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Eco-Compatible Use of Olive Husk as Filler in Thermoplastic Composites

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A study on the possibility of recycling waste materials, such as olive husk, the solid phase derived from an olive oil mill, in blend with thermoplastic polymers to produce new materials for manufacturer of, for example, containers and formworks, has been carried out. The present paper describes the methodology used for the preparation and the characterization of composite samples prepared by mixing various percentages of olive husk and polypropylene. A screening on the chemical-physical characteristics of the olive husk is reported, as well as a set of tests applied to evaluate the mechanical properties of the manufactured products obtained.

KEY WORDS: Olive husk; eco-compatibility; thermoplastic matrix.

INTRODUCTION

Council Directive 91/156/EEC on waste has established that in order to achieve a high level of environmental protection, the Member States must, in addition to taking action to ensure the responsible removal and recovery of waste, take measures to restrict the production of waste, particularly by promoting clean technologies and products that can be recycled and reused, taking into consideration existing or potential market opportunities for recovered wastes.

According to Council Directive 91/689/EEC, which defines as "hazardous" a series of wastes featuring on a list drawn up in accordance with the procedure laid down in article 18 of Directive 75/442/EEC, the solid wastes produced by edible oils processing are classified as non-hazardous wastes and therefore are suitable for recycling operations such as blending with other materials. Furthermore, the Italian legislation D.L. 05-02-1997 n.22 establishes that the practice of reusing, recycling, and recovering of raw materials from solid wastes is preferred to other kinds of waste disposal (landfilling, incineration, etc.).

Natural fibers, used to fill and reinforce both thermoplastics and thermosets, represent one of the fastest-growing types of polymer additives. Wood is the main natural fiber used, followed by other fibers such as kenaf, jute, hemp, flax, and sisal [1].

Although polyethylene, polyvinyl chloride (PVC) and polypropylene are the dominant polymers utilizing natural fibers, their use is also common in phenolics, polyester, polystyrene, and several other polymer systems. In addition, uses are not limited to building products and automotive parts. Significant markets are also emerging in such diverse applications as railroad ties, flower pots, furniture, and marine piers [2].

Our project intends to optimize the technology for the production of new plastic composite manufactures containing olive husk (the solid portion remaining after pressing olives) as filler and recycled plastics. A cost benefit analysis revealed the following benefits:

(1) saving environmental resources by using recyclable materials;

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Table I. Granulometric Analysis

ASTM sieve	Wet olive husk minus sieve %	Dry olive husk minus sieve %
200 (0,074 m*M*)	1,1	1,0
80 (0,177 m*M*)	4,7	4,9
40 (0,42 m*M*)	11,1	11,8
20 (0,84 m*M*)	21,5	19,1
10 (2,00 m*M*)	50,2	44,4
4 (4,76 m*M*)	99,1	98,2
3/8 (9,52 m*M*)	100	99,5
3/4 (19,1 m*M*)	—	100

Table II. Olive Husk Chemical-Physical Analysis Results Minus Sieve (<1,2 m*M*)

Parameter	Unit	Value
Humidity	%	13,62
Residual at 550°C	%	8,47
Residual at 1,000°C	%	8,07
Insoluble residual	%	3,39
Density	g/mL	0,605
Oils and fats	%	0,54
Calcium oxide	% CaO	0,31
Magnesium oxide	% MgO	0,15
Potassium oxide	% K_2O	0,86
Sodium oxide	% Na_2O	0,03
Iron oxide	% Fe_2O_3	0,17
Aluminium oxide	% Al_2O_3	0,22
Carbonic anhydride	% CO_2	<0,01
Sulphuric anhydride	% SO_3	<0,01
Oversize Powder (<3,5 m*M*)		
Parameter	Unit	Value
Humidity	%	14,10
Residual at 550°C	%	2,41
Residual at 1,000°C	%	2,16
Density	%	0,696
Sugar content	%	0,2

(2) preventing deterioration of the countryside and occupation of utilizable land;
(3) reducing the manufacturing cost because the olive husk is very cheap.

Today wood is the main material used in the construction of containers and frameworks. Several studies are reported in literature about the interaction among wood fibers dispersed in the polypropylene matrix [3–5]. This study reports on the attempt to replace wood with another lignocellulosic fiber, olive husk, to obtain a new, highly resistant composite material suitable for extrusion. Mechanical properties, flexural strength, and modulus of the extruded manufactures are reported.

