Original Article

High-density polyethylene/mollusk shell-waste composites: effects of particle size and coupling agent on morphology, mechanical and thermal properties

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\textbf{Abstract}
Composites based on high-density polyethylene (HDPE) and mollusk shell-waste (MSW) particles, with several concentrations and two different micro-sizes, were prepared by melt compounding and injection molding. The matrix flow behavior was not altered by the MSW incorporations. SEM analyses revealed weak filler/matrix interfacing and the presence of agglomerates (in the composites with higher particle concentrations). For the 2 wt% composites, good filler dispersion and distribution was observed in the HDPE matrix. The crystallinity of the matrix increased approximately 10% when adding lower MSW concentrations. For the composites with higher MSW concentrations and finer particles the thermal degradation temperature of HDPE (at a 20% mass loss) increased by approximately 26 °C. The tensile modulus increased by approximately 10% for the 2 wt% and 8 wt% composites with coarse particles. With lower MSW concentrations and finer particles, the flexural modulus increased by more than 37%. The composites modified with titanate presented properties similar to unmodified composites. Molecular interactions were verified by the presence of a band at 1030 cm\textsuperscript{-1}, yet were not sufficient to promote improvements in the mechanical properties of the modified composites.

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1. Introduction

The majority of common household, electronic and automotive applications of thermoplastics involve mixtures with mineral fillers, such as calcium carbonate (CaCO$_3$), talc, mica, wollastonite, glass beads, silica, rice husks and clays. Adding such fillers to polymers is very economical and improves the properties of polymeric matrices. Apart from reducing the price of the final material, mineral fillers can also help improve stiffness, and reduce both flammability and molding shrinkage, which are principal limitations of bulk thermoplastics [1–4]. In polyolefins, calcium carbonate is commonly used as filler with particle sizes varying from macro to nano scales. Calcium carbonate confers toughness and rigidity to the composites [5,6]. HDPE with particulate fillers is of great interest in industrial applications because it is easily processed, and it accepts different types of natural and synthetic fillers [7]. The effects of inorganic filler additions on the mechanical and thermal properties of polymeric matrices have been widely studied [8–12].

Using a coupling agent to improve the interfacial interactions between inorganic fillers and a polymeric matrix, Monte [13] proposed a mechanism to explain interlinking between the inorganic filler, the polymer, and the titanium derived coupling agents. Briefly, the hydrolysable portion of the titanate molecule reacts with free protons or hydroxyl groups on the inorganic surface, leading to formation of organic monomolecular layers. As a result, dispersion of inorganic filler in an organic phase is enhanced due to compatibilization at the interface: substituting hydrating water at the inorganic surface with a monomolecular layer before establishing titanate coupling. Consequently, a compatible inorganic/polymer interface promotes elimination of unwanted air voids in the composite, and dispersion of filler into the matrix.

Researchers around the world [14,15] have studied the structural features of different types of mollusk shells in great detail. Most shells are natural composites composed of stacked platelets (0.5 μm) arranged as if they were a brick and mortar microstructure, with an organic matrix interlayer (20–50 nm). The crystalline structure of mollusk shell is composed of aragonite and calcite, both are polymorphs of CaCO$_3$, and its chemical composition is 97.5372% calcium oxide [16]. Similar findings have been reported for other types of seashells [15,17].

Recently, the need to develop materials that are easily recyclable and that contribute less to greenhouse gas emissions has motivated research involving wood residues and shells as bio-fillers for polymeric matrices [17,18]. This motivated us to investigate HDPE polymeric bio-composites with recycled mollusk shell-waste particles. The use of treated shells for polyolefins with cetyltrimethylammonium bromide [17], furfural [19], furfural and hydrochloric acid [20] has been well documented, as tests of polymeric composites mixed using twin-screw extruders [17,19,20]. Varied authors have studied seashells as bio-fillers in polymeric composites. The peculiar properties of these materials depend largely on processing, shell-waste surface treatments, and the polymeric matrix. In addition, shells differ in respect to chemical composition. As an example, silicon dioxide is present in Brazilian mollusk shells [16], yet is lacking in Korean oyster shells [17]. Along the coasts of Brazil and other parts of the world there is great abundance of shell-waste, which is an environmental hazard lacking storage/disposal. On the Brazilian coast, human consumption drives commercial extraction of mollusks and the eventual production of shell-wastes. Once the mollusk is consumed, the majority of shells are discarded on river banks.

