Industrial Crops and Products 62 (2014) 491–498

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Composite materials from unsaturated polyester resin and olive nuts residue: The effect of silane treatment

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ARTICLE INFO

Article history:
Received 13 July 2014
Received in revised form 22 August 2014
Accepted 5 September 2014

Keywords:
Olives nuts
Composites
Unsaturated polyester
Mechanical properties

ABSTRACT

Olive nuts flour (ONF) from the solid waste of the olive oil extraction was used as a cost–effective filler to reinforce unsaturated polyester resin matrix composites. Composites with filler loading from 10 to 60 wt% were prepared by compression molding using untreated and γ-mercaptopropyltrimethoxysilane (MRPS)-modified ONF. The evolution of mechanical performance, dynamic mechanical properties, impact properties and water absorbance, were investigated as a function of the filler content. The changes in the mechanical properties as well as the water absorption behavior were shown to be greatly affected by the silane treatment of the filler. A better enhancement in the stiffening effect and a reduction in water absorption were noted when silane treated ONF was used. Evidence of the improvement of the interfacial adhesion following the silane modification was supported by dynamic mechanical analysis (DMA) and SEM observation. These results were explained in terms of the improvement in the interfacial adhesion between the filler and the matrix through the aptitude of the MRPS to provide a chemical connectivity between the two phases.

1. Introduction

Olives are among the most extensively cultivated fruit crops in the world. The total world production of olives and virgin olive oil was reported to be 20.8 and 3.27 million tons, respectively, for the year 2010 (FAOSTAT, 2012). Olive cultivation is particularly widespread throughout the Mediterranean region and plays an important role in its economy, local heritage and environment protection. The largest olive-producing countries are located in the Mediterranean and Middle Eastern regions providing 98% of the total cultivated surface area, and 99% of the total olive fruit production (Niaounakis and Halvadakis, 2006).

Tunisia is ranked among the leading olive-oil producers, with over 65 million olive trees grown on 1.7 million hectares and an average annual production amounting to 200 thousand tons. However, a major problem which significantly affects the environmental sustainability of this agricultural activity is the disposal of residues generated from the industrial extraction of olive oil. Indeed, the extraction process generates an ‘aqueous sludge’ and a solid residue called ‘olive cake’, which is obtained after extracting the oil from the fruit. Generally, from 100 kg of olives, about 20% of oil is recovered, 30% of olive cake and about 50% of aqueous liquor were generated. Due to their high phenolic content, the latter two fractions are not easily degradable by natural processes, and their disposal creates a major environmental issue in the main olive-producing countries. Among the negative effects resulting from the spread of olive solid waste in the field, we can cite (i) the inhibition of microorganisms' activities, (ii) reduction in the seed germination (Cardelli and Benitez, 1998), (iii) alteration of the soil characteristics in terms of the porosity and the humus concentration. Accordingly, research into finding new possible uses for olives by-products, particularly the solid ones, is of a great relevance not only to the economy, but also to the environment.

Given the growing environmental awareness, sustainable development and eco-friendly materials have become of great interest to preserve the environmental resources, while improving economic activities (López et al., 2012). The utilization of biomass for the development of novel composites has attracted the attention of material scientists thanks to its eco-friendly and renewable character, low density, good thermal insulation, reduced tool wear and low price (Bajwa et al., 2011). Although wood flour remains the main lignocellulosic filler (La Mantia and Morreale, 2011), among the natural reinforcements, the use of agricultural by-products as a source of renewable filler in the production of bio-based composites might constitute an alternative for woody filler for countries lacking wood resources (Jawaid et al., 2011). The olive nuts flour, obtained after grinding the solid waste, contains a great amount of cellulose, hemicelluloses, and lignin, which gives them

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http://dx.doi.org/10.1016/j.indcrop.2014.09.012
0926-6690/

unique properties similar to those of wood or natural fibers. They also offer many potential advantages such as sustainability, low price, biodegradability and renewability. Therefore, it might be expected that the incorporation of ONF into polymer matrices may contribute to produce cost–effective and eco-friendly composites with enhanced mechanical properties. Meanwhile, it will provide an opportunity to transform agricultural by-products into useful industrial resources, with benefits on both environment and economy.

So far, the utilization of solid byproducts generated by the olive oil extraction has been limited as an energetic source after burning. The use of the solid residue from the olive oil extraction as fillers in polymer-based composite materials has not been so much investigated (Naghmouchi et al., 2014; Ihemouchen et al., 2013; Amar et al., 2011; Djidjelli et al., 2007), especially in a thermoset based matrix (Papanicolaou et al., 2012). Accordingly, further work is needed to better assess the effect of the incorporation of solid wastes from olive oil extraction on the mechanical properties of the ensuing composites and how their presence affects the water sensitivity of the composite.

