foot. The barks were transported for the Area of Environmental Existence of the Company, for a previous drying to the air, being stored later in plastic sacks of 50 liters. The material was directed to the Laboratório de Química da Madeira, Departamento de Produtos Florestais, Instituto de Florestas – UFRRJ, where it was fragmented in hammer mill, drizzled and stored in plastic sacks. In the extraction of the tannins of the barks, particles were used that crossed the sieve of 4,37 mm and that it was kept in the one of 0,61 mm.

Extraction of the Tannins

The bark was extracted in autoclave, with capacity of 15 liters and cover endowed with manometer and thermometer, in the Laboratório de Tecnologia da Madeira (DPF/IF/UFRRJ), for 2 hours, being used relationship liqueur: bark same to 15:1 and sulfito of sodium in the concentration of 5%. After each extraction, the material was filtered in crucible of glass, put in glass trays and position in dry kiln to 103° ± 2°C for 8 hours, for a previous drying of the extract. After, the material was removed even for dry kiln to 60°C completes drying, when then the material was scraped and grounded being obtained the tannin powder.

Properties of the Resins

It was determined some properties of the synthetic resins phenol-formaldehyde - HL 2080, it modification with tannin extract of *Pinus oocarpa* and the resin based on tannin of the bark of *Pinus oocarpa*. The modification of the phenol resin was made through the substitution in the reason of 10% of the resin for a solution of tannin extract to 45%. For each resin it was determined the following properties: viscosity, solids content, gel time and pH.

The viscosity was determined through the equipament Rheo-Viskometer according to Höppler (it Haake Medingen GmbH).

The solids content was certain being weighed a small resin bracket and being determined the humid weight. Later the material was taken to the dry kiln to 103° ± 2°C for drying for approximately 15 hours where it was determined dry and percentile weight of solids.

For the gel time determination 10 g of resin was weighed in a test tube, being added a formaldehyde solution for 37% (catalyst) in the proportion of 20% on the solids content contained in the tannin resin. The mixture was homogenized with glass stick in hot water to the temperature of 90°C to the gel point.

The pH of the resins was determined through digital pH-meter.

Production of Plywood

For manufacture of those plywood sumaúma veeners were used (*Ceiba pentandra* (L.) Gaertn), with medium thickness of 27 mm and 9% of humidity, donated by the Estadual Office of Forests of the Government of the State of Acre.

In the determination of density of the veeners and sumaúma wood was used ABNT NBR 9485 (1986).

Manufacture of Plywood

The panels were made with the dimensions of 50 x 50 x 0,61 cm and apparent density average of 0,46 g/cm^3. A total of 13 panels was produced constituted by three sumaúma veeners. The adhesive was dispersed in an uniform way, with the aid of a spatula, in single line.

The panels were hot pressed, being used hydraulic presses, of horizontal plates with electric heating, time of closing of 35 seconds and pressure of 10 kgf/cm^2. The experimental plans for the used resins and the variables of the process of making of the panels are presented in the Tables 1, 2 and 3.

Table 1. Experimental plain for the panels made with phenol-formaldehyde resin and it modification with 10% of tannin extract of *P. oocarpa to 45%*

Assemblage:	20 minutes
Press Temperature:	140 ºC
Press Time:	10 minutes
Amount of glue:	380 g/m^2
Formulation (resins x flour x water):	100 x 10 x 10
Catalyst: Solution of K_2CO_3 to 60%	6% on the solids contet of the resin

Table 2. Experimental plain for the panels made with tannin-formaldehyde resin

Assemblage:	15 minutes
Press Temperature:	140 ºC
Press Time:	10 minutes
Amount of glue:	380 g/m^2
Formulation (resins x flour x water):	100 x 10 x 10
Catalyst: formaldehyde solution to 37%	20% on the solids content of the resin

Table 3. Description of the treatments for making of plywood

Treatment	Resin
T1	Phenol-formaldehyde
T2	Phenol-formaldehyde + 10% Tannin to the 45%
T3	Tannin-formaldehyde to the 45%

Mechanical Test of Panels

The properties of the panels were appraised for the following tests:

- Static bending, DIN 52371 (1982), ([25.thickness + 5] x 5 cm);
- Resistance of the glue line shear (RLC), DIN 52.255 (1982);

Statistical analysis

The used delineament was casual entirely with five repetitions. After the tests of test pieces, the medium data regarding each appraised tests were submitted to the variance analysis. Having rejection of the nullity hypothesis for the test F, the test Tukey was applied at the level of 5% of significance for comparison among the averages.

Results and Discussions

Viscosity, solids content, gel time and pH

The medium values of the viscosity, solids content, gel time and pH for the solution of tannin extract of *Pinus oocarpa* bark, phenol-formaldehyde resins and it modification with tannin extract of *Pinus oocarpa* bark are presented in the Table 4.