EXPERIMENTAL

Materials

Samples were prepared by mixing different percentages of the following materials: polypropylene (Moplen 2005 HEXP); olive husk derived from an olive oil processing plant; chopped glass strands PPG 3299 (13 micron diameter, 4.5 m*M* length); GF-polypropylene (Hostacom) reinforced with 30% chopped glass strands; and recycled plastics (mainly wasted tires).

Olive Husk Chemical Composition

Several tests were carried out to evaluate the olive husk composition and eco-compatibility:

(1) *Olive husk granulometry* was evaluated. Table I reports the data obtained on both wet and dry (in an oven at 120°C for 3 h) olive husk. The analysis was carried through a sifting-machine using ASTM standard sieves (Table 1). The oversize fraction is very rich in lignin and represents a good filler for plastics; on the other hand the undersize fraction, because of its dimension, is more suitable for homogeneous dispersion in the thermoplastic matrix. Several unsuccessful attempts were made, in our research, to introduce the oversize fraction into the polypropylene composite, but the dispersion of the powder was very low and not uniform; only the undersize fraction, which is instead easily dispersed into the melted polypropylene, was considered.
(2) *Chemical-physical analyses* were performed by traditional analytical methods. The obtained data are reported in Table II;

Olive Husk Characterization

As the preparation of the composite manufactures underwent a thermal process, in order to understand the olive husk dehydration and degradation profile, we performed thermal gravimetric analysis using a TA 3000 Mettler System. Furthermore, extraction methods were applied to determine both the lignin (a substance that together with cellulose forms the woody cell wall of plants) and organic content, to verify whether their presence can influence olive husk behavior when processed with polypropylene. The organic phase was determined through solvent extraction using a Soxhelet extractor

Table III. Sample Composition

Mixture	Husk (%)	PP (%)	Recycled Plastics (%)	Glass Strand (%)
Sample 1	50	50	—	—
Sample 2	40	40	20	—
Sample 3	30	40	30	—
Sample 4	40	20	30	10

under diethyl ether for 14 h. The percentage of extracted phase was determined by weighing the sample before and after the extraction (weight 13, 5%). The same procedure was applied to another olive husk sample after dehydration in oven at 180°C (extracted amount 8, 42%). The lignin content was determined according with the "Hagglund" method through dissolution in sulphuric acid.

Sample Preparation

To find the best conditions for the preparation of the mixtures a set of parameters was considered:

(1) the olive husk humidity content;
(2) the olive husk thermal behavior;
(3) the olive husk granulometry;
(4) the ratio olive husk/PP;
(5) the ratio of olive husk/PP/glass strands;
(6) the ratio of olive husk/PP/glass strands/recycled plastics; and
(7) the moisture permeability of the final product.

Because the olive husk obtained from the olive treatment plant contains a reasonable amount of water (over 14% humidity), and this causes the creation of voids in the mixture, the olive husk was subjected to a thermal pretreatment process before using.

The undersize fraction obtained after sifting the olive husk was first dehydrated at 120°C and then stored into a mass-flow bin. The dry material was carried through a pipe system into the head of the extruder, where it was mixed with polypropylene that had been previously softened at 190°C. The temperature in the head of the extruder is kept in the range of 180–190°C. The composition of the mixture varied depending on the mechanical results obtained and is reported in Table III. Each mixture was processed into the extruder; the final product was a panel with the following dimensions: 28 m*M* × 1820 m*M* × 780 m*M*.

The moisture permeability, which is the measure of the rate of steady passage of moisture through panels whose faces are at different relative humidity, was evaluated. To improve the final water resistance of the composite panel, the melted mixture was sandwiched, during the extrusion process, between two sheets of Teflon fabric.

Table IV. Mechanical Test Results

Sample	σ_f^a(MPa)^c ISO	E_f^b(MPa)^c ISO
1	25.12	1,980
2	27.42	2,280
3	32.27	3,000
4	34.21	3,500

[a]Flexural stress $\sigma_f = 3FL/2bh^2$
(F = applied force in Newton; L = span, in millimetres; b = width, in millimeters, of the specimen; h = thickness, in millimeters, of the specimen).
[b]Flexural modulus E_f.
[c]Mean value referred to five specimens.

