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Characterization of hydrothermally treated wood in relation to changes on its chemical composition and physical properties

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ABSTRACT

The modification of wood by hydrothermal treatments causes characteristic changes in its chemical composition. The determination of these specific changes was carried out by wet and instrumental chemical analyses. It could be confirmed that the polyoses were the first degraded components in a range from 45.40% to 47.64%. The lignin fraction also showed a significant reduction, increasing with the severity of the treatment, with a degradation rate from 8.65% to 45.39%. Besides, the pyrolysis fingerprints were highly variable due to simultaneous degradation via different pathways as well as to the existence of isomers, and to small structural differences between homologous compounds. Those reactions cause significant physical alterations and wetting phenomena in wood surface with a remarkable hydrophobic effect in modified samples, thus obtaining higher contact angle values than in unmodified samples.

1. Introduction

The methods for modifying the chemical composition of wood are broadly used worldwide and have been successfully marketed the last decades [1]. Among different modification methods is highly interesting to emphasize the hydrothermal process where chemicals are not added. The process consists of heating the wood slowly at temperatures up to 170–240 °C during 35–120 h (depending on the wood species) within an airtight chamber at reduced or inert atmosphere to facilitate the reaction process [2,3].

The cell walls create stable structures in green plants and particularly in woody plants, where they produce wood. This natural tissue is composed mainly of three biobased chemicals called cellulose, hemicelluloses (polyoses) and lignin, forming together a composite material of rigid cellulose fibers embedded in a cross-linked matrix of lignin and hemicelluloses that bind the fibers [4].

In addition to lignocellulosic structures, wood contains a variety of low molecular weight organic compounds called extractives, a group of cell wall chemicals formed of resins, phenols, fatty acids, fatty alcohols, terpenes, steroids, waxes, and many other minor organic compounds which can be extracted using solvents. [5].

The changes occurring in chemical composition of wood during thermal modification of timber (TMT) are mainly due to the autocatalytic reactions of the cell wall constituents. The polyoses, which are hydrolyzed into oligomeric and monomeric structures, are the most reactive components forming carbonic acids as result of cleavage of the acetyl groups. Subsequently, the monomeric sugar units are dehydrated to aldehydes such as furfural, formed from pentose. At the same time hydroxyl-methyl-furfural is formed out of dehydration of hexose sugar units [6,7].

The lignin complex reacts in smaller proportions and the reactivity increases only at high temperatures where could disintegrate into highly concentrated phenol groups as well as could take place several condensation reactions with aldehydes [7].

Moreover, wood always undergoes slight changes in moisture content due to its structure, and it is unlikely to preserve its dimensional stability in the environment where is maintained. The sorption of moisture by each cell wall polymer depends not only on its hydrophilic nature but also on water accessibility to the hydroxyl groups through hydrogen bonds [8].

Wood must be suitably prepared to obtain satisfactory treatments and good performance, this preparation involves quick drying of the wood when green (no shrinkage) to the fiber saturation point (25–30% moisture content) to avoid decay and insect damage. In this process, no change in the cell wall volume occurs, and only free water is lost. However, when the wood is dried further, bound water is removed from the cell walls and shrinkage of the wood begins [4].

In order to enhance the natural conditions of wood, such as different physical properties related to wood durability and dimensional stability, TMT is exposed to high temperatures. As a result, the wood resistance to pathogens increases and the moisture content is stabilized; in addition, during this treatment the hygroscopicity of wood can be substantially reduced [6].

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However, loss on mechanical strength on TMT has been one of the main drawbacks toward commercial use for this type of modification of wood, due to diverse changes in mechanical strength depending on the treatment temperature and sample length [9].

The main purpose of this study is to examine changes occurring on wood chemical composition during the hydrothermal treatment process (TMT) and to correlate these changes with certain physical properties and performance of this polymeric material.

2. Materials and methods

2.1. Wood material and treatment

Monterey pine (*Pinus radiata*) and English oak (*Quercus robur*) samples were industrially heat treated in the airtight chamber under inert N_2 atmosphere according to the industrial production standards in *Termogenik*© Orozko, Spain. Untreated samples were used to compare all analytical characterizations.

The modification process begins with a fast increase of chamber temperature up to 100 °C which allows the drying of the wood to 3–4% of moisture content. Subsequently steam is sprinkled in order to avoid damage in wood and the temperature in chamber is raised to its maximum level; on *Quercus robur* samples underwent a heat treatment of approximately 55 h at temperatures up to 170 °C, while *Pinus radiata* samples were treated for 60–70 h at temperatures up to 190 °C and 210 °C.

The last stage is the cooling down and stabilizing of the samples. In order to avoid abrupt temperature and pressure fluctuations, this stage takes about 24 h at controlled relative humidity until room temperature. The temperature gradient between surface and inner site of the samples did not exceeds of 15–20 °C with the purpose of retain the wood quality.

