Polymer Testing 59 (2017) 430–440

Contents lists available at ScienceDirect

Polymer Testing

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

Material Properties

Valorization of olive husk flour as a filler for biocomposites based on poly(3-hydroxybutyrate-co-3-hydroxyvalerate): Effects of silane treatment

Leila Hassaini [a], Mustapha Kaci [a], Naima Touati [a], Isabelle Pillin [b], Antoine Kervoelen [b], Stéphane Bruzaud [b], *

[a] *Laboratoire des Matériaux Polymères Avancés (LMPA), Université de Bejaia, 06000, Algeria*
[b] *Institut de Recherche Dupuy de Lôme (IRDL), FRE CNRS 3744, Université de Bretagne-Sud, Rue Saint Maudé, 56321 Lorient Cedex, France*

ARTICLE INFO

Article history:
Received 29 January 2017
Accepted 4 March 2017
Available online 8 March 2017

Keywords:
PHBV
Olive husk flour
Biocomposites
Silane treatment
Compatibility

ABSTRACT

The paper deals with the influence of surface treatment of olive husk flour (OHF) by trimethoxyoctadecylsilane (TMOS) on the morphology and physical properties of bio-composites based on poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). Biocomposites based on PHBV/OHF: 80/20 (w/w) before and after filler treatment were prepared by melt compounding, while the modification of OHF surface by TMOS was performed by thermo-chemical vapor deposition. Scanning electron microscopic observations showed that modification of OHF by TMOS led to homogeneous and finer dispersion of the filler particles in PHBV matrix, indicating improved compatibility between the two components. Further, TGA data revealed an increase in thermal stability of treated PHBV/OHF biocomposites. An increase in the crystalline index determined by DSC was also observed due to the nucleating effect of OHF in the polymer matrix, however more pronounced for the treated biocomposites. The latter exhibited better tensile properties, as confirmed by DMA results, showing higher reinforcing effect of OHF for the treated biocomposites. This study highlighted significant improvements of the properties of PHBV/OHF biocomposites through silane treatment of OHF.

1. Introduction

Interface bonding between wood filler and polymeric matrix is the key to stress transfer from the matrix to the filler throughout the interface [1,2]. There are three essential strategies available to improve the properties of wood-plastic composites; polymer [3] or filler modification [4–6], or the addition of a third component, i.e. a coupling agent such as maleic anhydride grafted polymers [5–7]. In the current paper, olive husk flour (OHF) was chemically modified by organosilane and its effect on the morphology and functional properties of PHBV/OHF biocomposites was studied. A decrease in the hydrophilic OHF character through the reduction of hydroxyl groups would be expected, thus improving affinity between matrix and filler. Many publications have been reported [8–15] on the effects of chemical modification of wood fillers on the properties of biocomposites. Among these techniques, the most successful and cost effective include filler treatment by organosilane [8,16]. Javadi et al. [8] investigated the effects of alkali- and silane-treatments of coir fiber to improve its adhesion with PHBV. They indicated that silane treatment was the most effective one by improving specific toughness and strain at break of PHBV/coir fiber composites. Srubar et al. [9] pointed out that silane treatment of oak wood flour leads to improved mechanical properties of PHBV-based composites.

The objective of this work was to investigate the influence of chemical modification of OHF by trimethoxyoctadecylsilane (TMOS) on the morphology and physical properties of PHBV/OHF: 80/20 (w/w) biocomposites prepared by melt compounding. Several techniques were used to characterize the morphology as well as the thermal, mechanical, viscoelastic and gas barrier properties of the samples before and after silane treatment.

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* Corresponding author.
E-mail address: stephane.bruzaud@univ-ubs.fr (S. Bruzaud).

http://dx.doi.org/10.1016/j.polymertesting.2017.03.004
0142-9418/

2. Experimental part

2.1. Materials used

PHBV was manufactured by Tianan Biological Materials Co. Ltd. (China) under the trade name ENMAT Y 1000P with the following physical characteristics: density = 1.25 g cm^{-3}, T_g = 8 °C and T_m = 165 °C.

TMOS was provided by Sigma-Aldrich (France).

Olive husk was collected from the olive treatment plant in the Bejaia (Algeria) region. The olive husk was first washed with hot water to remove the pulp and fat, followed by air-drying for two weeks, and ground into very fine particles. The size fraction selected after sifting has a maximum average diameter of 50 μm. The major constituents of OHF were determined from dry substances using chemical procedures [17], i.e. cellulose = 39 ± 0.5 % wt, lignin = 20.52 ± 0.4 %wt, organic content = 8.5 ± 0.8 %wt and mineral filler = 3 ± 0.2 %wt. The moisture content of the filler was 7 ± 0.3 wt %.

