# PERMEABILITY MEASUREMENTS OF BRAZILIAN

# PINUS ELLIOTTII

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## ABSTRACT

The liquid and gas phase permeability of Brazilian *Pinus elliotti* was studied with a custom built gas and liquid flow rate analysis chamber. The longitudinal gas phase permeability is shown to be six times greater than the radial permeability. There is no statistically significant difference between the longitudinal permeability of water versus wood preservative. Scanning Electron Microscopy (SEM) images confirm that the reported permeability properties are due to the wood itself rather than to blocked pores or other artifacts of the sample cutting process. Wood composition analysis shows that the samples of *Pinus elliotti* grown in Brazil are similar to other species of Pinus grown in tropical climates. Specifically, the *Pinus elliotti* in this study is composed of 17% extractives, 0,27% ashes, 21% hemicellulose, 45% cellulose and 30% lignin. Results are discussed in the context of the continued search for effective wood preservatives for use in tropical climates.

KEY WORDS: wood permeability; Pinus elliotii, SEM and chemical composition

## **INTRODUCTION**

The urgent need to preserve the Brazilian tropical rainforests has received increasing recognition in recent years. The desire for preservation has, in turn, generated much interest in the use of wood coming from reforestation species such as Pinus. The genus Pinus (composed of 111 species) is an important source of wood in Brazil and worldwide because it is fast growing and adaptable to many different environments from the Tropics to nearly Arctic conditions. However, to use this resource wisely, and to select the best possible Pinus species for construction purposes, it is necessary to understand the basic physical and chemical properties of the wood, especially those that affect its preservation (Serpa and Vital 2004, Milota et

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al. 1995, Fengel and Wegener 1984, Sjöström 1981). Permeability and the distribution of preservative within wood are two fundamental properties that control how effectively one can preserve wood. In short, good penetration of preservative is necessary for long term preservation. Permeability of wood also affects processing time and product quality. Both of these features affect price, another key factor in selecting the correct wood for construction purposes (Hunt and Garrat 1963, Cassens 1995, Fenton and Degroot 1996, Eaton and Hale 1993, Rhatigan et al. 2003). Permeability is the measured flow of liquids or gas through pores in response to a pressure gradient. It involves penetration of a liquid or gas into the porous network of interconnected wood cells and its subsequent flow through the capillaries. The pressure gradient may be externally applied or internally created due to capillary attractive forces. Both penetration into the capillaries and flow through them are highly dependent upon capillary size and arrangement. Gas permeability is relatively simple to measure because the measurements are not hindered by problems with air blockages or suspended particles and because the measured values are independent of the type of gas used in the analysis. In contrast, the type of liquid used affects the measured liquid permeability. In the vast majority of cases, permeability is found to decrease with increasing liquid viscosity (Hansmann 2002, Minato et al. 2004, Lihra et al 2000).

### **EXPERIMENTAL**

*Pinus elliotti*, known in the US as Southern Pine, was selected for this investigation. To have representative specimens, the wood samples were obtained by cutting disks from a long trunk. These disks were then cut into pieces, which were sized appropriately for each of the different measurements. Prior to testing, the moisture content of the specimens was 14%. During the assays, the moisture content was 12% and the density was 0.46g/cm<sup>3</sup>. To maintain the moisture content at 12%, the specimens were kept in an acclimatized room during testing (norm NBR 7190/97). The preservative used in the permeability measurements was a diluted aqueous emulsion containing 0.1% Neem oil and 0.1% surfactant in distilled water. The surfactant was synthesized in house from the reaction between castor oil and dimethylamine; 2% hexametaphosphate was added to the surfactant mixture to decrease the viscosity. The viscosity of preservative is 4 mPa.s and the water is 0.98 mPa.s (Machado et al. 2006).

For the chemical characterization, the samples of wood were cut into pieces capable of passing through a 42 mesh screen (0.355mm pore size). Before each chemical assay, the moisture content of all samples was determined (in triplicate) according to a process established by the Tappi Standard 1999. Subsequent to moisture content determination, the samples were treated in a soxhlet extractor using water and organic solvents (cyclohexane and ethanol, P.A. grade). First, the extraction was realized by soaking the samples in ethanol for 4 hours at room temperature (25° C). Next, the samples were placed in a 1:1 cyclo-hexane/ ethanol solution for 8 hours in order to remove the hydrophobic substances. Next, the same samples were subjected to a 3 hour extraction in distilled water. Finally, the fibers were dried at 60°C. The extractive content was determined by the mass difference in the dry samples, before and after the treatment procedures.

