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Understanding the physicochemical properties of olive kernel to be used as a potential tool in the development of phenol-formaldehyde wood adhesive

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ABSTRACT

During olive oil production process, a great number of by-products are generated, including olive kernel. These by-products can be used for the development of new products for use in many different industrial applications. The evaluation of the physicochemical properties of these by-products constitutes a key factor in evaluating the potential reutilization of olive oil by-products. In the present study, the physicochemical properties of olive kernel were analyzed. Fourier transform infrared spectroscopy (FT-IR), cross-polarization magic angle spinning ^{13}C nuclear magnetic resonance (CP/MAS ^{13}C NMR), Brunauer, Emmett and Teller (BET), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) techniques were used. FT-IR and CP/MAS ^{13}C NMR analysis showed that olive kernel contained typical functions of cellulose, hemicelluloses and lignin. Morphological studies revealed different sizes and arrangements of cells, showing that olive kernel had an irregular structure. TGA showed that thermal stability was observed up to approximately 180 °C. In the present work it was found that olive kernel has the potential to act as a replacement material for up to 15% of base resin in a PF-based adhesive, whilst exhibiting similar or better adhesive properties than a commercial PF resin.

1. Introduction

The Mediterranean region provides 97% of total olive production around the world, with the olive oil industry an important activity, producing 95% of the world's olive oil [1]. During the last decade, olive oil production has been increasing globally, at about 4% per annum, and the International Olive Council predicts that this rate may increase in future years. The increase will be driven by the increasing demand for olive oil and other olive products in both existing and new markets as the health benefits become more widely understood. However, during the olive oil production process large quantities of waste and by-products are generated.

Morocco is the fourth largest olive oil producer in the world. This fact has led to both the food industry and food researchers in Morocco exploring new ways to valorizate these products. Most olive oil waste and by-products, including olive kernel, have demonstrated potential for high-added value compounds [2].

Olive kernel is a lignocellulosic material that mainly contains: cellulose, hemicelluloses and lignin. Because of its high heating power (combustion heat of 17.16 kJ/kg), olive kernel finds application mostly in thermal processes, being used for power generation in the electricity sector and for space heating in residential and commercial buildings [3]. Despite the environmental benefits of using this biomass as a fuel, some problems such as air pollution (carbon monoxide, nitrogen oxides, and particulates such as soot and ash produced by combustion) remain. A more recent utilization of olive kernel consists in its use as a biosorbent of heavy metal ions such as chromium (III) and (VI) and cadmium [3–6].

Conventional wood adhesives are mainly produced from petroleum-based polymers (phenol-formaldehyde (PF), urea-formaldehyde (UF, etc.) and they are known to release formaldehyde to the environment upon production and curing [7,8]. Moreover, formaldehyde is considered a priority pollutant by the United States Environmental Protection Agency. Since the beginning of the 21st century, increasing concern over environmental pollution has forced the adhesives industry to develop environmentally friendly adhesives. Protein, tannin, lignin, and polysaccharides are

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examples of interesting bio-based polymers that have been suggested for wood adhesives [9–11].

At this stage of development, there is a lack of information about olive kernel components and their potential uses. Therefore, there is a need to study and characterize in depth these important by-products. In this line, the determination of olive kernel physicochemical properties is a key factor in order to find potential applications of this by-product (i.e. potential reinforcement in PE resin). The main aim of this study was to seek a better understanding of the chemical and thermal properties of olive kernel and to assess their suitability for partial incorporation into phenol-formaldehyde resin. For this purpose, several techniques such as Fourier transform infrared spectroscopy (FT-IR), cross-polarization magic angle spinning ^{13}C nuclear magnetic resonance (CP/MAS ^{13}C NMR), Brunauer, Emmett and Teller (BET), scanning electron microscope (SEM) and thermogravimetric analysis (TGA) were used in an attempt to assess the chemical and thermal characteristics of this class of material.

2. Experimental methods

2.1. Biological material

Mature olive fruits were obtained from the Picholine variety, which is widely grown in Beni Mellal province, located in the center of Morocco. Picholine is the main olive variety cultivated in Morocco and it is used for the production of olive oil and table olives. Olive fruits were immersed in water (between 70 and 80 °C) for 8 min, and pulped by manual crushing. The olive kernels were air-dried for three days at room temperature (to 8–10% equilibrium moisture content) and then ground to pass a 1.0 mm size screen using a Retsch blade mill. Then, the samples were packed and kept under darkness conditions in polyethylene bags until analysis. All chemicals used were of analytical or reagent grade (Sigma-Aldrich, France). All experiments were done in triplicate.

