SCIENTIA
FORESTALIS

# Wettability and surface free energy on heat-treated *Pinus* sp. and *Erisma* sp. woods

## Grau de umectação e energia livre de superfície em madeiras *Pinus* sp. e *Erisma* sp. tratadas termicamente

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*Resumo*

Este estudo tem como objetivo investigar a molhabilidade (grau de umectação), polaridade de superfície e perda de massa de duas madeiras de florestas plantadas, *Pinus* sp. (*softwood*) e *Erisma* sp. (*hardwood*) após tratamento térmico. As amostras de madeira foram tratadas termicamente a 100 °C, 140 °C e 180 °C e comparadas às amostras em temperatura ambiente, 25 ºC. A fim de obter o ângulo de contato, foram depositados diferentes solventes nas superfícies das madeiras tratadas com calor. A partir dessas medidas, foram calculados os valores de energia livre de superfície, em termos dos componentes polares e dispersivos, pelo método Owens-Wendt-Rabel-Kaelble. As madeiras se mostraram hidrofóbicas em temperaturas abaixo de 180 °C, isto é, com relativamente altos ângulos de molhabilidade e baixa polaridade superficial, mas sem alterações visuais e dimensionais mais drásticas. O impacto do tratamento térmico nas propriedades de superfície de *Pinus* sp. e *Erisma* sp. foi também verificado por meio da inoculação de um fungo (*Pycnoporus sanguineus*). As madeiras *Erisma* sp. tratadas termicamente, quando comparadas com *Pinus* sp., apresentaram melhores propriedades, tais como estabilidade de massa, polaridade superficial e grau de umectação.

**Palavras-chave**: energia livre de superfície, ângulo de contato, degradação por fungo, umectação.

*Abstract*

This study aims to investigate wettability, surface polarity, and mass loss in two reforestation woods, *Pinus sp.* (softwood) and *Erisma sp* (hardwood), after heat treatment. The wood samples were heated to 100 °C, 140 °C and 180 °C, meanwhile a control group was kept at a fixed temperature of 25 °C. Different test liquids were employed in order to obtain the contact angles (wetting angles) formed on the heat-treated sample surfaces. From such measurements, the values of surface free energy, in terms of its polar and dispersive components, were calculated by the Owens-Wendt-Rabel-Kaelble approach. Temperatures far below 180 °C proved to be high enough to yield hydrophobic samples, *i.e.*, with relatively high wetting angles and low surface polarity, but without drastic visual and dimensional changes. The impact of heat treatment on the surface properties of *Pinus* sp. and *Erisma* sp. was also verified by fungal inoculation (*Pycnoporus sanguineus*). Compared to *Pinus* sp., heat-treated *Erisma* sp. showed improved properties, such as mass stability, surface polarity and wettability.

**Keywords**: surface free energy, contact angles, decay fungi, wettability.

## INTRODUCTION

There are many methods of heat treating wood aiming at improving durability and mechanical resistance (OLIVEIRA et al., 2010; SRINIVAS; PANDEY, 2012). However, relatively high temperatures (225-325 °C) may produce irreversible deterioration of wood, causing drastic color changes, loosening of fibers, dimensional changes, and surface cracks (ESTEVES; PEREIRA, 2008; KUTNAR et al., 2013; OLIVEIRA et al., 2010). The most common protocols for the heat treatment of wood describe

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temperatures ranging from 160 °C to 240 °C, but biologically durable timbers can be obtained with reduced capability for moisture absorption. Heat-treated woods become surface protected even at temperatures far below 200 °C, which are high enough to produce hydrophobic, water-repellent surfaces by the removal of volatile extractives (KOCAEFE et al., 2015; OLIVEIRA et al., 2010).

Studies on surface properties are still far from being exhaustive as far as woods with different compositions are concerned (softwoods and hardwoods). Our group has studied *Araucaria angustifolia* and *Pinus elliottii* before and after thermal treatment from 20 °C to 200 °C (OLIVEIRA et al., 2010; SOARES et al., 2011). Here, *Pinus* sp. (softwood) and *Erisma* sp. (hardwood) were studied up to reach a lower temperature, 180 °C. Such species are chemically different, widely available, and applied in the construction, paper and pulp industries. Calculation of surface free energy for wood samples from results of contact angles enables ones to evaluate how surface polarity varies with the heat treatment. Surface free energy and its components are critical parameters aiming at revealing differences in wood/liquid interface characteristics (MANTANIS; YOUNG, 1997). The presence of volatile extractives and products formed by oxidative pyrolysis of wood are able to produce hydrophobic surfaces and reduce surface polarity, which should be properly measured. Inasmuch as thermal modification in woods fundamentally yields different surface features, the susceptibility of *Pinus* sp. *a*nd *Erisma* sp. was also studied with regards to fungal decay (*Pycnoporus sanguineus*).