Once the extractive-free samples were obtained, the ash content was established according to norm TAPPI T211 om-93 1985. The lignin content was determined by the sum of the soluble and insoluble lignin fractions according to norms TAPPI T222 om-98 and TAPPI T250 1985, respectively. High performance liquid chromatography (HPLC) was used to analyze the cellulose and hemicellulose content, as specified in TAPPI T 249 cm-85 1985. A minimum of three samples were tested in order to establish a standard deviation in the method.

Measurements of the radial and longitudinal air and liquid permeability of *Pinus elliotii* were carried out in an in-house built apparatus as depicted in Fig. 1. Twenty cylindrical specimens of 20 mm in diameter and 50 mm in length were cut from the same piece of timber. All the measurements were performed at room temperature (25°C). During gas and liquid measurement, the specimen was placed in the apparatus so that the sample thickness (or length for the longitudinal permeability specimens) was parallel to the flow direction. The cylindrical surfaces of the specimens were coated with epoxy resin to restrict flow in the longitudinal direction. The permeability assays were performed by placing the sample in the apparatus, pulling a vacuum, and then measuring the flow rate of the fluid through the sample.



Fig. 1: Apparatus for gas (a) and liquid (b) permeability measurement

For gas permeability, Fig. 1a, the apparatus consisted of three rotameters (flow meter) to measure the airflow rate. These rotameters measured in the ranges of 20 to180 ml/min, 10 to 100 l/h and 100 to 1100 l/h.

Before beginning each measurement, a vacuum of 98 kPa was applied for 2 minutes in order to stabilize the system. After the system was stabilized, the airflow rate on the rotameter was measured. Applying a similar procedure and using the apparatus shown in Fig. 1b, the liquid permeability was measured. Tests were performed with samples of water and with the Neem oil preservative. To measure the liquid permeability, the vacuum was applied and the liquid was put inside the burette and passed through the sample until the moment a constant flow was obtained. Once a constant flow was obtained, the amount of time necessary to drain 25 ml of liquid from the burette was measured. The gas and liquid permeability was determined by applying Darcy's law (Siau JF 1971) relating fluid flow rate to permeability through a porous medium.

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Samples of *Pinus elliotti* were examined by scanning electron microscopy (SEM) using a Zeiss-Leica instrument model 440 at an electron beam acceleration of 20 kV. All samples analyzed were gold coated in a BAL-TEC (MED 020) coating system.

Statistical methods (ANOVA and Tukey test) available in the SAS statistical software package were used in this study to analyze and interpret data. The Tukey test was used to show which samples exhibited statistically significant differences.

### **RESULTS AND DISCUSSION**

The results of the wood composition analysis are shown in Tab. 1. The extractives are defined as the sum of all compounds soluble in organic solvent plus those soluble in water. The inorganic salt content is termed "ashes". As is evident from Tab. 1, the majority of the wood samples' masses is derived from extractives, hemicellulose, cellulose and lignin. Ash contributes only a few tenths of a percent to the wood mass.

Compound	%		
Extractives	16.56 (±0.71)		
Ashes	0,27 (±0.01)		
Hemicellulose	21 (±0.82)		
Cellulose	45 (±1.73)		
Lignin	29,53 (±1.13)		

Tab. 1: Pinus elliotti characterization

PS: Values in parentheses are thestandard deviation of the means.

Although chemical analyses of some commonly found species of Pinus have been reported in the literature, chemical analyses of *Pinus elliotti* are rarely reported. Since there is a limited number of related studies (which do not provide adequate elements for comparison for the present data (Irbe et al. 2006, David et al. 2006, Jankowsky and Galvao 1979, Baldock and Smernik 2002, Bortoletto and Moreschi 2003)) the present chemical analysis of *Pinus elliotti* provides new insight. This new data shows that the chemical composition of *Pinus elliotti* is similar to what has been previously observed for other species of Pinus, particularly those grown in the tropics. Specifically, Pinus generally possesses a relatively low ash content. In fact, in tropical countries the ash content of this species is rarely less than 0.2% or greater than 1% (Fengel and Wegener 1984). Tab. 1 also shows that the extractive content is about 17%. The extractives can constitute up to 8% of the mass of dry wood in temperate climate species, and up to 20% in tropical species (Fengel and Wegener 1984). The greatest percentage of the wood mass is made up of lignin and polysaccharides. These include cellulose (45%), lignin (30%) and hemicelluloses (21%).