2.2. Olive kernel characterization

To obtain information about the olive kernel elemental composition, carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) contents of olive kernels were measured using a CHNS Analyzer (CHNS 932, LECO, Michigan, USA). The percentage of oxygen was calculated by subtracting the C, H, N and S contents from 100%.

The moisture content was measured gravimetrically by drying the sample in an air oven at 105 °C until reaching a constant weight. The corresponding weight loss was ascribed to moisture. The ash content was determined gravimetrically after heating the sample in a muffle furnace at 600 ± 2 °C for two hours, according to the TAPPI T211 om-07 standard (TAPPI, 2007).

FT-IR measurements were performed in an ABB Bomem FTLA 2000-102 instrument by direct transmittance using the KBr pellet technique. The concentration of the olive kernel in KBr was maintained between 0.3% and 1%. Each spectrum was recorded over 20 scans, in the range from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1}. Background spectra was collected before each sampling. KBr powder was previously oven-dried to avoid interferences due to the presence of water. The characteristic bands of olive kernels were assigned according to the literature.

^{13}C NMR measurements were obtained at room temperature by using a BRUKER 400 MHz spectrometer. Powdered samples were packed in a 4-mm zirconia rotor, sealed with Kel-FTM caps and spun at 7 kHz and at a contact time of 3.5 ms. Chemical shifts were determined relative to tetramethyl silane (TMS) used as control and expressed in parts per million (ppm).

TGA was used to determine the thermal stability and degradation of the olive kernel samples using a TGA Q50 thermogravimetric apparatus. Ten milligrams of each dried sample were placed on a balance located in the furnace and heat was applied over the temperature range from room temperature to 600 °C at a heating rate of 5 °C/min in air, in order to ensure no significant further changes above this top limit. Mass losses versus temperature thermograms were obtained showing the different decomposition processes.

The specific surface area and pore size of olive kernels powder were measured using BET method with a Quantachrome Autosorb Automated Gas Sorption Instrument (Vers. 1.27, Boynton Beach, Canada). The analysis was carried out through an adsorption of N_2 gas (gas effluent temperature = 75 °C versus bath temperature = 77.35 °C).

Scanning electron microscopy (SEM) was used to obtain SEM images of olive kernels. SEM images were obtained with a Jeol JSM-7000F BRUKER instrument operating at 15 kV accelerating voltage, after conventional vacuum coating of olive kernel particles with a carbon film.

2.3. Preparation of resin formulation

A phenol-formaldehyde (PF) resol (solid content 46%, viscosity ~450 cP) was prepared using a 2.2:1 formaldehyde:phenol ratio and 7.3% (w/w) of sodium hydroxide. Resols were prepared in a 2-L glass reactor with mechanical stirring and temperature control. The appropriate amount of the reagent was added to the reactor according to the established formulation. When the operating temperature was reached (90 °C), the extension of reaction was monitored, measuring resol viscosity at 25 °C. The olive kernels/PF adhesives were prepared by copolymerization of olive kernels (variable amounts with PF resin) at room temperature. Three different weight ratios of the olive kernel to the PF resin were chosen for the formulations, i.e. 7/93, 15/85, and 20/80 (w/w).

2.4. Plywood manufacture and testing

Five ply laboratory plywood panels of dimensions 250 mm × 250 mm × 10 mm were prepared from 2 mm thick Maritime pine (*Pinus pinaster*) veneers of 4% moisture content at a glue mix spread of 225 g/m^2 single glue line. Before pressing adhesive coated veneers were allowed to stand at room temperature for 15 min prior to panel assembly. Plywood bonded with olive kernel/PF resin based adhesives were assembled and hot pressed under 12 bar at 160 °C for 6 min. The fixed bonding conditions (pressing temperature of 160 °C and 12 bar) were selected to reproduce the industrial conditions used to bond plywood panels. A longer pressing time (6 min) than would normally be used in industrial practice was used to assure full reaction. Mechanical properties commonly taken into consideration in the general usage areas of plywood panels were investigated. Dry tensile strength and modulus of elasticity values of plywood panels were determined according to EN 314 (1993) [12] and EN 310 (1993) [13], respectively. The maximum dry shear strength and modulus of elasticity values were recorded. Forty specimens were used for each test method.

2.5. Formaldehyde emission by desiccator's method

The formaldehyde emissions from the plywood were determined according to the European Norm (ISO/CD 12460-4) [14] using a glass desiccator. The 24-h desiccator method uses a common glass desiccator with a volume of 10 L. Eight test pieces, with