## MATERIAL AND METHODS

*Pinus* sp. (*Pinus Taeda*) and *Erisma* sp. (Qualea albiflora Warm.) from planted forests were donated by LaMEM, EESC/USP, São Carlos-SP (Brazil), and obtained from the outer, sapwood parts of trees. The woods were cut into (5.0x3.0x0.5) $cm^3$ pieces, and were dried in a conditioning chamber at 103±2 °C for 6 h (*Erisma* sp.) and 9 h (*Pinus* sp.) from a green state (anhydrous mass) to a point of equilibrium moisture content of 12%, which is recommended for wood-based products (CALIL JUNIOR et al., 2003). A set of samples was treated in an oven from room temperature to operating temperatures of 100 °C, 140 °C, and 180 °C for 10 h at 3 °C $min^{-1}$. This heating protocol was chosen based on our previous results (OLIVEIRA et al., 2010; SOARES et al., 2011). All wood samples were weighed and stored under vacuum at 25 °C. A set of samples was left untreated (control samples).

Contact angles (θ) were measured for untreated (25 °C) and heat-treated samples (100 °C, 140 °C, and 180 °C) by the sessile drop method (OLIVEIRA et al., 2010; SOARES et al., 2011). Drops of 8.0 µL of four test liquids: water, ethylene glycol, formamide, and diiodomethane were deposited at different positions on the wood surfaces. The droplet images were analyzed using the arithmetic means of three contact points for the drop profiles by software *Cam2008*.

Surface free energy (γ) was calculated by considering the solid (S)-liquid(L) interactions in equilibrium with the vapor phase. Total surface energy ($\gamma^t$) was obtained as a sum of non-polar, dispersive (d), and polar (p) contributions (LAMPROU et al., 2010), and the values of θ were related to γ via the Owens-Wendt-Rabel-Kaeble (OWRK) approach (QIN et al., 2015; QIN et al., 2014; VÁZQUEZ et al., 2011), Equation (1):

$$\left(\frac{\gamma_L(\cos\theta+1)}{2\sqrt{\gamma_L^d}}\right)=\sqrt{\gamma_S^d}+\left(\frac{\sqrt{\gamma_L^p}}{\sqrt{\gamma_L^d}}\right)\sqrt{\gamma_S^p}$$

where $\gamma_L^p$ and $\gamma_L^d$ are the polar and dispersive components of $\gamma^t$, and can be calculated from the values of θ in water (W), ethylene glycol (E), formamide (F), and diiodomethane (D) using a commercial spread sheet software program. Since there are two unknowns, $\gamma_L^p$ and $\gamma_L^d$, in Equation (1), at least two liquids are necessary to be used in the calculation; one with a predominant polar component and the other, with a predominant dispersive component. The component $\gamma_L^p$ has a major contribution in water, while it is zero in diiodomethane; $\gamma_L^d$ predominates for formamide and ethylene glycol (QIN et al., 2015). Surface polarity was calculated by taking the $\gamma_L^p/\gamma^t$ ratio such as proposed for wood species (MANTANIS; YOUNG, 1997).


**Sci. For., Piracicaba, v. 45, n. 113, p. 161-167, mar. 2017**
**DOI: dx.doi.org/10.18671/scifor.v45n113.16**

For accelerated decay tests, a white-rot fungus, *Pycnoporus sanguineus*, donated by Universidade Federal de Pernambuco (Brazil), was used for inoculation (class: Basiodiomycetes, species: *P. sanguineus*). The culture medium was a mixture of Sabouraud-dextrose agar dissolved in 400 mL of hot water, which was autoclaved (Phoenix Luferco, AVplus) at 121 °C for 15 min, and deposited onto sterile Petri dishes in a laminar flow hood to prevent contamination (ZIGLIO; GONÇALVES, 2014). The fungus was inoculated by means of a swab onto the wood surfaces, which were subsequently placed into Petri dishes with nutrient agar at room temperature for 16 weeks. After this period of time, the samples were autoclaved for sterilization at 121 °C for 20 min, cleaned with a brush, and stored in a desiccator until reaching a stable value of mass. The values of mass loss ($\Delta m$) were obtained for the samples before and after the fungal decay. Such experimental conditions were chosen based on our previous results (ZIGLIO; GONÇALVES, 2014).

