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Olive Pomace Flour as Potential Organic Filler in Composite Materials: A Brief Review

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Abstract The use of natural renewable fibers such as olive stone flour as novel organic fillers in polymer matrices is investigated. Properties of olive stone flour such as abundance, biodegradability, easy processing, low density and low cost make it apt to act as a promising novel organic filler. Environmental issues and the need for versatile polymer-based materials have led to increase interest in polymer composites filled with biodegradable natural-organic fillers. Interfacial filler-polymer adhesion and processing temperatures are the main obstacles facing composite productions. The use of coupling agents, thermal stabilizers, plasticizing agents and/or chemical modifications of the filler can overcome such limitations. This review covers novel works related to the most significant polymer types which are used as matrices for olive stone flour as a filler to prepare a bio-composite material.

Keywords Olive stone flour, Filler, Polymer composite

1. Introduction

Olive stone is an important by-product generated in the olive oil extraction industry [1-3]. The main components of olive stone are hemi-cellulose, cellulose and lignin as well as protein, fat, phenols, free sugars and polyols composition [4-6]. The main use of olive oil by-product waste is in producing heat and/or electric energy [7-10]. Other uses such as activated carbon, [11-12] furfural production [13], polymer filler [14-15], abrasive [16] and cosmetic materials [17-19]. Moreover, an emerging potential uses such as biosorbent [20-21], animal feed [22-23] or resin formation have been proposed by few studies [24].

In this article, a brief review of olive stone flour (OSF) used as filler material in polymeric materials is described for the first time. In addition, this review discusses the potential use of this filler material based on several candidate polymer matrices. A new approach to olive stone as a reinforcement material with particle size ranging from 10 to 100 μ is described.

In the last decade only limited number of articles discussing issues related to the characterization (Table 1) and potential use of olive stone as a filler material in polymer matrices. Research works are still in need to cover and investigate further potential applications of olive stone as a promising filler in various polymer matrices. The following sections summarize the main polymeric materials used as matrices for the OSF as filler.

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Table 1. Polymer matrices filled with OPF composites and their measured properties

Polymer	Measured properties	Ref
PLLA	Mechanical.	26
	DSC, TGA, SEM.	27
	Tg, Tm, Tcc.	28
	Plasticizer, crystallization.	29
PP	Phase compatibility, filler high %content.	30
	Tensile, impact, wear resistance, water absorption.	31
	Elastic modulus.	32
	Thermal, phase compatibility.	33
	Young's and flexural modulus.	34
PVC	Mechanical strength.	35
Polyester	Interfacial adhesion, biodegradation.	36
	Extrusion and thermal behavior.	37-38
Unsaturated polyester	Interfacial adhesion, mechanical.	39
Epoxy resin	Thermal, bending strength and modulus.	40,41
Chitosan	Tensile strength.	42,43
Wheat gluten	Young's modulus, tensile strength, water uptake.	44,45
HDPE	Mechanical, morphological, water absorption.	46,47

2. Olive Stone Flour (OSF)

Olive stone particle size distribution

The suitability of wastes from olive oil production industry for subsequent use in polymer composites was studied. In particular, residues of olive wet husk and olive pits were investigated. A wide particle size distribution was predicted in case of olive wet husk compared to olive pits which showed a narrower particle size distribution and better stability against thermal degradation. Moreover, pit and husk olive parts favor the compatibility with polar polymer matrices [25].

3. Polymer Matrices

Polylactic acid (PLA)

Fully biodegradable composites made out of (polylactic acid, PLA) reinforced with olive pit powders were manufactured and mechanically characterized. It was shown that with filler loading, an increase in the tensile modulus but a decrease of the flexural strength may be due to the poor interfacial bonding between olive pit powder and PLA [26].

Various amounts of olive stone flour (0-25% OSF) were incorporated with poly(L-lactide) polymer (PLLA) to form a biodegradable (PLLA/OSF) composite material by using Brabender mixer and hot press. Thermal properties of (PLLA/OSF) composites were investigated. Differential scanning calorimetry (DSC) analysis showed a decrease in cold crystallization temperature which may account for certain kinds of interactions between the filler and the polymer under certain conditions. On the other hand, the glass transition temperature (T_g) and the melting temperature (T_m) values of PLLA in the composites were unaffected by the filler loading which may be due to poor interaction between filler and PLLA polymer matrix. Degradation of the filler-polymer composite was studied by using thermogravimetric analysis (TGA); PLLA degrades in one-step, PLLA/OSF composites in two and OSF in three decomposition steps. Thermal stability of PLLA decreases as OSF loading increases. Weak interactions between PLLA matrix and OSF were confirmed by the morphological studies carried out by scanning electron microscopy SEM [27]. The effect of the OSF filler content and plasticizer on the thermal properties of PLLA composite were investigated. It was found that the filler material in the absence of plasticizer material in PLLA polymer composite have no effect on the values of T_g, T_m and T_{cc} (cold crystallization temperature) of the polymer composite. On the other hand, PLLA polymer plasticized with tributyl citrate (TBC) and tributyl acetyl citrate (TBAC) (without filler) showed a lower T_m when compared to the plasticized polymer (with filler). Moreover addition of filler (OSF) and plasticizer (TBC & TBAC) individually to the PLLA polymer matrix increases crystallinity of the polymer composite and this increase is greater in case of using plasticizer with filler material [28].