2.2. Methods

2.2.1. Surface modification of olive husk flour by TMOS

Before OHF treatment by TMOS, the filler was subjected to Soxhlet extraction in a solvent mixture of toluene/ethanol: 3/2 for 24 h according to the procedure reported in Ref. [18] in order to eliminate the presence of any waxes, contaminants or impurities on the filler surface. OHF was air dried for 24 h at 105 °C. A thermo-chemical vapor deposition technique was employed for the OHF treatment to ensure that silane was sufficiently chemisorbed onto the OHF particles. Prior to processing, 100 g of OHF were weighed and introduced into a small crystallizer and then placed in a desiccator. Above the OHF, 2 mL of TMOS were measured and placed in a small aluminum tray. The desiccator was sealed and then completely covered with aluminum foil and placed in a *Thermo Scientific Heraeus Vacutherm* vacuum-assisted oven operated at 120 °C under atmospheric pressure for 48 h. After 48 h of the thermo-chemical treatment, 1 g of OHF was extracted from the bottom of the desiccator and tested with a drop of distilled water by means of a pipette in order to check the hydrophobic character of the treated flour. If the flour absorbed any amount of water droplets, the treated-OHF was placed back into the desiccator and the desiccator was sealed and placed in the oven and tested for hydrophobicity periodically in 3 h increments. The silane solubility in ethanol was verified; thus, random TMOS treated-OHF samples were subsequently refluxed with ethanol in a Soxhlet and retested for hydrophobic behavior to ensure that silane was covalently bound to the filler surface. This method was adapted from Srubar et al. [9].

OHF particles before and after silane treatment are shown in Fig. 1. It is clearly observed that the silane treatment mainly results in the darkening of wood tissues. Maillard-Amodori mechanisms suggest that the presence of lignin and tannins can result in the formation of colored compounds after chemical reaction due to heating [19].

2.3. Preparation of PHBV/OHF biocomposite samples

OHF was first dried in an oven under vacuum at 105 °C for 24 h in order to reduce the humidity content to less than 3 wt%. PHBV was dried under vacuum at 60 °C for 24 h to remove moisture and, therefore, to minimize the hydrolytic degradation during processing. Two blend compositions based on PHBV and 20 wt. % of OHF before and after silane treatment were prepared by melt compounding using a Brabender Plasticorder mixer (model W 50 EHT). Table 1 summarizes the compositions prepared. All components of the biocomposites were first mixed by tumbling in a plastic bag for 5 min and then fed into the Brabender mixer. The mixing temperature, screw speed and residence time were maintained at 180 °C, 40 rpm and 10 min, respectively. The extruded materials were ground into pellets which were dried at 60 °C under vacuum overnight, and then compression molded in a Carver hydraulic press at 180 °C under a pressure of 10 metric tons for 2 min.

. Samples for tensile tests were cut in the form of 4 mm dumbbell of width and 45 mm of length. Rectangular bars were cut for Charpy impact tests (80 × 10 × 4 mm), and Dynamic Mechanical Analysis (DMA) (30 × 4 × 2 mm). In addition, the determination of oxygen and water vapor transmission rates was performed on film samples with average thickness of 100 μm.

2.4. Techniques

2.4.1. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of untreated and TMOS-treated OHF were recorded using a Shimadzu 8400 M FT-IR spectrometer at 4 cm^{-1} resolution and 40 scans. All spectra were recorded in the absorbance mode in the 4000-400 cm^{-1} region. The samples were analyzed using the KBr pellet method.

2.4.2. Scanning electron microscopy (SEM)

The fractured surfaces were analyzed using a Jeol JSM-6031 scanning electron microscope. The neck region for the broken specimens fractured in liquid nitrogen was parallel to the draw direction in order to reveal the internal morphology. Initially, the fractured surface of the composite samples was sputter-coated with a thin gold layer (Edwards Sputter Coater). For the characterization of the fillers before and after silane treatment, Energy dispersive X-ray (EDX) point shooting was performed on the same SEM machine.

2.4.3. Contact angle measurements

Contact angle measurements were performed using a Digidrop (GBX) contact angle instrument [7]. Measurements were taken at 20 °C and 48% RH. The volume of the sessile drop was maintained as 1 μl in all cases using a micro-syringe. For precision, contact angle was measured for at least five specimens of each composite, and the measurements were repeated 5–10 times on different pieces of the same sample. With the help of several different liquids, (water, formamide and tricresylphosphate (TCP)) for measurement of contact angle, the dispersive and polar components of

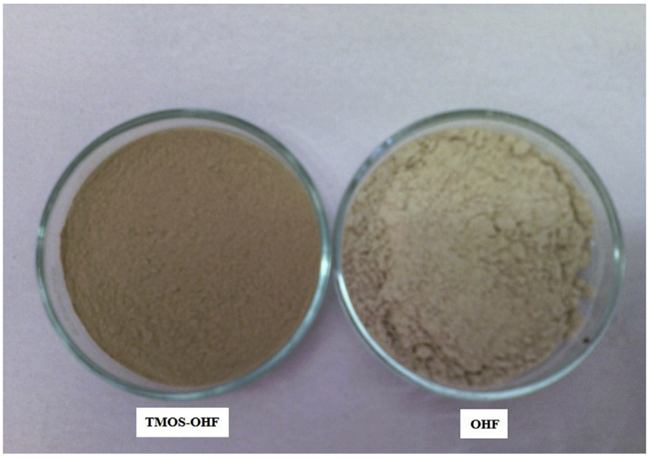

Fig. 1. OHF before and after TMOS treatment.