Mechanical Test

Flexural strength testing of plastics was performed using the ASTM D790 and ISO 178 systems. The flexural strength of a material is its ability to resist deformation under a load. For materials that do not break, the load at yield, typically measured at 5% deformation/strain of the outer surface, is reported as the flexural strength. Test results with the ASTM D790 and ISO systems do not vary significantly.

Test Conditions

	ASTM	ISO
Preferred specimen	Length: 127 m*M* Width: 12.7 m*M* Thickness: 3.2 m*M*	Length: 80 m*M* Width: 10 m*M* Thickness: 4 m*M*
Support span	Span to depth ratio of 16	Span/depth = 16
Support radius	5 ± 0.1 m*M* or 3.2 m*M* minimum, up to 1.5 times the depth for 3.2-m*M* specimen thickness	5 ± 0.1 m*M*
Loading nose	5 ± 0.1 m*M* or 3.2 m*M* minimum up to 4 times the depth	5 ± 0.1 m*M*
Radius	Up to 4 times the depth	
Test speed	1.3 m*M*/min ± 50% for the preferred specimen	2 m*M*/min ± 20%
Maximum strain	5%	3.5%

Five strips per sample were cut and tested. The specimen should be long enough to allow the overhanging on each end of at least 10% of the support span. The specimen is deflected until rupture occurs in the outer surface or until the maximum strain of 5% is reached, whichever occurs first. Flexural stress σ_f (MPa) and flexural modulus E_f (MPa) data are reported in Table IV.

RESULTS AND DISCUSSION

Processing Conditions

Olive Husk Thermal Analysis Results

The thermal behavior of the olive husk is the fundamental parameter that affects the whole process. It is extremely important to follow a profile of temperature for the extruder in all its parts and sections. The reason is the instability of the olive husk on heating, as shown in the thermal analyses graphs. Figure 1 shows the thermal behavior (TG and DTG analysis) of the olive husk (without dehydration pretreatment). The weight loss in the area of 100°C is due to humidity; this datum is confirmed by Fig. 2, in which it is shown that weight loss in the range of 100°C does not occur because the olive husk had previously been dehydrated. Between 120 and 200°C the olive husk is stable; this range represents the optimal temperature for the process. From 220–380°C a peak resulting from the loss of lignin is visible, while the peak in the range of 380–500°C corresponds to the loss of oils and resins. This interpretation is confirmed by the TG graph (Fig. 3) of the olive husk after extraction with diethyl ether, which removes the oil fraction. The thermograph shows a peak only at 220–380°C because of the lignin degradation. The consequence of the thermal behavior of the olive husk is that when the temperature of the extruder exceeds 200°C there is a reasonable production of volatile compounds, which are entrapped into the bulk of the mixture. The final product contains voids that drastically affect the mechanical properties of the material. To avoid this phenomenon, it was necessary to optimize the working conditions of the extruder:

- using only dehydrated olive husk (the humidity contributes to the formation of voids); and
- using a controlled range of temperature (180–200°C) during the whole producing process.

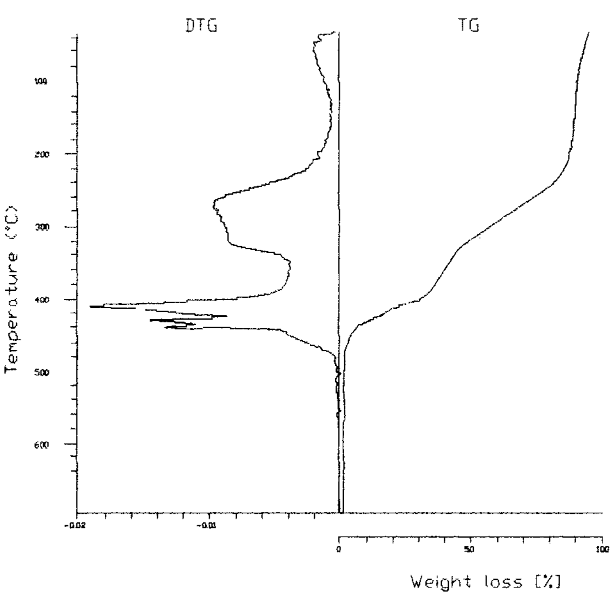

Fig. 1. TG/dTG diagram of nontreated olive husk.