The aim of this work was to prepare HDPE/shell-waste composites using two different grades of mollusk shell particles and a titanate coupling agent. We investigated tensile, flexural, and impact properties for the composites, together with flow behaviors, thermal properties, and morphological characteristics to find a new low cost way to recycle Brazilian shell-wastes.

2. Materials and methods

2.1. Materials

The polymer used in this study was high-density polyethylene (HDPE) IA58 supplied by Braskem. It has a density of 0.957 g/cm$^3$ and a melt flow index of 22.0 g/10 min (2.16 kg at 190°C). Mollusk shell-waste was collected after disposal on the banks of the Paraíba River by a riverside community in Paraíba State, Northeast Brazil. It was used as bio-filler for this study. The organic titanate coupling agent (isopropyl tri(diocetyl)phosphate)) is an industry grade powdered product, and was kindly donated by the Mag-Mix Company. This specific coupling agent was chosen due to its potential to improve the thermal stability, and mechanical-rheological properties of polyolefinic matrices.

2.2. Mollusk shell preparation

The shell-wastes were washed to remove superficial impurities and then dried outdoors. They were then milled on a disc mill (30 min) and sieved. Granulometric classification was performed using two different sieves: 200 (74 μm) and 325 (44 μm) mesh; the shell powder was respectively classified into two grades: coarse and fine.

2.3. Processing

After the shell-waste was washed, dried and sieved, one part of the shell-waste was mixed to 1.2% (m/m) with powdered titanate coupling agent. Using the coarse and fine grade composites, we then prepared 2, 5, and 8% (m/m) shell-waste particle mixtures. Composites using 5% (m/m) titanate modified shell-waste were also studied. The samples were melted into a compound using a 30 mm fluted single screw extruder (as proposed by Tadmor and Gogos [21]). The extrusion mixing process was performed at a temperature of 170–180 °C, with screw rotation speed at 50 rpm. A fluted screw was preferred because a single screw extruder is less expensive than a twin screw extruder, making processing more economic and attractive for recycling companies. The preparation of the test specimens from the compound composites occurred in a BATTENFELD HM45/210 injection molding machine. The
molding conditions were as follows: injection speed 75 cm/s; holding pressure 600 bar; hold time 15 s; and cooling time 30 s. The temperature profile used was 170–190 °C, and the mold temperature was maintained at 30 °C. Before processing, the materials were dried in an air circulating oven for 2 h at 60 °C. The particulate compositions are shown in Table 1.

### Table 1 – Sample labeling.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSW</td>
<td>Mollusk shell-waste particles</td>
</tr>
<tr>
<td>MSH2</td>
<td>2.0% MSW (200 mesh)</td>
</tr>
<tr>
<td>MSL2</td>
<td>2.0% MSW (325 mesh)</td>
</tr>
<tr>
<td>MSH5</td>
<td>5.0% MSW (200 mesh)</td>
</tr>
<tr>
<td>MSL5</td>
<td>5.0% MSW (325 mesh)</td>
</tr>
<tr>
<td>MSL5T</td>
<td>5.0% MSWT (200 mesh)</td>
</tr>
<tr>
<td>MSW8</td>
<td>8.0% MSW (200 mesh)</td>
</tr>
<tr>
<td>MSW8</td>
<td>8.0% MSW (325 mesh)</td>
</tr>
</tbody>
</table>

2.4. **Characterization**

#### 2.4.1. Particle size distribution

The particle size distribution curves for both particle samples were obtained by laser diffraction using a Cilas laser diffraction analyzer in wet mode with distilled water.

#### 2.4.2. Fourier transform infrared spectroscopy (FTIR)

The analyses were recorded on an IR-Prestige 21 spectrophotometer from Shimadzu, accumulating 32 scans with 4 cm⁻¹ resolution in the 4000 to 1000 cm⁻¹ region. The samples of mollusk shell-waste and titania coupling agent using approximately 1 wt% were prepared as KBr pellets. Analyses of the ground composite samples were performed in attenuated total reflectance (ATR) mode by direct analysis on a ZnSe crystal. The FTIR spectra were baseline and ATR-corrected.