Table 4. Medium values of the Viscosity (V), Solids Content (SC), Gel Time (GT) and pH of phenol-formaldehyde resins, it modification with tannin and pure resin of tannin extract of *Pinus oocarpa* bark to 45%

Treatment	V (cP)	SC (%)	GT (min)	pH
Phenol-formaldehyde	760,16	45,97	9,69	12,31
Phenol-formaldehyde + 10% Tannin	1.006,14	41,03	18,59	12,51
Tannin	691,86	41,26	2,21	4,47

The addition of tannin extract of *Pinus oocarpa* bark to the phenol-formaldehyde resin increased viscosity. That can be attributed to the occurrence of competitiveness between the phenols of the tannin and phenols of the synthetic resin for the molecules of free formaldehyde.

The tannin extract of *Pinus oocarpa* bark presented low viscosity, contrasting with the literature that tannin extracts usually present high viscosity in the concentration of 40% - 50% (Weissmann, 1985).

The solids content found was close to the expected, once tannin solution was made to 45%. Mori (2000) and Tostes (2003), they worked with solids contet of 42% and 40,47%, respectively, in solutions of eucalyptus tannin. The same authors observed superior viscosity to the found for *Pinus oocarpa*.

Regarding the gel time, there was an increase tendency in the value with the addition tannin extract of *Pinus oocarpa* bark. Gonçalves (2000) and Tostes (2003) observed this same behavior analyzing the modification of the phenol resin with 10% of tannin extract of mimosa and eucalyptus, respectively.

The gel time depends in a large part of the pH. Studies with tannin extracts of *Pinus halepensis* showed that the largest values of gel were found in pH 4 - 4,5 (Tisler et al., 1983). The authors also showed that the extracts in pH minor (below 3) or more alkaline (above 7) they presented smaller gel times.

With the extract addition to the phenol-formaldehyde resin there was a subtle elevation in the pH value. The pH interferes in the reactivity and viscosity of tannin solutions, being important the control of this variable to impede an accelerated polymerization and consequent pre-cure of the resin.

Apparent Density of the Wood and Panels

The average of the apparent density of sumaúma wood, made calculations to 12% of humidity, was of 0,30 g/cm3. The Table 5 presents the medium values of the apparent density of the panels for treatment.

Table 5. Medium values of the apparent density of the panels (MAD-g/cm3)

Treatment	MAD (g/cm3)
Phenol-formaldehyde	0,45^{NS}
Phenol-formaldehyde + 10% Tannin	0,46
Tannin-formaldehyde	0,45

NS = No significant at the level of 5% of probability;

The medium values obtained for apparent density of the panels in different treatments are not differed statisticly at the level of 5% of probability, there wasn´t necessity to do covariance analysis in the obtained properties of panels.

Static Bending (MOR and MOE), Glue Line Strenght (GLS)

The medium values found for the modulus of rupture in the parallel and perpendicular grain sense of the external veeners of panels made with the phenol-formaldehyde resin, its modification with 10% of tannin extract to 45% and tannin-formaldehyde resin of *Pinus oocarpa* bark are presented in the Table 6.

Table 6. Medium values obtained for modulus of rupture (MOR) in the parallel and perpendicular grain sense of the external sheets of panels made with phenol-formaldehyde resin and its modification with 10% of tannin extract and tannin-formaldehyde resin of *Pinus oocarpa* bark

Treatment	Static Bending	
	MOR (kgf/cm^2) Parallel	MOR (kgf/cm^2) Perpendicular
Phenol-formaldehyde	350,29 A *	95,84 A
Phenol-formaldehyde + 10% Tannin	332,14 A	87,68 A
Tannin-formaldehyde	241,62 B	60,04 B

* Following averages for the same letter, inside of a same column, they don't differ statisticly amongst itselves at the level of 5% of probability for the Tukey test.

Regarding the parallel rupture module they were observed that the panels made with the phenol-formaldehyde resins and phenol-formaldehyde modified presented the best results, not having significant difference among the treatments. The resin tannin-formaldehyde pure presented the smallest results modulus of rupture, being differed statisticly of the other found values. The same tendency found for the parallel modulus of rupture was observed, in the perpendicular module of rupture. It was evident that the addition of tannin extract to phenol resin didn't affect the resistance of panels, being possible to substitute part of the onerous phenol resins for tannin extract.

The values modulus of rupture, parallel and perpendicular, observed were inferior to the found for Pio (1996) in compensated *of Eucalyptus scabra* and *E. robust* made with phenol resin, being them: 1221,8 kgf/cm^2 and 968,0 kgf/cm^2; 614,5 kgf/cm^2 and 426,3 kgf/cm^2, respectively. This great variation in the found values is due to use of different species, besides the panel to be composed by five veeners, what also increases its resistance.

