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A comparison between bio- and mineral calcium carbonate on the properties of polypropylene composites

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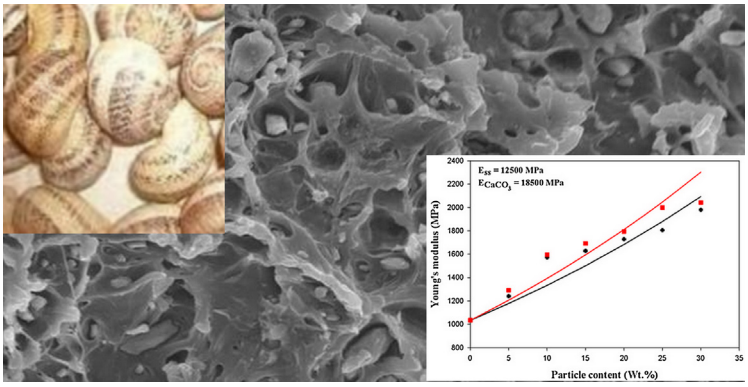
HIGHLIGHTS

- Biocomposites of polypropylene were reinforced with snail shell (SS) particles.
- Biocomposites were manufactured using extrusion and injection techniques.
- Biocomposites of PP and SS particles were characterized by different techniques.
- Thermal and mechanical properties were increased with SS filler content.

GRAPHICAL ABSTRACT



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ABSTRACT

In the first part of this study, snail shell (SS) particles were characterized in terms of thermal, structural and morphological properties. Then, the particles were used as a bio-filler and compounded with polypropylene (PP) to produce bio-composites. As a base of comparison, samples were also produced under the same conditions using a low cost mineral filler: calcium carbonate ($CaCO_3$). The samples (SS/PP and $CaCO_3$/PP) were compounded by extrusion with various filler content (5, 10, 15, 20, 25 and 30% wt.) and injection molded. The results show that SS addition substantially improved the thermal and mechanical properties of the composites. For example, adding 20% SS improved the thermal stability by 21 °C, while at 30% the tensile modulus increased by 91% compared to neat PP. Overall, SS particles could be a good substitute for commercial $CaCO_3$ as they offer an ecological alternative to upgrade the valorization of an abundant and unexploited Moroccan resource. In addition, SS particles as a bio-filler appear to be a good alternative to obtain environmentally friendly products, especially in the plastics industry.

1. Introduction

Over the last decade, the field of composite materials still received a great deal of attention with a focus on polymer matrices. But most of the resins used are derived from the petroleum indus-

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try and generate high amounts of wastes and contaminants needing treatment to limit their environmental impact [1,2]. For these reasons, a growing effort has emerged to develop composites based on bio-fillers [3–5]. These composites contain at least one component derived from renewable resources such as fibers: hemp [6], coir [7], alfa [8], pine cone [9] and doum [10], or shells: argan [11], almond [12] and eggs [13].

In general, the physical and mechanical properties of composites depend on various factors, including those intrinsic to each component and their interactions, as well as the processing conditions [14]. Today, several investigations on composite materials are based on polyolefin matrices like polyethylene [7,15] and polypropylene [16,17]. But the lack of compatibility between these hydrophobic matrices and hydrophilic bio-fillers leads to poor adhesion and the formation of aggregates during processing, leading to a loss of mechanical properties [7,8]. To partially solve this problem, inorganic fine powder are used to increase the surface contact area in several industrial products such as paper, paints, rubbers and polymers. The particles can also be surface treated to improve their compatibility with the continuous phase (matrix). The most commonly used fillers are calcium carbonate [18] and talc [19]. These particles are available, low cost and were found to improve some mechanical properties and dimensional stability [20].

With respect to sustainable development concepts and biomass revalorization, most of the bio-fillers used today are residues from primary transformation industries. These locally available materials can be used as reinforcement to produce polymer composites and this is the case for snail shells (SS). Snail shells contains a high amount of calcium carbonate [21,22], which may be suitable as a calcium carbonate substitute for the production of polymer composites. But snail shells also contains various organic compounds. The hypostracum is a form of aragonite, which is a type of $CaCO_3$. The ostracum is built by several layers of prism-shaped $CaCO_3$ crystals with embedded proteid molecules. The periostracum, the outermost shell layer, is not made of $CaCO_3$, but of an organic material called conchin which is a mixture of organic compounds mostly based on proteids. Conchin not only makes the outer shell layer, but is also embedded between $CaCO_3$ crystals inside deeper layers [22,23]. So the chemical composition and availability of snail shells make them a potential source of bio-based $CaCO_3$ and a good candidate for commercial $CaCO_3$ substitute [21]. For example, SS was shown to be more easily and homogeneously dispersed in polypropylene (PP) than mineral calcium carbonate [20].

The main objective of this work is to show that snail shell (SS) particles are a good filler for polypropylene (PP) and a substitute for commercial $CaCO_3$. To do so, composites based on polypropylene (PP) were made to compare the effect of both particles and their concentration (5 to 30% wt.). Here, the comparison is made in terms of morphological, physical, mechanical, rheological and thermal properties. From the results obtained, the Tsai-Pagano model was used to determine the mechanical rigidity of SS and $CaCO_3$ particles.

