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Utilization of natural montmorillonite modified with dimethyl, dehydrogenated tallow quaternary ammonium salt as reinforcement in almond shell flour–polypropylene bio-nanocomposites

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ABSTRACT

The main goal of this work was to evaluate the technical feasibility of almond shell flour (ASF) as wood substitute in the production of wood–plastic composites (WPCs). The effects of organically modified montmorillonite (OMMT), as reinforcing agent, on the mechanical and physical properties were also investigated. In order to improve the poor interfacial interaction between the hydrophilic Lignocellulosic material and hydrophobic polypropylene matrix, maleic anhydride grafted polypropylene (MAPP) was added as a coupling agent to all the composites studied. In the sample preparation, OMMT and ASF contents were used as variable factors. The morphology of the specimens was characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The results of mechanical properties measurements indicated that when 3 wt.% OMMT were added, tensile and flexural properties reached their maximum values. At high level of OMMT loading (5 wt.%), increased population of OMMT lead to agglomeration and stress transfer gets blocked. The addition of OMMT filler decreased the water absorption and thickness swelling of composites. SEM study approved the good interaction of the almond shell flour with the polymer as well as the effectiveness of OMMT in improvement of the interaction. TEM study revealed better dispersion of silicate layers in WPCs loaded with 3 wt.% of OMMT. The improvement of physico-mechanical properties of composites confirmed that OMMT has good reinforcement and the optimum synergistic effect of OMMT and ASF was achieved at the combination of 3 and 50 wt.%, respectively. The findings indicated that almond shell as agro-waste material is a valuable renewable natural resource for composite production and could be utilized as a substitute for wood in composite industries.

1. Introduction

Nowadays, in the polymer industry, natural fibers and nanomaterials have been gaining increasing attention due to two reasons. One is to develop 'environmentally friendly materials' through utilizing natural fibers as alternative to synthetic fibers in fiber-reinforced composites. Another is to improve the properties of polymer matrix by adding nanoparticles.

The growing global environmental concerns and increasingly social pressure for the use of less harmful composites materials have aroused a paradigm shift towards using natural fibers as substitute for synthetic and nonrenewable reinforcements [1]. Natural fibers compared with conventional reinforcement materials such as glass, carbon and aramid fibers have more advantages such as low cost, low density/light weight, non-toxicity, non abrasive during processing and use, fully biodegradable, recyclability, sustainability, versatility, wide availability, high specific strength and modulus, and minimum waste disposal problems [2–5].

Faced with serious shortage of wood resources in Iran, the wood industry is showing increased interest in production of ligno-cellulose based composites from other materials. Agricultural residues, which are produced with large quantities annually throughout the world, are the main renewable alternative resources [6,7]. The high cost of collection, storage, transportation, and handling of agricultural residues are the foremost obstacles to the production of composite materials from these wastes that can be overcome by establishing small-scale plants close to rural areas [8].

Several researchers in Iran have investigated the suitability of agro-waste materials as fillers or reinforcement in thermoplastic

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composites, including fibers of bagasse [9,10], hemp [11], corn stalk, reed stalk, and oilseed stalk [12], rice husk [13], rice straw [14], wheat straw [15], as well as walnut shell [2].

Fruit shells can be considered as a good potential for biomass feedstock [16]. Almond is one of the most valuable crops in Iran and also in the world. Approximately 2.00 million tons almond is being generated annually in the world. According to Table 1, Iran after USA, Spain and Australia is the 4th largest almond producer by annual production of about 100,000 tons [17].

Since almond shell comprises 35–75% of the total weight of the fruit, consequently; around 0.7–1.5 million tons of almond shell is left behind each year [6]. Almond shells have no economical value or industrial usage in Iran and normally are incinerated or dumped without control due to logistic problems such as seasonal production in small scale factories, transport costs, and lack of energetic plants. As an annual agricultural waste, almond shell is a lignocellulosic material with chemical composition similar to wood; regarding its quantity in Iran, evaluation of its feasibility for producing polymer based composites is of high importance [2].