2.2. Analytical characterizations

2.2.1. Physical properties

The properties investigated have been measured in reference samples (*P. radiata* and *Q. robur*) and hydrothermally treated samples (*Q. robur170*, *P. radiata190*, *P. radiata210*) respectively, using samples of 25 mm × 25 mm × 10 mm or milled samples depending on the test to be performed.

The moisture content was carried out in accordance with UNE-EN 13183-1 (oven dry basis), the dry density (ρ_0) and normal density (ρ_{12}) were determined according to DIN 52182; also characteristic density (ρ_k) was calculated in accordance with EN 384 European Standard. In addition, the volumetric shrinkage (β_v) was obtained using the UNE 56533-77, and the coefficient of anisotropy (β_t/β_r) was determined as the ratio between the tangential and radial shrinkage.

2.2.2. Wood chemical composition

The chemical analysis of the hydrothermal and reference samples was done by wet chemistry according to the standard methods; ashes (TAPPI T211 om-93), ethanol-toluene soluble extract content (TAPPI T264cm), lignin (TAPPI T222 om-98), holocellulose [10] and α-cellulose and hemicelluloses [11]. All analyzes were carried out threefold.

2.2.3. Soluble carbohydrate content

In order to determine the composition of monosaccharides presented in wood, samples were ground to pass a 4–6 mm mesh screen, and hydrolyzed according to the method of Saeman [12]. 0.35 g of meshed wood were hydrolyzed using 5 mL of sulfuric acid (72%, w/w) at 30 °C for 45 min, then 140 mL of distilled water was added and it was autoclaved for 1 h at 121 °C.

Afterwards, the hydrolyzed sugars were analyzed by high performance liquid chromatography (HPLC) determined by a Jasco LC-Net II/ADC equipment with a photodiode array detector MD-2018Plus, refractive index detector RI-2031Plus and Rezex ROA Organic Acid H^+ (8%) column. Dissolution of 0.005 N H_2SO_4 with 100% of deionised and degassed water was used as a mobile phase. The conditions of the samples injection were 40 °C, 0.35 mL/min flow and volume of 20 μL.

2.2.4. Wood chemical composition by Py–GC–MS

Milled wood samples (treated and reference), were characterized by pyrolysis–gas chromatography–mass spectroscopy (Py–GC–MS), where each sample was thermally degraded in the absence of oxygen, and its macromolecules break down at specific lower bonding energy points forming volatile fragments that provide useful structural information about the macromolecule as a whole.

The *Py–GC–MS* was carried out using a commercial pyrolyzer (Pyroprobe model 5150, CDS Analytical Inc., Oxford, PA). Small sample (in the μg range) was pyrolyzed in a quartz boat at 650 °C for 15 s with a heating rate of 20 °C/ms (ramp-off) with the interface kept at 260 °C. The pyrolyzates were purged from the pyrolysis interface into the GC injector under inert conditions using helium gas. The fused-silica capillary column used was an Equiy-1701 (30 m × 0.20 mm × 0.25 μm). The GC oven program started at 50 °C and was held for 2 min. Then it was raised to 120 °C at 10 °C/min and was held for 5 min after that raised to 280 °C at 10 °C/min, was held for 8 min and finally raised to 300 °C at 10 °C/min and was held for 10 min.

The identification of the pyrolysis products was accomplished using a *GC–MS* instrument (Agilent Techs. Inc. 6890 GC/5973 MSD). The obtained mass spectra were compared to the mass spectra of National Institute of Standards Library (NIST) and with those compounds reported in the literature.

2.2.5. Chemical structure by Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectroscopy is a very useful technique for analyzing the structure of wood components and the chemical changes induced by hydrothermal treatment. Various wood samples were ground to obtain a specific diameter (4–6 mm) and different chips from the same wood sample were analyzed in order to ensure that the obtained spectra represent the whole board.

Infrared spectra were collected using milled samples measured in Nicolet Nexus 570 equipment by direct transmittance in a single-reflection ATR System (ATR top plate fixed to an optical beam condensing unit with ZnSe lens) with an MKII Golden Gate SPECAC instrument at a resolution of 4 cm^{-1} for 32 scans in the range from 700 cm^{-1} to 4000 cm^{-1}.

2.2.6. Thermal stability

Dynamic thermogravimetric measurements were carried out in order to observe the behavior of wood samples (treated and reference) with increasing temperature.

Thermogravimetric analysis (TGA) of were carried out under nitrogen atmosphere using a Mettler Toledo TGA/SDTA RSI analyzer with a dynamic scan from 25 to 600 °C at 10 °C/min Approximately 5–10 mg of wood sample were placed in a crucible. For the quantitative calculations, the response factors between the weight gain (TG) and the mass loss rate (DTG) were determined.

2.2.7. Surface wettability

In order to determine the impact of hydrothermal treatment on the wood surface wettability, samples were cut from treated and reference wood with the following dimensions 25 mm × 25 mm × 60 mm (tangential, radial and fiber directions)