Fig. 2 shows SEM micrographs of the samples prepared for the permeability assay. As is evident from the micrographs, *Pinus elliotti* presents a relatively simple and homogeneous

anatomical structure consisting essentially of two types of cells: tracheids and rays. The tracheids are elongated hollow tubes with characteristic thin areas (pits) in their side walls. In the living tree, these cells have the dual function of sap conduction and mechanical support. Thus, they are expected to play a key role in the impregnation of preservative. In contrast, the rays of the living tree serve chiefly for storage and horizontal conduction of food materials. They may also have a secondary water-conduction function. While these latter cells may be expected to facilitate radial movement of preservatives into the wood, even under the best conditions, they play only a subordinate role in the impregnation of softwoods (Hunt and Garrat 1963). As such, the longitudinal permeability is expected to be the value most relevant to the impregnation of preservative in wood preservation.

In all permeability tests, the top of the sample was cut with a razor blade so as to allow the pores of the wood to remain unblocked for fluid transport. Fig. 2 (a) displays test-pieces before cutting with a razor blade. As is shown in the micrograph, the pores are completely obstructed in the longitudinal and radial direction. After the cutting process, the opened pores of the tracheid, longitudinal direction, and ray cells, radial direction, can be observed (Fig. 2b). Thus, the SEM images indicate that this method of sample preparation assures that the permeability values to be discussed below are due to the intrinsic properties of the wood and not to any sample preparation artifacts such as blocked pores.



a - longitudinal direction



a - radial direction



b - longitudinal direction



b - radial direction

Fig. 2: Test-pieces (a) without and (b) with surface treatment to unblock pores. 100x magnification was used for scale bar corresponds to  $101\mu m$ 

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Table 2 shows the gas and liquid permeability results in both radial and longitudinal directions. The gas permeability in the longitudinal and radial directions displays a statistically significant difference (to the  $\alpha$ =0.05 level). The higher permeability occurs in the longitudinal direction due to the presence of tracheid cells, in accord with previous observations that gas transport is dominated by the longitudinal cells with the ray cells playing only a secondary role (Hunt and Garrat 1963). By statistical analysis of the measured results using the SAS software (ANOVA follow by Tukey test, with the confidence level set at 95%), it was found that the permeability of the gas is significantly greater than that of the liquid permeability.

Permeability	Air		Distilled water	Preservative
(9,87x10 <sup>-10</sup> m <sup>3</sup> .m/N.s )	longitudinal	Radial	Longitudinal	longitudinal
Mean	141.71	23.52	5.45	4.13
Std Deviation	14.44	6.07	2.5	1.89

Tab. 2: Permeability measurement of Pinus elliottii

No liquid or air transport was detected in the transverse direction. Interestingly, the mean liquid permeabilities of preservative and water along the longitudinal direction were similar. A Tukey test indicated that there was no statistically significant difference between the longitudinal permeability of water and preservative. These results were expected because the preservative is very dilute (only 0.1% active ingredient). As such, the difference between the viscosity of water (0.98 mPa.s) and that of preservative (4 mPa.s) may not be great enough to lead to measurable permeability rate differences.

In the context of wood preservation, some protection for wood can be obtained with surface coatings. However, the products used (paint, varnishes and lacquers) may be destroyed under external conditions. In a relatively short time, the action of ultraviolet rays, rain and cycles of drying and humidification can destroy superficial protective films. Therefore, it is necessary to renew the coating periodically. Because of this, the most reliable method to protect wood is impregnation with preservatives. The treatment methods used include vacuum pressure impregnation and diffusion. For both methods of impegnation, the permeability value is important information both in choosing the type of wood and in properly executing the impregnation procedure.

The present information about the permeability of *Pinus elliotti* is particularly important in Brazil and in other tropical developing nations. The demand for construction materials in developing nations is huge and often outstrips the availability of native species. In the absence of alternative woods from reforestation species, the need for wood results in the decimation of old growth forests. In Brazil, *Pinus elliotti* is currently being used as an alternative wood (particularly in the south and southwest). However, it is sometimes used without preservative due to skepticism about the potential efficacy of the preservation process and due to lack of knowledge about appropriate process conditions for *Pinus elliotti* impregnation. Because of the structural similarities between *Pinus elliotti* and other tropical Pinus species, it is suggested that methods conventionally used for impregnation of Pinus can also be used for *Pinus elliotti*. Further, the penetration rate measurements presented above can be used to develop a robust impregnation process.