#### 2.4.3. Melt flow

The processability of the filled HDPE composites was determined with a Modular Line CEAST melt flow indexer according to ASTM 1238-10. A load of 2.16 kg at 190 °C was used for the measurements. At least five specimens for each composition were tested. Before analysis, the samples were dried in an air circulating oven for 2 h at 60 °C.

#### 2.4.4. Differential scanning calorimetry (DSC)

Thermograms were obtained using a Shimadzu DSC 60 calorimeter. Calibration was done with indium and sapphire in the temperature range of 0–350 °C. The sample weight was approximately 6.0–6.4 mg. For each test, the sample was first heated to 200 °C at 10 °C/min and then annealed for 5 min to ensure an identical thermal history. The sample was subsequently cooled to 30 °C at a cooling rate of 10 °C/min for data collection. In the second heating scan, the sample was heated from 25 to 200 °C at 10 °C/min in a nitrogen atmosphere. The crystallization temperature (Tc) was determined during cooling, and the peak temperature of the second heating scan was taken as the melting temperature of the polymer. The peak area was used to determine the melting enthalpy using constant integration limits. The degree of crystallinity (Xc) was determined using the following equation:

\[
X_c(\%) = \frac{\Delta H_m}{(1 - W_f) \times \Delta H_{100\%}} \times 100
\]

where \(\Delta H_m\) is the melting enthalpy per unit weight of HDPE in the composition; \(W_f\) is the fractional weight of shell-waste particles in the composite; and \(\Delta H_{100\%}\) denotes the enthalpy per unit weight of 100% crystalline HDPE, which was assumed to be 293 J/g [22].

2.4.5. **Thermogravimetric analysis (TGA)**

The curves were obtained using a Shimadzu DTG-60H Simultaneous DTA-TG apparatus. The sample weights were approximately 10–11 mg, and samples were loaded and heated from 30 to 900 °C at 10 °C/min in an argon atmosphere.

2.4.6. **Scanning electron microscopy (SEM)**

The morphologies of the composites were investigated using a ZEISS LEO 1430 scanning electron microscope; observing dispersion and interfacial adhesion of the mollusk shell-waste particles to the HDPE matrix. The injected composite specimens were immersed in liquid nitrogen, after several minutes fractured cryogenically, and then covered with a thin layer of gold for analysis of the fracture surface. The images were obtained with different magnifications at an electron beam accelerating voltage of 15 kV.

2.4.7. **Mechanical properties**

Tensile, flexural, and impact tests were performed on the HDPE/mollusk shell composites to analyze the effects on the mechanical performance of adding the differently sized mollusk shell-waste particles. For each compound, five samples were tested, and mean values were considered. The tensile tests were carried out using a universal testing machine; Shimadzu model AG-X 10KN, according to ASTM D 638 at an extension rate of 50 mm/min. The three-point bend flexural test was conducted conforming to ASTM 790 using the same universal testing machine; Shimadzu model AG-X 10KN, at a deflection rate of 2 mm/min. Izod impact tests were performed in accordance with ASTM D256 using a CEAST Resil 5.5 machine and a 2.75J pendulum impact tester.

3. **Results and discussion**

In this work, composites with low concentrations of shell-waste were investigated. The single fluted screw extruder in laboratory scale did not permit mixing with a shell-waste concentration above 8% (m/m). Chong et al. [17] has studied recycled polyethylene/shell-waste composites with various higher concentrations without observing changes relevant to the mechanical matrix properties. Though other authors [19,20] have employed pretreatment for shell-wastes using a sodium hydroxide solution, this was not done in the present study. Our proposal was to prepare low cost composites without shell-waste pretreatments, and to investigate the influence of low concentration shell-wastes (in two different
particle sizes) on the flow, thermal, mechanical, and morphological characteristics of polyethylene/bio-filer compositions.

3.1. Particle size distribution

The particle size distribution curve for the 325 mesh sample is shown in Fig. 1; the results for the 200 mesh sample had already been investigated in a previous study [16]. Comparing the results, the 325 mesh sample presented a 50% diameter (D50) of 5.27 µm, this was compared to the 50% diameter (D50) of 6.49 µm obtained from the 200 mesh sample, resulting in a diameter decrease of approximately 23%. The same tendency was observed for particles with diameters at 90% (D90); resulting in a diameter decrease of approximately 28%.