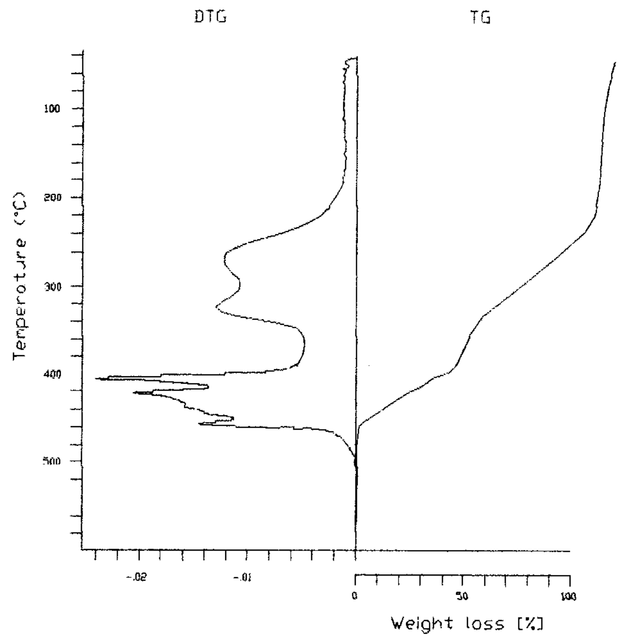

Fig. 2. TG/dTG diagram of dehydrated olive husk.

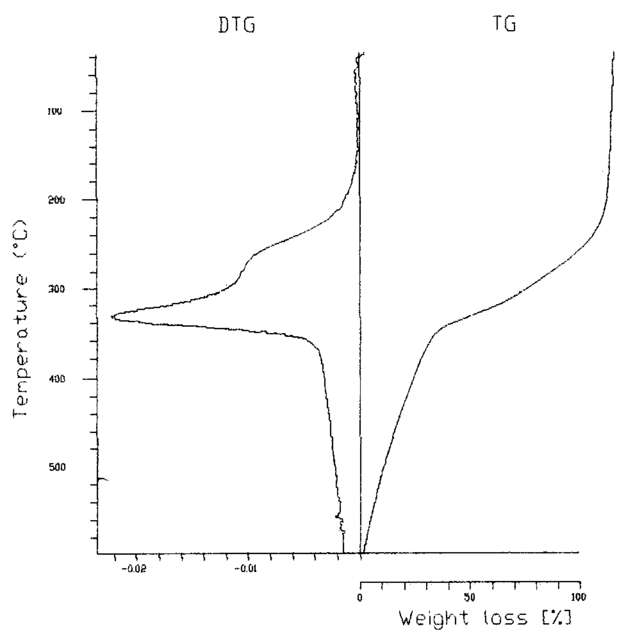

Fig. 3. TG/dTG diagram of olive husk after extraction in diethyl ether and dehydration.

Mechanical Test Results

Mechanical test results, reported in Table 4, give clear evidence of the effectiveness of the mixture under investigation. Sample 2, containing olive husk/virgin PP/recycled plastic, shows a higher elastic modulus (E_f = 2,280) compared to virgin polypropylene (E_f = 1,750). The presence of 10% glass strands in the mixture drastically improves the mechanical properties (E_f = 3,200).

The optimized mixture was also tested for the production of frameworks and containers. All of the tests were positively passed. For these applications (frameworks and containers), the material commonly used is polywood (PP/wood powder; E_f = 2,500–3,000), but in the near future this material must be replaced both for ecological and technical reasons. Polywood frameworks and containers have a very short life (they cannot be reused and are wasted after one use); the consequence is a great demand for wood to produce new manufactures. Wood resources, which have largely fueled the industrialization of many countries are facing significant problems: governments continue to restrict access to the timber lands; the quality of timber available is lower than it used to be; the price of timber is rising [6]. But the market continues to demand low-maintenance, durable building materials. In this contest the material under our investigation becomes very interesting: olive husk/PP frameworks and containers are very resistant to humidity and stress conditions. For this reason they can be used several times before becoming waste. Furthermore, as waste they easily can be recycled by grinding and added as filler in the preparation of new mixtures. These two conditions contribute to increase interest in the study of the chemistry (mechanism involved in the reactions, use of different fibers and matrix, etc.) and the technology of the process.

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