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Thermochemical and physical properties of two fast-growing eucalypt woods subjected to two-step freeze–heat treatments

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ABSTRACT

In this study, the effect of two-step freeze–heat treatments on the thermochemical and physical properties of two *Eucalyptus* wood were investigated. Five treatments were performed and compared to untreated control: freezing (WF), freezing followed by heat treatment at 180 and 200 °C (WFT180 and WFT200) and heat treatment at 180 and 200 °C (WT180 and WT200). The freeze step was performed at −22 °C for 72 h and the heat step was performed at 180–200 °C for 3.5 h. Thermochemical (wet chemical analysis, FTIR and TGA), physical (water absorption and ASE) and surface properties (wettability) were measured. The two-step freeze–heat treatments changed the holocellulose and extractives contents, and stabilized the 1% NaOH solubility. Dimensional stability increased and hygroscopicity of thermally treated eucalypt wood decreased. The two-step treatments resulted in lower chemical changes than the application of a heat treatment only. The apparent contact angle of thermally treated wood increased, confirming the improvement of wood hydrophobicity.

1. Introduction

Wood is a polymer composed by a three-dimensional interconnected network of cellulose, hemicelluloses, lignin and minor amounts of extractives and inorganic compounds. The wood cell wall is composed mainly for carbohydrates (65–75%) and lignin (18–35%). In general, elemental composition of wood consists of 50% carbon, 6% hydrogen and 44% oxygen [1,2].

Specific modification of some wood compounds by thermal treatment can be very useful to improve their properties, such as dimensional stability, hygroscopicity and decay resistance [3]. Cademartori et al. [4] affirmed heat treatments up to 220 °C result in physical and chemical changes that, consequently, increase wood hydrophobicity. In addition, the authors highlighted the absence of chemical products in heat treatments, which characterizes as an eco-friendly modification of wood. On the other hand, the influence of a freeze step on the wood's chemical structure was not fully explored, since the main discussion was related to mechanical [5], physical and anatomical changes [6,7].

Changes in components of both the wood cell wall and extractives have been observed after heat treatments [8,9]. Nevertheless, the level of modification depends on temperature and time of treatment, atmosphere, type of system (open or closed; dry or wet) and dimension of the samples [10]. In general, the modification of the wood's chemical structure after a heat treatment occurs firstly through the breaking of H bonds between water and wood, followed by the evaporation of volatile extractives (<100 °C). The second stage is the decomposition of hemicelluloses at low temperatures (~150 °C), as it is the most thermal unstable wood compound [11,12]. After that, the fraction of crystalline cellulose increases due to the thermal degradation of amorphous cellulose, and the extractives are thermally degraded, forming new compounds due to the decomposition of the polysaccharides [8]. Simultaneously, autocondensation of lignin via cross-linked bounds [3,11] and a cleavage of β-O-4 linkage (depolymerization) [13–15] occur during the heat treatment at high temperatures.

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Although there are many studies about wood thermal treatments, there is a lack of information about the influence of the freeze step (combined or not with a heat step) on the wood's chemical structure. Few studies [7,16] have reported on the decreased extractives content in the wood cell wall after the freeze step. Nevertheless, in some cases this variation of extractives is small and insignificant. According to Hart [17], Ilic [7] and Awoyemi et al. [18], specific extractives tend to rearrange or to migrate toward the inside of the wood cell wall, increasing the radial permeability and possibly creating more pathways through the pits.

The combination of thermal phenomena can result in more significant changes on the materials' structure than if they are individually applied. A successful combination of thermal treatments has been reported in the literature, such as hydrothermolysis followed by heat treatments at high temperatures [19,20], and wood freezing as a pre-treatment followed by heat treatments [18,21]. Thus, this study aimed to evaluate the effects of two-step freeze–heat treatments on thermochemical and physical properties of fast-growing Rose gum (*Eucalyptus grandis* Hill ex Maiden) and Gympie messmate (*Eucalyptus cloeziana* F. Muell.) woods.

2. Material and methods

2.1. Raw material

Six Rose gum and six Gympie Messmate trees from experimental plantations (29°43′0.39″ S, 53°43′46.03″ N) with 21 years of age and spacing of 2 m × 3 m were cut according to the American Society for Testing and Materials – D5536-94 [22] standard. The soil type used in the forest plantation is Arenic Kandiustults [23].