## RESULTS AND DISCUSSION

Wood is rich in a large variety of colored compounds, which allows one to visibly distinguish different species. The process of thermal degradation of wood produces changes in color due to dark-brown quinones formed after oxidation of phenolic compounds (CARVALHO et al., 2014; MOURA; BRITO, 2011). *Pinus* sp. and *Erisma* sp. became darker from yellow to brown and light brown to dark brown, respectively, under treatment from 25 °C to 180 °C (Figure 1), which are not drastic color changes for these temperature variations.

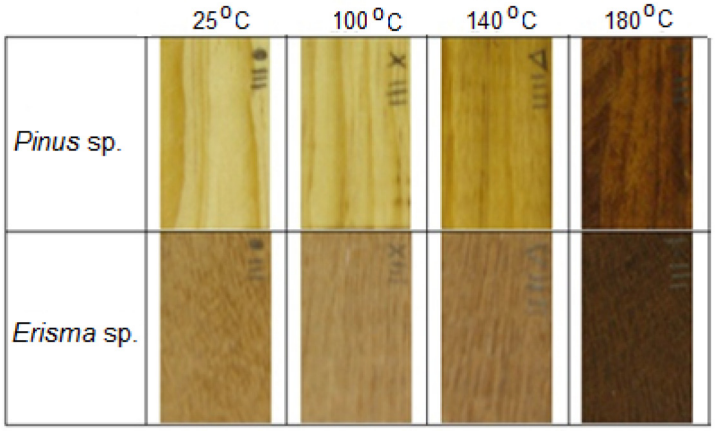


**Figura 1**. Cores de *Pinus* sp. e *Erisma* sp. quando tratadas termicamente em diferentes temperaturas.
**Figure 1**. Colors of *Pinus* sp. and *Erisma* sp. when heat treated at different temperatures.

From Figure 1, it can be assumed that *Pinus* sp. and *Erisma* sp. are not dark enough to indicate significant effects of pyrolysis on their surface properties. However, even without considerable color changes, they suffered deterioration for some extent at relatively low temperatures so far as results of wettability and surface polarity have indicated.

The contact angles (θ) were obtained for *Pinus* sp. and *Erisma* sp. at a wood/liquid interface by using different testing liquids: water (W), formamide (F), ethylene glycol (E), and diiodomethane (D) (Figure 2).

The values of θ in Figure 2 are characteristically different for *Pinus* sp. and *Erisma* sp., in particular when testing with water (W). *Erisma* sp. shows the highest values of θ at 180 °C, thus evidencing a hydrophobic character. Values of θ close to zero, on the other hand, implicate on complete wettability, such as obtained for *Pinus* sp. at lower temperatures. Besides, the values of θ were typically different in probes such as diiodomethane (nonpolar solvent), water and formamide (polar solvents).

Figure 3 shows the changes in surface free energy for untreated (control group) and heat-treated *Pinus* sp. and *Erisma* sp., and which were calculated from the values of θ (Equation 1). Surface polarity was also obtained as the ratio of the polar component of the surface free energy to the total surface free energy (dark-brown quinones $\gamma^p/\gamma^t$).

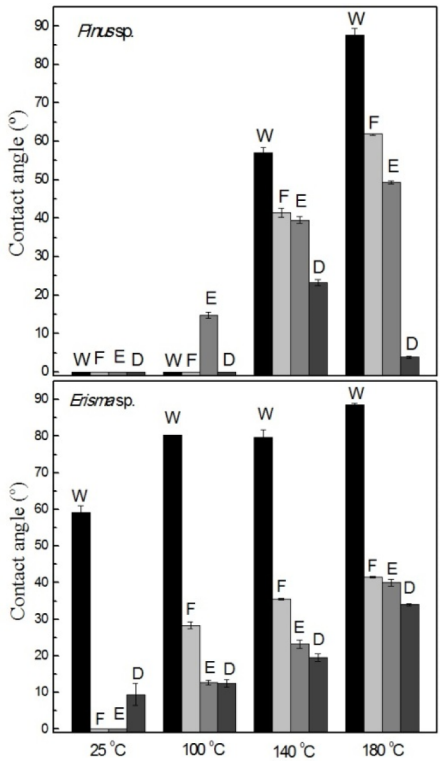


**Figura 2**. Variação do ângulo de contato em função da temperatura para *Pinus* sp. e *Erisma* sp. medidos com diferentes tipos de solventes (água, etilenoglicol, formamida e diiodometano).
**Figure 2**. Variation of contact angle versus temperature for *Pinus* sp. and *Erisma* sp measured by using different liquid probes (water, ethylene glycol, formamide, and diiodomethane).