Unsaturated polyester (UP) resins are one of the most commonly used thermosetting polymers, which are generally made up of a condensation reaction between a glycol and an unsaturated dibasic acid. Thanks to their easy processability, excellent mechanical properties, and low price, UP resins have been extensively used in a variety of applications, ranging from automobile and water tanks to packaging and building materials. To the best of our knowledge, the use of ONF as filler for unsaturated polyester matrix has not yet been explored in literature. In this context, the present study aims to investigate the effect of the incorporation of the ONF up to 60% loading in UP on the flexural properties, impact strength, thermomechanical properties and water absorption behavior. The ONF was prepared from the exhausted solid olive oil mills after mechanical grinding treatment.

2. Materials and methods

2.1. Materials

The unsaturated polyester (Synolite 1408-P-2) is an orthophatlic unsaturated polyester liquid resin from DSM with a solid content of 57% in styrene. The silane γ-mercaptopropyltrimethoxysilane (MRPS) is a commercial product from Aldrich.

2.2. Methods

2.2.1. Olive nuts flour preparation

Olive nuts flour (ONF) used as filler for unsaturated polyester composites was kindly provided from Ecolivarum. It was an industrial product produced by grinding the solid waste of olive oil industry. In brief, after the separation of the olive oil, the residue was composed of skin (epicard), pulp (mesocarp) and stone (endocarp). Water was discarded and the solid residue was extracted with hexane to recover the remaining oil. The residue was then dried, and separated into shell and stone by screening ventilation. The hard material, separated from the soft skin was grounded into fine flour using industrial grinding mill machine. The nuts called the woody endocarp represent about 18–25% of the olive weight and it is mainly composed of lignin, hemicellulose and cellulose.

2.2.2. Surface modification of olive nuts with MRPS

The procedure adopted for the filler treatments with MRPS is as follows: the ONF was added in an ethanol/water (50/50, v/v) solution to form a suspension with a solid content of 20%, then the MRPS (3% based on the ONF content) was added and the pH was adjusted to 4.5–5 by the addition of acetic acid to catalyze the hydrolysis of the trialoxysilane. Afterwards, the suspension was kept under mechanical stirring for 3 h to ensure the adsorption of the silane onto the ONF particles. Then, the modified filler was recovered by filtration and dried at 70 °C for 12 h.

2.3. Filler characterization

The biomass used in this study consisted of olive nuts crushed and sieved to obtain finer particles from 50 to 200 μm size.

2.3.1. Chemical composition

The determination of the basic chemical composition was conducted following TAPPI standard protocols (TAPPI T257 cm-02, 2002). Samples were first submitted to Soxhlet extraction with ethanol/toluene and water. Then the chemical contents were determined using the following methods, ash (Tappi T 211 om-93, 2000), extractive (Tappi T264 om-07, 2007), Klason lignin (Tappi T222 om-83, 1999), and hemicelluloses (Tappi T249-cm-85, 1999).

The length and aspect ratio of ONF filler was determined by Morfi analysis using a TECHPAP LB 01 Morfi equipment (fiber content of 0.300 g/L).

2.4. Infrared spectroscopy

The FTIR analysis was performed using a Perkin–Elmer Paragon 2000 FTIR spectrometer. DRIFT spectra of the sample before and after treatment were obtained using the diffuse reflectance accessory. Each spectrum was recorded with a resolution of 4 cm^{-1}, with a total of 40 scans. Background scans were obtained using the KBr powder. The spectra were plotted according to the Kubelka-Munk function.

2.5. Preparation of the composite

Composite specimens with different filler loadings ranging from 0 to 60% were fabricated using the hand lay-up technique. First, the ONF and UP resin were mixed in different weight ratios until complete wetting of the ONF, then 2% methyl ethyl ketone peroxide was added as a free-radical initiator. Immediately, the mixture was poured into a metal mold coated with a thin layer of wax as a release agent and cured at a temperature of 110 °C and a pressure of 5 MPa for 20 min. These conditions were shown to ensure rapid and full hardening of the composite.

2.6. Mechanical characterization

The processed materials were assayed after 48 h conditioning at room temperature and 50% relative humidity. Three-point bending tests and Charpy impact strength were measured according to ASTM D790 and ASTM D6110, respectively, using a Pegasil (ZIPOR) testing machine with a cell load of 2KN and a Zess apparatus provided with a hammer of 2.074 kg in weight and 382 mm in arm length. The final results were given as the average of at least five samples.

2.7. Dynamic mechanical thermoanalysis

The dynamic mechanical analysis was conducted in a flexural mode using a Diamond (Perkin–Elmer). The temperature scans were run from 20 to 120 °C at a heating rate of 2 °C/min, frequency of 1 Hz, and amplitude deformation of 10 μm. The storage (E') and the loss (E'') modulus of the sample as well as the loss factor tan $\delta = (E''/E')$ were measured as a function of temperature. The sample dimensions were about 20 mm in length, 5 mm in width, and 2 mm