3.2. FTIR

Fig. 2 presents the FTIR spectra of the titanate coupling agent and composites, detailing the interaction between mollusk shell-waste and HDPE in composites with 5 wt% concentrations. The mollusk shell exhibits absorptions bands at 1475 cm\(^{-1}\), 1080 cm\(^{-1}\), and 858 cm\(^{-1}\) and a split peak at 710 and 700 cm\(^{-1}\) being characteristic bands of aragonite [23]. The titanate coupling agent spectra present absorption bands at 2930 cm\(^{-1}\) and 2850 cm\(^{-1}\), which are respectively related to CH\(_2\) and CH\(_3\) group stretching. Additionally, a broad absorption band at 3500–3100 cm\(^{-1}\) was observed, which is characteristic of OH groups. The bands at 1720 cm\(^{-1}\) and 1462 cm\(^{-1}\) are attributed, respectively, to C=O stretching vibration and bending vibrations of methylene groups. The sharp and strong band at 1030 cm\(^{-1}\) is related to the Ti-O-C linkage of the titanate coupling agent. The composite spectra present the characteristic bands of polyethylene related to the methane groups near 2900 cm\(^{-1}\) and 1470 cm\(^{-1}\) and a strong sharp doublet in the 730–700 cm\(^{-1}\) region. Looking at the region of 1300–800 cm\(^{-1}\), the composite spectra present a band near 858 cm\(^{-1}\) related to the mollusk shell particles. The band at 1030 cm\(^{-1}\) was evident only in the spectra of composites modified with the titanate coupling agent, and may also be related to the Ti-O-Ca linkages, as has been suggested for ZnO [24] and CoZ ferrite particles [25].

3.3. Melt flow index (MFI)

Table 2 shows the melt flow rates (2.16 kg at 190 °C) of the composites previously presented in Table 1. Adding MSW to the HDPE (up to 8 wt%) did not significantly alter the melting flow rate. Thus, the mollusk shell particle size variations (on the micron scale) with diameters at 50% (between 5.27 µm and 6.49 µm) did not significantly modify the flow rates of the composites. This behavior is completely different from other observed nano-particulate composites. For example, certain authors [26,27] have observed a considerable increase in the melting flow rate for thermoplastic/nano-CaCO\(_3\), which was attributed to nano-particle rolling (bearing-like), which reduced interlayer interactions in the nanocomposites when melted. Jang, Keon-Soo [28] observed that large talc particles

Fig. 1 – Particle size distribution of mollusk shell-waste (325 mesh samples).

Fig. 2 – FTIR spectra for the titanate coupling agent, MSH5, MSH5T, MSL5 and MSLST composites in the 4000 to 1000 cm\(^{-1}\) region.

Table 2 – MFI for pure HDPE and its composites.

<table>
<thead>
<tr>
<th>Designation</th>
<th>MFI (g/10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>22.0 ± 0.50</td>
</tr>
<tr>
<td>MSH2</td>
<td>21.8 ± 4.01</td>
</tr>
<tr>
<td>MSL2</td>
<td>21.7 ± 2.89</td>
</tr>
<tr>
<td>MSH5</td>
<td>22.5 ± 1.28</td>
</tr>
<tr>
<td>MSL5</td>
<td>22.7 ± 0.98</td>
</tr>
<tr>
<td>MSH5T</td>
<td>22.4 ± 2.08</td>
</tr>
<tr>
<td>MSL5T</td>
<td>22.7 ± 1.56</td>
</tr>
<tr>
<td>MSH8</td>
<td>20.8 ± 2.65</td>
</tr>
<tr>
<td>MSL8</td>
<td>21.8 ± 3.98</td>
</tr>
</tbody>
</table>
act as flaws, which due to their flattened shape tend to slide, yet they reduce the melt flow in composites with higher concentrations. The mollusk particles do not present a definitive shape (as shown in the Figs. 5 and 6). Further, the composites were studied without addition of any flow aids, and the maximum MSW concentration used in the composites was limited to 8 wt%. However, recycling of these wastes as filler for polymeric composites is possible.