The medium values found for the modulus of elasticity in the parallel and perpendicular grain sense of the external veeners of tpanels made with the phenol-formaldehyde resin, it modification with 10% of tannin extract to 45% of *Pinus oocarpa* bark and the tannin-formaldehyde resin are presented in the Table 7.

Table 7. Medium values obtained for Modulus of Elasticity (MOE) in the parallel and perpendicular grain sense to the of the external veeners of the panels made with the resin phenol-formaldehyde, phenol-formaldehyde and it modification with 10% of tannin extract to 45% of *Pinus oocarpa* bark and the tannin-formaldehyde resin

Treatment	Static Bending	
	MOE (kgf/cm^2) Parallel	MOE (kgf/cm^2) Perpendicular
Phenol-formaldehyde	49.014 A *	2.355 B
Phenol-formaldehyde + 10% Tannin	29.698 B	2.583 B
Tannin-formaldehyde	32.731 B	5.229 A

* Following averages for the same capital letter, inside of a same column, they don't differ estatisticamente amongst themselves at the level of 5% of probability for the test Tukey.

The largest value of parallel modulus of elasticity found was obtained with the phenol-formaldehyde resin and the smallests were observed in the phenol-formaldehyde resins modified and pure tannin-formaldehyde. Regarding the perpendicular modulus of elasticity the smallest results were observed in panels made with phenol-formaldehyde resins pure and modified, the panels made with the tannin-formaldehyde resin presented the largest values of modulus of elasticity.

Bortoletto Júnior (2003), evaluating phenols plywood composed by five veeners of eleven species of eucalyptus, it found values of modulus of elasticity varying out 125.789 kgf/cm^2 to 197.114 kgf/cm^2 for it parallel MOE and of 34.861 kgf/cm^2 to 55.949 kgf/cm$_2$ for perpendicular modulus of elasticity.

The medium values found for resistance of the glue line shear of the panels made with the phenol-formaldehyde resin, phenol-formaldehyde and it modification with 10% of tannin extract to 45% of *Pinus oocarpa* bark and the tannin-formaldehyde resin are presented in the Table 8.

In the Table 8 it can be observed that there was significant difference in the glue line strength, in the acclimatized samples, among the different treatments. The appraised treatment that obtained the best acting was with the phenol-formaldehyde resin and the worst was obtained with the tannin-formaldehyde pure resin. The same behavior can be observed in the samples submitted to the treatment with cold water.

Table 8. Medium values obtained for Glue Line Strenght (GLS) of panels made with phenol-formaldehyde resin, it modification with 10% of tannin extract to 45% of *Pinus oocarpa* bark and the tannin-formaldehyde resin

Series	**1****	**2**	**3**
Treatment	GLS (kgf/cm^2)	GLS (kgf/cm^2)	GLS (kgf/cm^2)
Phenol-formaldehyde	31,18 A*	27,57 A	25,27 A
Phenol-formaldehyde + 10% Tannin	20,95 B	18,28 B	15,06 B
Tannin-formaldehyde	17,71 C	9,31 C	10,36 B

*1 = acclimatized samples of 12% humidity; 2 = Samples submerged in cold water by 6 hours and put at climatization room by one week; 3 = Samples submerged in hot water (80° C) for 4 hours, being after having put for 2 hours in cold water and acclimatized by one week.
 * Following averages for the same capital letter, inside of a same column, they don't differ statisticly amongst itselves at the level of 5% of probability for the Tukey test.

In the samples submitted to the hot water, the best results were found with the phenols resin, the smallest medium values were observed for the phenol modified resins and pure tannin. The samples made with tannin-formaldehyde pure resin submitted to cold water as for submitted them to the hot water suffered delamination, and that percentile one was of 55% and 50%, respectively. The high index of delamination of panels made with the tannin-formaldehyde pure resin submitted to humid tests can be explained by the fact of occured a pre-cure of the resin and subsequent formation of a weak and brittle glue line, that consequently didn't resist to the action of the water. It is evident also that the addition of tannin extract to the phenol resin reduced the quality of the bonding and consequently the resistance in the glue line strength in all of the samples.

Dix & Marutzky (1985) they used tannin extracts of *Pinus sylvestris* and *Picea abies barks* in mixtures with the phenol-formaldehyde resins in bonding of plywood. According to authors, it was possible a substitution of the phenol for tannin of up to 60% in the case of *Pinus* without the strength properties to shear (dry test) they were altered negatively. Unlike observed it in the glue line strength test of the submerged samples in cold water for 24 hours, the allowed maximum of substitution was of 20%.

Carneiro et al. (2001), analyzing different formulations of adhesives based on tannin of *Eucalyptus grandis* bark found strength values of the glue line in dry tests varied out 33,4 kgf/cm^2 to 41,0 kgf/cm^2.