Different processing procedures applied to (PLLA/OSF) polymer composite production resulted in different thermal behavior of the polymer composite, whereas different kinds of plasticizers showed same thermal behavior effect on polymer composite. The results of DSC analysis indicate that thermal properties of the samples were greatly affected by processing procedure, regardless of any differences among the chosen plasticizers. The addition of OSF filler was reported to make only marginal effects on thermal properties of PLLA whereas filler loading greatly influences its crystallization behavior. Addition of a plasticizer to PLLA polymer was found to decrease its thermal transition temperatures while increasing its crystallinity. TGA analysis revealed that filler addition to PLLA polymer reduces thermal stability of the composite while plasticizer addition improves it. The weak interactions between PLLA and OSF phases with and without TBAC plasticizer were reported by studying SEM images of the polymer composite. Mechanical properties such as strength and flexibility were investigated. It has been found that the flexibility and strength of the polymer composite decrease with the increasing filler loading level. On the other hand, plasticizer (TBAC) reduces the strength but improves the flexibility of the PLLA polymer. Crystallization and melting behavior of PLLA affect the thermal properties of the polymer composite which in turn depend on the ageing process during the polymer composite production. Biodegradation of PLLA and its composite in soil environment was studied. PLLA filled with OSF and TBAC degraded more easily compared to version PLLA polymer [29].

Polypropylene (PP)

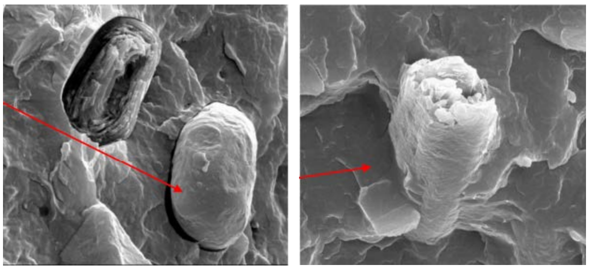

Figure 1. SEM of the tensile fractured surface for OSF filled PP composite in the absence (left), and in presence (right) of MAPP coupling agent (magnification 2000x) [30]

Melt processing and injection molding techniques were used to prepare polypropylene composites with (OSF) filler loading up to 70 wt. %. Phase boundary related drawbacks and incompatibility between polymer and filler (Figure 1) were reduced by using maleated polypropylene (MAPP) as a coupling agent at loading level of 5%, with respect to the filler. Coupling agent inclusion improved the modulus along with preservation in the tensile strength of the OSF filled polypropylene composite up to 60% filler content. An improvement in the composite properties make OSF a good candidate as a cheap reinforcement agent for polypropylene polymer [30].

The mechanical and physical behavior such as tensile and impact strength, wear resistance and water absorption of the polymer composite (OSF/PP) as a function of filler loading were investigated. It was found that the use of coupling agent enhances the mechanical performance of the polymer composite and reduces the adverse effect of water absorption on the whole composite properties. The morphology of the filler material is an important factor that enhances, in the presence of coupling agent, the compatibility with the polymer matrix. As a result filler morphology would affect the composite properties by reducing the effect of water absorption [31].

Olive husk as a filler material in thermoplastic PP polymer matrix was produced and studied. The mechanical behavior in addition to chemical and physical properties was reported. It was shown that the elastic modulus of the composite increased by 30% compared to that of the version PP polymer [32]. The interfacial adhesion improvement between olive husk flour (OHF) as a filler and PP polymer matrix was reported. Two types of chemical treatment were used to enhance polymer composite adhesion properties. Vinyl triacetoxy silane (VTAS) and maleic-anhydride polypropylene (PPMA) compatibilizer agents were included in polymer composite modification. Chemically treated and untreated OHF with 10 and 20% wt. filler loading levels to PP matrix were prepared. The thermal stability of the polymer composite treated with (PPMA) coupling agent showed a better thermal performance when compared to that of untreated or (VATS) treated polymer composites [33]. Olive pomace filled polypropylene composites were fabricated and characterized by Atagur et al, olive pomace with fine particle size (~21μ) of different weight fractions (up to 40%) were loaded into polymer matrix using high speed thermal mixer. An increase in Young's and flexural modulus by 62% and 19% was reported, respectively. In contrast, tensile and flexural modulus were decreased upon filler loading %. On the other hand, thermal stability and decomposition behavior were enhanced upon filler loading [34].