The first log from each tree was cut into wood samples with 20.0 × 20.0 × 50 mm^3 (radial, tangential and longitudinal, respectively), all of them with straight grain and made only of heartwood, with the absence of warps.

2.2. Two-step freeze–heat treatments

Wood samples prepared for the freezing step were immersed in water in order to obtain full saturation. Other samples were oven-dried with forced air circulation at 40 °C to reach 15% of humidity. Subsequently, wood samples were kept in a climatic chamber at 20 °C and 65% of relative humidity to reach the equilibrium moisture content, which was the initial condition for the heat treatments.

Parameters of thermal treatments performed in this study were defined based on a pilot experiment and previous scientific works [4,7,12,18,19,21].

Five thermal treatments were performed – a control treatment was used (Table 1). The freeze step (WF) was performed from room temperature to −22 °C, at a freezing rate of 0.04 °C min^{-1}. The time of treatment was measured after temperature stabilization at −22 °C. After this step, all the samples were unfrosted to 0 °C with a rate of 0.6 °C min^{-1} for six hours and were dried at 40 °C in an oven with forced air circulation.

The heat treatment (WT) was performed in an oven with forced air circulation. Wood samples were put inside the oven at 100 °C and, subsequently, the oven temperature was increased to 180 and 200 °C (0.90 °C min^{-1} heating rate). After reaching the desirable temperature, wood samples were thermally treated for 3.5 h. After this step, temperature was reduced to 100 °C and all the samples were kept in a climatic chamber (20 °C and 65% RH). Two-step freezing–heat treatment (WFT) was performed considering the same parameters described above for the freezing and heat treatments.

2.3. Chemical characterization

For the chemical characterization, twenty samples of each treatment were used. Milled wood samples (40–60 mesh) [24] were used to quantify in triplicate the ethanol–toluene extractives [25], Klason lignin [26] and hollocelulose [27].

ATR-IR spectra were collected in a Nicolet Nexus 470 spectrophotometer equipped with MKII Golden Gate SPECAC instrument. The equipment was set for 32 scans at a resolution of 4 cm^{-1} in the range of 4000–700 cm^{-1}. Before the tests, the light of the equipment was aligned and the background spectra were collected. A peak at 1029 cm^{-1} was used as the standard to determine the peak ratios. This peak corresponds to deformation on the plane of CH structures and to the symmetric stretching C—O of cellulose [28,29], highly stable structures when subjected to thermal and chemical treatments.

2.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out using a DTG-60 Shimadzu equipment in a dynamic nitrogen atmosphere (gas flow of 50 ml min^{-1}) at 25–600 °C with a heating rate of 10 °C min^{-1}, wherein 5–6 mg of each sample was kept in a platinum pan. The derivative thermogram of mass loss was illustrated as a function of temperature (dw/dt).

2.5. Physical analysis

Water absorption was determined according to Eq. (1). Wood samples (twenty each treatments) were oven-dried at 103 ± 1 °C to reach constant mass. Subsequently, wood samples were immersed in water. The increment of mass was measured after 1, 2, 3, 4, 5, 6, 7, 8, 10, 12 h of immersion and at full saturation.

$$\mathrm{WA} = \frac{(w_f - w_i)}{w_i} \cdot 100 \quad (1)$$

where w_f is the sample mass after immersion in a different time; w_i is the dry mass.

Table 1
Thermal treatments performed in Rose gum and Gympie messmate woods.

Treatment	Freeze step			Heat step		
	Natural condition	Temperature (°C)	Time (h)	Natural condition	Temperature (°C)	Time (h)
Control	–	–	–	–	–	–
WF	Wet	−22 ± 2	72	–	–	–
WFT180	Wet	−22 ± 2	72	Climatic chamber (20 °C and 65% RH)	180 ± 1	3.5
WT180	–	–	–	Climatic chamber (20 °C and 65% RH)	180 ± 1	3.5
WFT200	Wet	−22 ± 2	72	Climatic chamber (20 °C and 65% RH)	200 ± 1	3.5
WT200	–	–	–	Climatic chamber (20 °C and 65% RH)	200 ± 1	3.5

W: wood; F: freeze treated; T: heat treated.