3.4. **Differential scanning calorimetry (DSC)**

To study the effect of particle size on the thermal properties of HDPE composites, DSC studies of the non-isothermal crystallization and melting behavior were performed. A DSC cooling scan of the exothermic transition was performed after heating and annealing for 5 min. Fig. 3a shows the DSC cooling scan of the exothermic transition; Fig. 3b shows the DSC heating scan obtained after cooling under controlled conditions. The thermograms of both composites with small (44 μm) and large (74 μm) particles were similar, thus, only those with large particles are shown in the Fig. 3. Calculating the degree of crystallinity was achieved using Eq. (1). The melting enthalpy was obtained in the second heating (Fig. 3b). Table 3 shows the values for crystallization and melting temperature, melt enthalpy, and degree of crystallinity for all of the samples. The HDPE crystallization temperature (Tc) was not altered, remaining at approximately 114 °C, for every mollusk shell-waste particle concentration or all of the compositions studied. None of the particle sizes used for filler participated in HDPE nucleation, even when the initial crystallization temperature (T_{onset}) was increased for the composite concentrations below 5 wt%. The increase in T_{onset} did however accelerate the crystallization process for these composites. The MSW additions did not alter the melt behavior of HDPE, and the influence of particle size was insignificant. However, the degree of crystallinity for the MSH2 and MSL5T composites increased by approximately 10% with respect to that of the pure polymer. This increase was not supported by the Tc(peak) results, as the values did not change. Nevertheless, crystallization was initiated in the MSH2 composite at a temperature above 4 °C (with respect to that of the pure polymer), which could have led to modifications in its crystal structure. Consequently, these potential changes were insufficient to increase either Tc or Tm, but may have contributed to crystallinity increases in the composites. Bartczak et al. [7] have demonstrated that it is possible to obtain higher crystallinity for HDPE/calcium carbonate (CaCO3) composites using a slight increase in Tc. This is attributed to a reduction in the thickness of the HDPE lamellae, and formation of a new fraction of very thin crystallites within it. Further, the effects of inorganic fillers as nucleation agents in thermoplastic matrices have been well documented in the literature for other composites filled with nano or micro-particles (among them, calcium carbonate) [7,11,12,26,29]. Comparing the effects of particle size and coupling agents on T_{onset} and degree of crystallinity for the MSL5T and MSH5T composites, it was observed that the composites, when using the 44 μm particle size filler, presented better results than with 74 μm particles. In fact, the results reveal that by increasing the specific MSW area, (by decreasing the particle size to 44 μm), the coupling agent was more efficient. When the concentration of the mollusk shell particles increased (in the MSH8 and MSL8 composites), no significant changes were observed in their thermal characteristics in relation to HDPE.

3.5. **Thermogravimetric analysis (TGA)**

To investigate the effect of shell-waste filler particle size on the thermal stability of the HDPE matrix, TGA measurements were performed. Both components showed only one stage of decomposition. The temperatures obtained at mass losses of 20% and 50% are shown in Table 4. At 20% mass loss, the respective pure polymer and MSW temperatures were equal.
Table 4 – TGA test results for HDPE and its composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature at 20% mass loss (°C)</th>
<th>Temperature at 50% mass loss (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>434.13</td>
<td>469.98</td>
</tr>
<tr>
<td>MSH2</td>
<td>456.46</td>
<td>469.15</td>
</tr>
<tr>
<td>MSL2</td>
<td>458.11</td>
<td>471.27</td>
</tr>
<tr>
<td>MSH5</td>
<td>462.57</td>
<td>469.15</td>
</tr>
<tr>
<td>MSL5</td>
<td>455.05</td>
<td>472.68</td>
</tr>
<tr>
<td>MSH5T</td>
<td>448.23</td>
<td>469.81</td>
</tr>
<tr>
<td>MSL5T</td>
<td>460.92</td>
<td>471.27</td>
</tr>
<tr>
<td>MSH8</td>
<td>412.75</td>
<td>469.15</td>
</tr>
<tr>
<td>MSL8</td>
<td>460.12</td>
<td>471.27</td>
</tr>
<tr>
<td>MSW</td>
<td>711.19</td>
<td>715.00</td>
</tr>
</tbody>
</table>