Polyvinyl chloride (PVC)

Melt compounding and injection molding processing techniques were used to produce polymer composite from OSF and PVC up to 50 wt. % filler loading level.

OSF incorporation to PVC matrix reduces the mechanical strength to values not less than 30 MPa, which is still an acceptable value on the industrial scale to produce plastic-based articles [35].

Polyester thermoplastic

Polyester resins filled and compounded with OSF at various loading levels were prepared. The physical and chemical properties of the obtained polymer composite were studied. The biodegradation behavior for the mentioned composite material was also evaluated. An early study on the preparation of the cost effective and environmentally friendly biodegradable polymer composite was achieved by utilizing the ligno-cellulosic waste flours OHF, as a source of filler. Bionolle 3020, commercial biodegradable polyester, was used as matrix for a natural waste filler. The interfacial adhesion between natural waste flour and polymer matrix was enhanced by chemical treatment, acetylation and propionylation, of the filler. Moreover, a compatibilizer produced from the polymer matrix itself by anhydride-grafted Bionolle would promote the adhesion effect between polymer and filler in the polymer composite matrix. As a result, there was an improvement in mechanical performance of such composite.

The chemical treatment of the flour (as a filler) with acetic and propionic resulted in a significant reduction of composite material water uptake. Moreover, increasing the waste flour loading level percentages in the polymer matrix resulted in enhancement of biodegradation rate [36]. In searching for environmental friendly food packaging application, a biodegradable olive pomace filled polyhydroxybutyrate-co-valerate (PHBV) composite material was fabricated and characterized. A decrease in mechanical stress and the elongation at break for (PHBV) biocomposite was pronounced at high olive pomace content. Thermal decomposition of the polymer composite during extrusion process may result in a decrease in mechanical performance [37-38].

Unsaturated polyester resin

The weak interaction between non polar polymeric matrix material and filler from ligno-cellulosic materials is considered the main problem facing such filler material. A study on the enhancement of the interfacial adhesion between unsaturated polyester resin and silane treated OSF was carried out. Composite materials loaded with 10-60 wt% filler were mixed and molded by compression molding technique using untreated and γ-mercapto propyl trimethoxy silane (MRPS)-modified OSF. Silane treated OSF filled polymer matrix showed better mechanical performance and reduction in water uptake [39].

Epoxy resins

The mechanical properties of epoxy resin filled OSF composite were evaluated under the effect of thermal shock cycling. The bending modulus increased by 48% and the bending strength remained unaffected by the amount of the filler incorporated into the polymer matrix [40].

Pyrolytic char from olive kernel was used as a filler to reinforce epoxy resin. Different filler loading levels were compounded with the polymer matrix. Produced composite was mechanically characterized by using three point bending test. Both bending and elastic modulus of the reinforced epoxy resin increased by 60% for each compared to that of the neat unfilled resin material [41].

Chitosan

Cellulose nanocrystals (CNC) and 2, 2, 6, 6-tetramethyl-1-piperidinyloxyl- (TEMPO-) oxidized cellulose nanocrystals (CNC-TEMPO) were prepared from OSF processing. Obtained nanocrystals were then used as reinforcing agents in chitosan matrix to prepare nanocomposites. The mechanical properties especially the tensile strength of the nanocrystals filled chitosan material showed better performance when compared to that of unfilled one. The use of cellulose nanocrystals in chitosan/hydroxyapatite (Hap) composite enhance the deposition of new Hap when compared to the same composite in the absence of cellulose nanocrystals [42-43].

Wheat gluten

Blending technique was used to prepare new boicomposites from wheat gluten plasticized by 35% of glycerol, containing 0–20% of Clean Olive Pomace, Esterified Clean Olive Pomace, or Mercerized Clean Olive Pomace powders. Mercerization process resulted in an improvement in the thermal stability of the powder. Inclusion of Clean Olive Pomace powder in plasticized wheat gluten significantly enhanced the young's modulus of the composite compared to that of unfilled wheat gluten material.

Water uptake of 20% reinforced composite was decreased by 29% less than that of unfilled wheat gluten. A decrease in Young's modulus and tensile strength of 5% Esterified Clean Olive Pomace was reported. On the other hand increasing of Mercerized Clean Olive Pomace content resulted in a decrease in elongation at break of the biocomposite. A decrease in thermal stability was noticed for 20% Clean Olive Pomace biocomposite. Thermal stability of the biocomposite did not alter upon using chemically modified Esterified Clean Olive Pomace and Mercerized Clean Olive Pomace fillers [44].