2. Materials and methods

2.1. Materials

The polypropylene (PP) matrix PPH03BPM was supplied by TASNEE, Saudi Arabia, which is an extrusion/co-extrusion grade with a melt flow index (MFI) of 3.0 g/10 min (ASTM 1238), a density of 0.90 g/cm^3 (ISO 1183), and a Vicat softening temperature of 156 °C (ISO 306). The commercial calcium carbonate powder ($CaCO_3$) was supplied by Sigma-Aldrich, with an average diameter of 10 μm. Ground snail shell was selected as the bio-filler. The snails were collected from the rural areas of Morocco (Rabat) and their shells were removed carefully. The shells were first washed with tap water to remove mud, sand and other impurities. Then, the cleaned shells were dried in an oven at 80 °C during 24 h, before being ground in a laboratory precision grinding Disk Mill machine (FRITSCH Pulverisette 13) down to 0.05 mm. The material was finally sieved to keep only particles below 10 μm to be similar as the commercial $CaCO_3$.

2.2. Composites processing

To study the effect of filler (SS and $CaCO_3$) content on the properties of polypropylene, six different concentrations were used: 5, 10, 15, 20, 25 and 30% wt. Compounding was done on a Leistritz ZSE-18 twin-screw extruder (Leistritz GmbH, Germany). Mixing was performed using a screw speed of 125 rpm. PP was fed at the main hopper (zone 1) and the particles through a side-feeder (40 rpm screw speed) located at zone 3. The temperature profile was set at: 200, 200, 200, 200, 180, 180, 180 and 180 °C [24]. The compounds were cooled in a water bath at the die exit and then pelletized (Thermo Fisher, UK). Finally, the samples were produced on an injection molding machine (Engel e-Victory). The temperature of the injection barrel was fixed at 200 °C, while the nozzle was set at 180 °C with a mold at 45 °C. The mold dimensions are according to ISO 527-1:2012 [24,25].

2.3. Characterization

2.3.1. ATR-FTIR analysis

Infrared spectra were recorded on an ABB Bomem FTLA 2000-102 spectrometer (ATR: SPECAC GOLDEN GATE) using the attenuated total reflectance (ATR) technique. The transmittance range of the scan was 4000–500 cm^{-1}. The spectra were obtained by an accumulation of 16 scans with a resolution of 4 cm^{-1}.

2.3.2. Scanning electron microscopy (SEM)

Morphology was evaluated using a scanning electron microscope (SEM) (FEI, Quanta 200-ESEM) operated at 20 kV. To obtain clean and clear cross-sections, the biocomposites were frozen in liquid nitrogen and cryo-fractured before being coated by a thin conductive gold layer.

2.3.3. Thermal stability

The thermal stability of the materials was evaluated by thermogravimetric analysis (TGA) using a Q500 instrument from TA Instruments (UK). Roughly 10 mg of each sample was placed in a platinum pan and heated under air from room temperature to 800 °C at a heating rate of 10 °C/min to yield the onset decomposition temperature.

2.3.4. Tensile testing

Tensile testing of five specimens was performed according to ISO 527-1:2012 [25], and the average values are reported with standard deviations. The tensile tests were performed on a universal testing machine INSTRON 8821S (Instron, USA) at a crosshead speed of 3 mm/min using a 5 kN load cell.

2.3.5. Torsion testing

Torsion tests were performed on an ARES-LS rheometer (TA instruments, UK) using the rectangular torsion mode. The sample dimensions were 5.5 mm width, 58 mm length and 2 mm thickness. The torsion modulus G* was obtained from low amplitude (0.002 strain) oscillatory tests (linear viscoelastic properties) performed at room temperature in the frequency sweep mode (0.1–40 Hz).

2.3.6. Dynamic rheological measurements

Small amplitude oscillatory shear tests were performed on a MCR 500 (Physica, Germany) rheometer equipped with a CTD600 device (melt state). The measurements were carried out at 180 °C under small amplitude oscillatory shear using a 25 mm parallel plate geometry with 2 mm thick samples. Frequency sweeps between 500 and 0.05 Hz were performed at a strain of 5%, for which the materials exhibit a linear viscoelastic behavior as verified by previous strain sweeps.

3. Results and discussion

3.1. Fourier transforms infrared spectroscopy (FT-IR)

Infrared characterization was carried out to get some information on the chemical composition of the snail shells. Fig. 1 shows that the spectrum can be divided into five regions with peaks around 1782, 1448, 1074, 853 and 708 cm^{-1} which can be associated to CO_3^{2-} ions in $CaCO_3$ [26–28]. The band at 1782 cm^{-1} could be attributed to C=O bonds of the carbonate groups [26], while the absorption bands around 1448 cm^{-1} are attributed to asymmetric stretching [27]. The band at 1074 cm^{-1} corresponds to the symmetric stretching in aragonite [27], while the bands at 853 cm^{-1} can be assigned to the out-of-plane bending vibrations [27].