Conclusions

The addition of tannin extract of *Pinus oocarpa* bark to phenol-formaldehyde resin there was increase in the values of the viscosity and gel time and reduction in the values of solids content and pH;

It is possible to add 10% of tannin extract to the phenol-formaldehyde resin without altering the mechanical properties (modulus of rupture and modulus of elasticity) of plywoods, except for the parallel modulus of elasticity;

The addition of 10% of tannin to the phenol-formaldehyde resin harmed the glue line strength of the panels;

References

ABNT – Associação Brasileira De Normas Técnicas. 1986. Painéis de madeira compensada: determinação da massa específica. Rio de Janeiro. (NBR – 9485)

Bortoletto Júnior, G.; Belini, U. L. 2002. Produção de lâminas e manufatura de compensados a partir da madeira de Guapuruvu (*Schizolobium parayba* Blake) proveniente de um plantio misto de espécies nativas. Cerne. 8 (2): 16 – 28.

Carneiro, A. C. O.; Vital, B. R.; Pimenta, A. S.; Mori, F. A. 2001. Reatividade dos taninos da casca de *Eucalyptus grandis* para produção de adesivos. Cerne. 7(1): 1 – 9.

Dalton, L. K. 1950. Tannin-formaldehide resins as adhesives for wood. Australian Journal of Applied Science. 1: 54 – 70.

Dalton, L.K. 1953. Resins from sulphited tannins as adhesives for wood. Australian Journal of Applied Science. 4: 136 - 145.

Dix, B. & Marutzky, R. 1985. Ersatz von Phenolharz durch fichten – und kiefer – Tanninformaldehydharze bei der Verleimung von furnierem. Hols als Roh – und Werkstoff. 44: 228.

DIN – Deutsches Institut Für Normung. 1982. Bestimmung der Bindefestigkeit von Sperrholzleimungen im Zugversuch. In: Normen für Holzfaserplatten, Spanplatten, Sperrholz. 3. Auflage, Berlin. (DIN 52.255)

DIN – Deutsches Institut Für Normung. 1982. Prüfung von Sperrholz-Biegeversuch. In: Normen für Holzfaserplatten, Spanplatten, Sperrholz. 3. Auflage, Berlin. (DIN 52.371)

Gonçalves, C. A. 2000. Utilização do tanino da madeira de *Mimosa caesalpiniaefolia* Bentham (Sabiá) como matéria prima alternativa para a produção de adesivos. Dissertação (Mestrado em Ciências Ambientais e Florestais) – Instituto de Florestas, Universidade Federal Rural do Rio de Janeiro, Seropédica. 100f.

Mori, F. A. 2000. Caracterização parcial dos taninos da casca e dos adesivos produzidos de três espécies de Eucaliptos. Tese (Doutorado) – Departamento de Engenharia Florestal, Universidade Federal de Viçosa, Viçosa. 73f.

Pio, N. S. 1996. Avaliação da madeira de *Eucalyptus scabra* (Dum-Cours) e *Eucalyptus robusta* (Smith) na produção de painéis compensados. Dissertação (Mestrado em Ciências Florestais) – Setor de Ciências Agrárias, Universidade Federal do Paraná, Curitiba. 101f.

Pizzi, A. 1983. Wood Adhesives: Chemistry and Technology. New York: Marcel Dekker.

Pizzi, A.; Mittal, K. L. 1994. Handbook of adhesive technology. New York: Marcel Dekker.

Plomley, K. F.; Gottstein, J. W.; Hills, W. R. 1957. Tannin-formaldehyde adhesives. CSIRO Australian Forest Products. Newsletter. 234: 6 – 8.

Roffael, E.; Dix, B. 1994. Tannine als Bindemittel für Holzwerkstoffe. Holz Zentralblatt. 20(6): 90 – 93.

Sellers, T. 2001. Wood adhesive innovations and applications in North America. Forest Products Journal**.** 51(6): 12 – 22.

Sellers, T.; Mcsween, J. R..; Nearn, W. T. 1995. La adhehrencia en la Madera y los adhesivos. Revista VETAS. : 74 – 77.

Tostes, A. S. 2003. Tanino da casca de *Eucalyptus pellita* F. Muel como fonte de adesivos para colagem de painéis de madeira aglomeradas. Dissertação (Mestrado em Ciências Ambientais e Florestais) – Instituto de Florestas, Universidade Federal Rural do Rio de Janeiro, Seropédica. 85f.

Weissmann, G. 1985. Analysis of acid and neutral sugars in bark extracts from *Pinus radiata* and *Larix decidua* by capillary gas liquid chromatrography. Holzforchung. 39: 245 – 247.

Acknowledgments

The authors express their gratitudes to the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Capes for the cession of the scholarship and to the government of the state of Acre for the donation of the sumaúma veeners used in this research.