MSL5T temperature was practically unchanged in comparison to the MSL5 composite. The maximum degradation temperatures of these composites were not altered. The composites with an 8 wt% MSW concentration, did not present the same tendency toward increased thermal stability of the matrix as did the other composites (2 wt% and 5 wt%). From morphological observations (Fig. 7), the MSH8 and MSL8 composites contained agglomerated particles, though the lower MSW concentration composites presented better particle distributions (Fig. 5). The improvement in thermal stability observed for HDPE upon addition of MSW is similar to that of other polymer composites obtained with other types of mineral particles, suggesting that thermal stability is enhanced when filler particles are well dispersed into the polymer matrix, impeding diffusion of volatile decomposition products due to the formation of carbonaceous char. Consequently, the filler has a physical barrier effect, hindering heat diffusion and degradation of volatiles from the bulk [7,11,32–34]. The agglomeration of MSW in the MSH8 and MSL8 composites may have blocked such particles, preventing their action as physical barrier to the HDPE decomposition.

3.6. Morphological aspects (SEM)

Figs. 5–8 present fracture surfaces and cross-sectional areas of the composites. The shell-waste particles are irregular in shape; and in the composites with lower filler concentrations, especially the 2% composites are well distributed and dispersed as shown in Fig. 5. Another important observation is the presence of voids in the interfacial region of all unmodified composites (Figs. 5 and 6). In addition to the voids observed around the particles, parts of their surfaces were attached to the polymer matrix, indicating that the particles were (in some cases) mechanically anchored. However, regardless of particle size, when the concentration was increased a strong tendency toward agglomeration could be observed (as shown by the black arrows) as seen in Fig. 7a and b. In these composites, the particles are only held in place by a thermal mismatch of the matrix during thermal processing, which induces a clamping effect. The morphological aspect of these composites corroborates the work of Wang et al. [35] with hydroxyapatite-polyethylene composites. Under static loading conditions, the weak interaction between the shell-waste and the HDPE matrix in such composites may not be sufficient to transfer the stress from the matrix to the particles. From this perspective, an improvement in the composite tensile strength would not be expected from higher concentrations of MSW.

Other authors [36] have observed agglomerates in the films of polypropylene composites prepared by casting with egg shell at 5 wt%, being this, the concentration limit for incorporation of such particles into the matrix resulting in mechanical property gains. One can observe the effect of the type of processing employed, in relation to dispersion and distribution of the shell particles in the polymer matrices. For example, egg shell composites prepared by casting process [36], snail composites prepared using twin-screw extruder [37], and in the present work, mollusk shell composites using fluted single screw. From these studies [37], it was concluded that mixtures are more effective when done using a twin-screw extruder.
Fig. 5 – SEM micrographs of the HDPE/MSW fracture surface: (a, b) MSH2 and (c, d) MSL2.

Fig. 6 – SEM micrographs of the HDPE/MSW fracture surface: (a,c) MSH5; (b,d) MSL5.
even if the composites have higher concentrations of in natura snail shell.

In this work, isopropyl tri(diocyl pyrophosphate) titanate coupling agent was used. It is important to consider that beyond its main function of forming a monomolecular layer, and consequently a compatible interfacial region between the shell-waste and HDPE matrix; its chemistry can also improve the thermal properties of HDPE/Shell-waste composites. As to the modified composites (MSHST and MSLST) with the titanate coupling agent, it is suggested that did not occur interfacial interaction between the modified shell-waste particles and the HDPE matrix. The presence of 1030 cm\(^{-1}\) band (Fig. 2) did not favor this interaction. The morphological details can be observed in Fig. 8a and b. In comparing Figs. 6a, b and 8, it can be seen that the voids around the particles were smaller, as seen in Fig. 8 for both modified composites.