The Effect of olive pomace load and ball milling process on properties of plasticized wheat gluten biocomposite was studied by Hammoui et al. High-energy ball milling and mixing process of wheat gluten and olive pomace were used to produce a biocomposite by the conventional blending method. Homogenous dispersion of olive pomace filler in wheat gluten matrix resulted from appropriate filler particle size, effective milling process, and suitable % loading led to a biocomposite with an optimum performance. Biocomposite moisture absorption increases with the increase in filler content whereas thermal stability decreases on loading %. Food packaging is a proposed application for such biodegradable biocomposite with optimum filler content below 15% above which phase discontinuity is a major problem [45].

High density polyethylene (HDPE)

In our laboratories HDPE filled with olive shell flour at 0-50 wt. % loading level in the absence and presence of 1% and 5% coupling agent (Fusabond M603 resin) were prepared (Figure 2). Composites were fabricated by extrusion and compression molding processes. Mechanical, morphological, and water uptake properties were investigated. Results showed that the tensile strength of the composite decreases with the increase of the filler loading; and increases in the presence of coupling agent. Composites, with low filler loading, showed good performance compared to composite with high filler content. The tensile stress and modulus of elasticity reduction at medium and high filler loading levels may be due to the poor interfacial bonding between olive shell flour and HDPE. Olive shell flour can be used as reinforcements in HDPE by the help of certain coupling agent. The developed OSF/HDPE polymer composite would be considered as alternative to conventional polymers in packaging application [46-47].

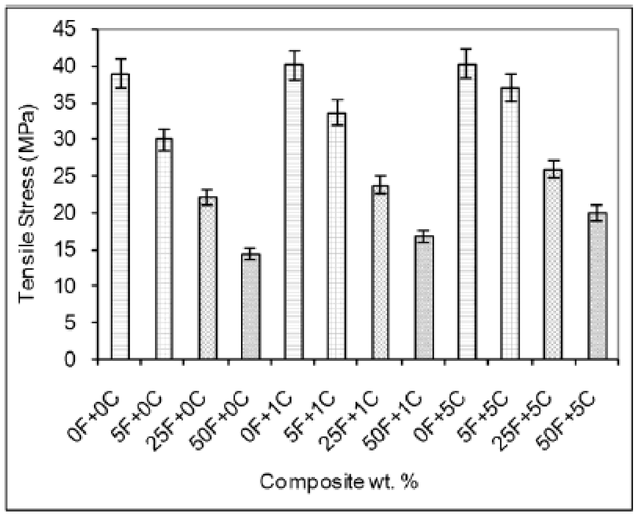

Figure 2. Comparison of tensile stress of OPF filled HDPE composite as a function of the filler and coupling agent loading level. F: olive pomace flour % and C: coupling agent % (maleated PE) [46]

Esterification of olive stone flour (OSF)

The chemical modification of lingo-cellulosic materials based on waste flour, using catalyst and solvent-free reactions with acetic and propionic anhydrides was studied. OSF treated with acetic anhydride resulted in higher ester content compared to the one treated with propionic anhydride. High content of lignin/hemicelluloses in olive husk flour was the main reason for the ease of the esterification process. As a consequence of the flour esterification process, moisture content reduction which is an indication of the decrease in the material’s hydrophilicity was noticed; in addition their thermal stability was also slightly decreased. Moreover, esterification process resulted in a slight decrease in the crystallinity of the flour [48].

Medium density fiberboard (MDF)

Olive mill sludge (OMS) as an alternative to wood in the manufacture of medium density fiberboard (MDF) was reported. With increasing OMS flour content (up to 50%), the flexural properties of the panels, modulus of rupture and modulus of elasticity, decreased by 31.0% and 29.2% compared to panels without OMS flour, respectively. However, water resistance was improved by addition of the OMS flour up to 20 wt. % content. According to the authors, the findings obtained showed that OMS was capable of serving as lingo-cellulosic raw material in the manufacture of MDF [49-50].

4. Conclusions

Availability and easy extraction of olive stone flour as a promising filler in olive oil mills makes it suitable for industrial manufacturing of bio-composites. The use of OSF as filler for several polymeric matrices was introduced. The effect of filler content, processing conditions, compatibilizing agent and plasticizer on the performance characteristics of bio-composites was partially investigated in literature. A completely biodegradable composite from OSF needs to be developed for future applications. The inclusion of such filler needs to be evaluated for many other existing polymers especially with those of biodegradable nature. Better bio-composite properties can be achieved through improvements in the interfacial adhesion between polymer and natural fillers to address the filler/polymer poor adhesion problems. Processing techniques and filler chemical modifications would be of significant importance to obtain a bio-composite with desired mechanical performance.

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