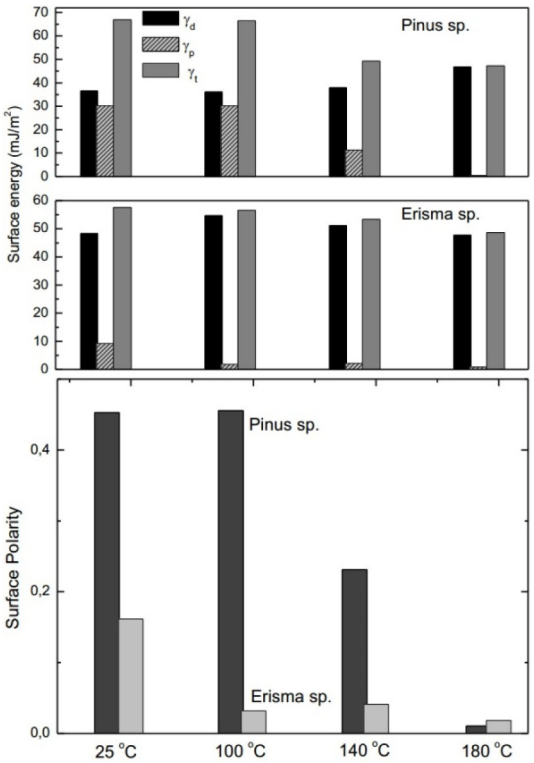


**Figura 3**. Energia livre de superfície e polaridade de superfície de *Pinus* sp. e *Erisma* sp. obtidos a partir das medidas de ângulo de contato.
**Figure 3**. Surface free energy and surface polarity of *Pinus* sp. and *Erisma* sp. as evaluated from the measurements of contact angles.

In addition to describing a wood surface as hydrophilic or hydrophobic, data in Figure 3 are even more conclusive. By comparing the values of total surface free energy ($\gamma^t$), for *Pinus* sp. *e.g.*, it can be verified they are practically the same for untreated samples and after being treated at 100 °C. In this case, since the values of $\theta$ used in the calculations of $\gamma$ are close to zero, they gave similar contribu-


Sci. For., Piracicaba, v. 45, n. 113, p. 161-167, mar. 2017
DOI: dx.doi.org/10.18671/scifor.v45n113.16

tions for both dispersive ($\gamma^d$) and polar ($\gamma^p$) components. However, for the samples heat-treated at 180 °C, the polar component ($\gamma^p$) decreases in detriment to the dispersive component ($\gamma^d$), producing values of surface polarity (p) close to zero. The values of $\gamma^t$ decrease about 30% from untreated to heat-treated samples at 180 °C. Such decrease in surface polarity (p) can be explained by effects of thermal expulsion of water from inner channels of wood, and also, from decomposition of lignin, which can make the wood more hydrophobic.

By comparing *Erisma* sp. and *Pinus* sp., the values of $\gamma$ are markedly different (Figure 3); for *Erisma* sp. treated at 180 °C, dispersive component ($\gamma^d$) contributes significantly to the value of $\gamma$. Such effect can be attributed to a process of thermal degradation of extractives and hemicelluloses, since polar components move away from inner to outer layers of wood. As a consequence, heat-treated woods are most likely related to higher contact angles and low surface polarities. The results obtained here are in agreement from previous data of wettability of heat-treated Jack Pine woods by different liquid probes (HUANG et al., 2012). In this work, it was assumed that structural changes in lignin and cellulose reduce absorption of liquids after heating, especially water [16]. In general, since the amount of free hydroxyl and acetyl groups in wood decreases during heating, this precludes the formation of a dense cross-linked network and more hydrophobic surfaces. Besides, thermal softening of lignin can also be related to water-repellent wood surfaces since its glass transition temperature usually occurs at about 90 °C (GUNNELLS et al., 1994; HAKKOU et al., 2005). Such effects justify small values in surface polarity for both untreated and heat-treated *Erisma* sp. as compared with *Pinus* sp. (Figure 3).