3.7. Mechanical properties

The mechanical test results for both unmodified HDPE and its composites are presented in Figs. 9 and 10. Both of the MSH2 and MSL2 composites presented better mechanical behavior, as there was an improvement of approximately 7% in yield tensile values as compared to HDPE, as seen in Fig. 9a. From a morphological aspect, the good dispersion, and distribution of the particles together with the mechanical anchorage contributed to impeding fissure propagation, making MSH2 and MSL2 more resistant. The irregular shapes of the mollusk shell particles helped their anchorage to the matrix, despite the voids present around them. Regarding the presence of particulate agglomerates in the MSL5 and MSL8 composites, the larger surface areas associated to the fine (44 \(\mu\)m) particles contributed to the yield tensile values making them practically the same as HDPE. However, a decrease by about 7% for this property occurred for the MSH5 and MSH8 composites with coarse (74 \(\mu\)m) particles, as they were more affected by the presence of particle agglomerations. Thus, in accordance with other authors [36,38], large particle agglomerates affect the ability of particulate composites to withstand loading. Load transfer from the matrix to the particles occurs more effectively in composites with higher specific area particles. Figs. 6 and 7 present debonding and pull out of particles, which took place in the composites (as indicated by red arrows). Accordingly, composites with finer particles present better results than those with coarser particles. Further, the coupling agent was not sufficient to improve the yield tensile of the composites modified with shell particles at 5 wt%. As shown in Fig. 10, for tensile modulus, the 2 wt% and 8 wt% composites presented improvements as compared to the HDPE matrix. It can be seen, that tensile modulus increases with particle concentration, the best results were observed with the 8 wt% composites. It is known from the literature that the tensile modulus of a polymeric matrix improves with the addition of rigid particles because the rigidity is generally much higher than that
of the organic polymers [39]. In this study, the composites with coarse particles presented higher tensile modulus values than those with finer particles. In Fig. 9c one can observe that tensile strength at break for the 2 wt% composites followed the same tendency as presented for yield tensile. It is noted that the composites with finer particles presented more strength than those with coarser particles (where values were reduced in relation to the value of pure HDPE). The mollusk shell particle sizes influenced the mechanical properties of the HDPE composites. The tensile strength at break of MSH8 was more affected by aggregated particles and voids around them, where dewetting of particles occurred more easily, leading these composites to early failure. It is common in particulate composites with agglomerates that failures begin with structural inhomogeneity of the material [28]. HDPE composite elongation at break was less affected by mollusk shell particle size and the 8 wt% composites were only negligibly decreased.

Under flexural stress (as shown in Fig. 10a and b), both flexural strength and modulus were improved for all composites when adding finer particles (44 μm). As an example, an increase in flexural modulus of about 35% was obtained for the MSL2 composite because of excellent particle dispersion and distribution. For the MSL5 and MSL8 composites, the mechanical properties were only mildly improved in relation to HDPE. Despite the morphological aspects of these composites, (with particle agglomerates), their higher crystallinity (as compared to pure matrix) may have overcome the negative effects of particle agglomeration. The impact strength of the composites improved when the particle size was 44 μm. However, a decrease of approximately 23% was observed for the MSH5 and MSH8 composites. Thus, coarse particles did not contribute to the impact properties of these composites. The results are in accordance with those of Bharathiraja et al. [38], whose composites (with particle agglomerates) had their capacity to carry load affected, reducing their impact strength. The fine mollusk shell particles played an important role in improving the flexural and impact mechanical properties of the HDPE/MSW composites.

4. Conclusion

In this study, mollusk shell-waste particles were added to HDPE in concentrations of 2, 5 and 8 wt%, using microparticles of two different sizes. Superficial modification of the particles was performed using a titanate coupling agent. Matrix flow behavior remained unaltered by the mollusk particle additions. Composites with lower concentrations of filler presented increased crystallinity when compared to HDPE. The degradation temperature (20% mass loss) of the matrix increased together with filler concentrations; however, finer particles were more effective in this respect. In general, the composites with titanate modified particles presented better thermal properties. The results were collaborated by molecular interactions verified by the presence of a band at 1030 cm⁻¹, that contribute to decrease void sizes around the particles. With the addition of lower concentrations of
filler, the yield tensile strength of the matrix increased by approximately 7%. The tensile modulus increased in the 2 wt% and 8 wt% particulate composites. Dispersion and distribution in the lower concentration composites was more effective; improving the mechanical tensile properties. Yet, composite elongation at break was practically unchanged, especially when finer particles were used. Strength and modulus under flexural strength testing, and impact strength were more affected by particle size; the composites with finer particles presented better performance. For HDPE, adding mollusk shell waste at concentrations of 2 wt%, (with finer particles) promotes improvement in both mechanical and thermal properties. Thus, recycling of this residue as a bio-filler for HDPE is promising, especially in ecological applications such as gardens. In addition, its use as a bio-filler in other polymeric matrices may help mitigate environmental problems on the banks of the Paraiba River.

Conflicts of interest
The authors declare no conflicts of interest.

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