The introduction of nanotechnology has opened new opportunities for the industries to develop a new generation of composites with high performance [18]. Amongst the nanoparticles used in nanocomposites, nanoclays or silicate layers have been much considered in polymer nanocomposites. This is due to the fact that nanoclay is an inexpensive natural mineral with a high aspect ratio (100–1000) and large surface area (750 m^2/g), along with high mechanical and thermal properties [19]. The high extent of nanoclay dispersion (exfoliation) within a polymer matrix, which is very hard to achieve because of the incompatibility of hydrophobic polymers with hydrophilic clays, plays the key role in the property improvement. In order to uniformly disperse clays within a polymer matrix, clay nanolayers must be modified with some hydrophobic surfactants by the exchange of metal ions in the intergallery regions with alkylammonium or alkylphosphonium ions. Clay modification lowers the surface energy of the clay layers and increases the polymer–clay interfacial interactions which lead to an increase in the distance between clay nanolayers (intercalated structure) and to subsequently complete separation of stacked clay layers (exfoliated structure) [20,21]. So, organically surface modified nanoclays (organo-nanoclays) were types of clays that were developed to have better dispersion in polymer matrices [22]. One example is the quaternary amine modified Montmorillonite clay series (Southern Clay Products) that are highly hydrophobic and were reported to be highly effective in improving mechanical properties of some polymer composites [23]. Presence of OMMT in polymers has also shown the ability to minimize moisture absorption in polymeric composites [24]. This ability has been attributed to inherent morphology of OMMT which prevent of moisture ingress during exposure [25].

According to serious shortage of wood resources in Iran, using of agro-waste materials (e.g. almond shell) that has no industrial usage and usually incinerated or dumped, alleviate the shortage of these resources, and can have the potential to start a natural fiber industry in countries where there are little or no wood resources left. The suitability of using almond shell as a bio-waste resource in wood based particleboard manufacturing have been studied before [6]. The main objective of this research was to study the potential of almond shell as reinforcing filler for WPCs in order to evaluate their suitability as an alternative for wood fibers. In addition, the effects of fiber loading and organically modified montmorillonite content on the physical and mechanical properties were studied.

2. Materials and methods

2.1. Materials

2.1.1. Lignocellulosic material

The lignocellulosic material for this study was almond shell flour (ASF). The almond shells supplied from dry fruit almond manufacturer in North Khorasan Province (Faroj County – Sfejir) of northeastern Iran. Prior to the use, the shells first cleaned of dirt and impurities, and then were ground into flour using a Thomas-Wiley miller. Particles manually screened to choose 40–60 mesh and oven-dried at 105 °C for 24 h to a moisture content of less than 3%. Table 2 lists the compositions of almond shell flour reported by Pirayesh and Khazaeian [6].

2.1.2. Polymer matrix

The polypropylene homo-polymer (Moplen V30S) pellets with a melt flow rate (MFR) of 18 g/10 min and a density of 0.92 g/cm^3 was supplied by Arak Petrochemical Co. (Iran).

2.1.3. Coupling agent

A maleated polypropylene (PP-g-MA) coupling agent (grade PP-G 101), in the form of powder with a density of 0.91 g/cm^3, a melt flow index of 64 g/10 min, and maleic anhydride of 2% was purchased from Kimia Javid Sepahan Co., Iran. MAPP was used to enhance the compatibility between PP and almond shell flour in the composite structures. Based on our pretests, optimum percentage of using PP-g-MA in mixture was 4%.

2.1.4. Nanoparticle

The commercial organically modified montmorillonite (Cloisite® 15A) used in the present study was supplied by Southern Clay Products (USA). The specifications of the montmorillonite are given in Table 3. Montmorillonite was modified with the quaternary ammonium salt shown in Scheme 1 (HT = hydrogenated tallow), with approximate composition (by mass) of 65% C_{18}, 30% C_{16} and 5% C_{14}.

2.2. Sample preparation

Composites were produced in a two stage process based on a literature procedure [26]. In brief, in the first stage, the mixtures were premixed before being fed into the first zone of the extruder. All the experiments were performed in a co-rotating twin-screw extruder. The temperatures of the first to the last chambers were

Table 1
The major almond producing countries in the world (Fao-2012).

Country	Production (tonnes)
USA	720,000
Spain	215,100
Australia	142,680
Iran	100,000
Morocco	99,067

Table 2
Chemical composition of the used almond shell (dry basis).(previous study).

Almond shell composition	Value (%)
Holocellulose	64.3
Cellulose	29.1
Lignin	32.7
Ash	3.4
Hot water solubility	9.1
Cold water solubility	6.3
NaOH (1%) solubility	30.2