In order to evaluate the resistance of heat-treated *Pinus* sp. and *Erisma* sp. to fungal decay (*Pycnoporus sanguineus*), measurements of $\theta$ were also made. However, values of $\theta$ with higher levels of uncertainty were obtained due to the presence of cracks or fissures in heat treated wood; they ranged from 67.1°±26.7° (*Pinus* sp.) to 88.9°±25.2° (*Erisma* sp.) in water. Although imprecise, these results have indicated that the samples change their surface characteristics from hydrophilic to hydrophobic after fungal decay. For *Erisma* sp., this result is even more evident, since the values of $\theta$ are closer to 90°, indicating that fungal decay involves predominantly consumption of polar components of wood. In this case, heat treatment reduces hygroscopicity, by decreasing chemical interactions with water, and, as a consequence, affects the performance of wood-decaying fungi (HOMAN et al., 2000). The ability of fungi to partly decay a variety of wood components depends on the action of ligninolytic enzymes, and white-rot fungi, such as *Pycnoporus sanguineus*, known for secreting enzymes and depolymerizing lignin (MEYSAMI; BAHERI, 2003), which is a structural biopolymer responsible for protecting cellulose. A wood surface can be considered to be predominantly polar (hydrophilic) if it contains accessible -OH groups in the cell walls, and hydrophilic, when it contains high amounts of highly polar cellulose, or hemicelluloses, as a compared to less polar lignin.

The mass loss obtained for the heat-treated samples, before and after exposure to *Pycnoporus sanguineus* (16 weeks), can be observed in Figure 4.

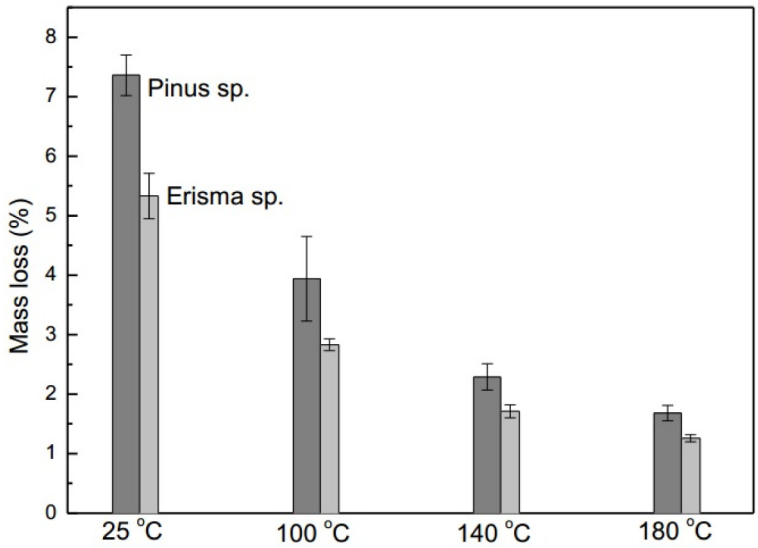


**Figura 4**. Perda de massa para *Pinus* sp. e *Erisma* sp. degradadas após tratamento térmico em diferentes temperaturas.
**Figure 4**. Mass loss for decayed *Pinus* sp. and *Erisma* sp. after heat treatment at different temperatures.

The mass loss decreased for the heat-treated samples, but both wood specimens have shown high resistance to white-rot fungal decay as compared with those untreated samples. Therefore, *Erisma* sp. is the most resistant wood to fungal decay, i.e., repellent to water; *Pinus* sp. is the most polar and more susceptible wood to deterioration in humid conditions. The methodology proposed here for obtaining the values of surface free energy and surface polarity is straightforward and non-invasive and can be applied to many heat-treated wood species.

## CONCLUSIONS

Surface free energy and surface polarity were compared for two wood species; *Pinus* sp. and *Erisma* sp., and they were related to changes on wettability after treatment from 25°C to 180 °C. Appropriate thermal treatments of woods make it easier to understand how surface modifications are induced by heating. This is a prerequisite for obtaining high quality woods with accurate properties, and which are necessary and in high demand in the market. Therefore, it is necessary to adapt analytical methods of characterization to control their surface quality and avoid expensive and time-consuming procedures. Here, it was verified that the thermal treatment used was able to change the hydrophilic nature of *Pinus* sp. and *Erisma* sp., which become rather hydrophobic, and with a non-polar character. These results show that temperatures higher than 180 °C, generally used for most common heat treatment of woods, are not necessary to modify their surface nature from hydrophilic to hydrophobic one. In this case, it takes place at lower temperatures without causing significant color and dimensional changes.

## ACKNOWLEDGEMENTS

The authors would like to thank the financial agencies FAPESP (proc. 2012/13003-5) (Brazil), CAPES (Brazil), and Lemann Institute for Brazilian Studies, University of Illinois at Urbana-Champaign (USA).

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Recebido em 08/03/2016
Aceito para publicação em 05/10/2016