## CONCLUSION

Results from this study demonstrate that *Pinus elliottii* has gas permeability about 6 times greater in the longitudinal direction than in the transverse direction. All samples have no transverse permeability for liquids. Statistical tests (ANOVA followed by Tukey test) show that there is no significant difference in the longitudinal permeability of preservative as compared to water. SEM images present no evidence for blocked pores indicating that the permeability values described above represent the true permeability of the wood. The wood component analysis shows that *Pinus ellioti* grown in Brazil has a similar composition as other species of Pinus grown in tropical climates. As such, it is expected that impregnation methods developed for other species of tropical Pinus may be useful in the preservation of *Pinus elliotti* wood in Brazil.

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# REFERENCES

- 1. ABNT, NBR 7190, 1997: : projeto de estruturas de madeira. Rio de Janeiro
- Baldock, J.A., Smernik, R.J., 2002: Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. Org Geochem 33:1093–1109. DOI 10.1016/S0146-6380(02)00062-1
- Bortoletto, J.r. G., Moreschi, J.C., 2003: Physical-mechanical properties and chemical composition of *Pinus taeda* mature wood following a forest fire. Bioresource Technol 87:231–238. DOI 10.1016/S0960-8524(02)00242-0
- 4. Cassens, D.L., 1995: Selection and use of preservative: treated wood, Forest Products Society, Madison
- David, J.P., Schimleck, L.R., Peter, G.F., Daniels, R.F., Clark, A., 2006: Nondestructive estimation of wood chemical composition of sections of radial wood strips by diffuse reflectance near infrared spectroscopy. Wood Sci Technol 40:709–720. DOI 10.1007/ s00226-006-0085-6
- 6. Eaton, R.A., Hale, M.D.C., 1993: Wood: decay, pests and protection, Chapman & Hall, New York
- 7. Fengel D., Wegener G., 1984: Wood: chemistry, ultrastructure reactions. Walter de Gruyter, New York
- Fenton, C.C., Degroot, R.C., 1996: The recycling potenticial of preservative treated wood. Forest Prod J 46(7-8):37-46
- 9. Hansmann, C., 2002: Permeability of wood a review. Drevarsky Vyskum 47(4):1-16
- 10. Hunt, M.G. Garrat, G.A., 1963: Wood Preservation, Mc Grawhill, New York
- Irbe, I., Andersons, B., Chirkova, J., Kallavus, U., Andersone, I., Faix, O., 2006: On the changes of pinewood (*Pinus sylvestris L.*) Chemical composition and ultrastructure during the attack by brown-rot fungi Postia placenta and Coniophora puteana. Int Biodeter Biodegr 57:99–106. DOI 10.1016/j.ibiod. 2005.12.002
- 12. Jankowsky, I.P., Galvao, A.P.M., 1979: Influência do teor de extrativos na umidade de equilíbrio da madeira. IPEF 18:1-33. O.D.C. 812.213
- 13. Lihra, T., Cloutier, A., Zhang, S.Y., 2000: Longitudinal and transverse permeability of balsam fir wetwood and normal heartwood. Wood Fiber Sci 32(2):164–178
- Machado, G.O., Calil, Jr. C., Polito, W., Pawlicka, A., 2006: Preservante natural de madeira para uso na construção civil: óleo de Neem. Minerva 3(1):1-8
- 15. Milota, M.R., Tschernitz, J.L., Verril, S.P., Mianowski, T., 1995: Gas permeability of plantation Loblolly pine. Wood Fiber Sci 27 (1):34-40
- Minato, K., Naruo, N., Konishi, J., 2004: How far does a gaseous reagent penetrate into wood. Holz Roh Werkst 62:120-125. DOI 10.1007/s00107-0030457-7
- Rhatigan, R.G., Milota, M.R., Morrell, J.J., Lavery, M.R., 2003: Effect of high temperature drying on permeability and treatment of western hemlock lumber. Forest Prod J 53(9):55-58
- Serpa, P.N., Vital, B.R. 2004: Propriedades da madeira de *Pinus elliottii*. Revista de Madeira 14(86):86-96
- 19. Siau, J.F., 1971: Flow in wood, Syracuse University Press, Syracuse

- 20. Sjöström, E., 1981: Wood chemistry: fundamentals and applications, Academic Press, London
- 21. Tappi Standard, 1985: T 211. Om-93. Ash in wood
- 22. Tappi Standard, 1985: T 222. Om-98. Acid-insoluble lignin in wood and pulp
- 23. Tappi standard, 1985: T 249. cm-85. Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography
- 24. Tappi Standard, 1985: T 250. Acid-soluble lignin in wood and pulp
- 25. Tappi Standard Methods, 1999: Preparation of wood for chemical analysis: T 264 cm-97. Atlanta, TAPPI PRESS

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