To Explore the Effect of Modified Seashell on the Thermo-Mechanical Properties of Polymer Matrix Composite

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Abstract

This research paper proposes a sustainable and feasible technique to utilize seashell waste. The utilization of seashells offers economic and environmental benefits because of their abundant, renewable, and cheap source of calcium carbonate. The technique will reduce the hazards of seashell waste generated to the environment and landfilling that cause risk to water sources and public health. Moreover, the synthesized $bio-CaCO_3$ will reduce the end-product cost of the polymer. The successful synthesis of bio-calcium carbonate powder ($bio-CaCO_3$) was carried out using a calcinations technique up to 800°C from seashells. The high-density polyethylene (HDPE) composite samples were prepared via the industrially preferred melt route by varying the shell powder content by 10% and 20% by weight. The composite was subjected to Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetric (DSC), and mechanical analysis. TGA confirmed the thermal behavior of synthesized $bio-CaCO_3$. The thermal degradation temperature of $bio-CaCO_3$ and virgin HDPE were distinctly observed at 734 °C and 443 °C, respectively, in composite samples. The thermal stability was increased by more than 37 °C in the composite sample at 20% $bio-CaCO_3$ loadings. The percent crystallinity also increased by 14% for higher $bio-CaCO_3$ loadings when compared to virgin HDPE. DSC analysis showed no significant changes in melting points and was not affected by the addition of $bio-CaCO_3$ and remained at about 134 °C in virgin and composite samples. This observation is attributed to the similar crystal structures in all samples. The HDPE composite sample showed higher tensile strength, about 25%, than virgin HDPE. In addition, HDPE10 and HDPE20 composite samples showed lower elongation at break when compared to virgin HDPE in accordance with the literature.

Keywords—High-Density Polyethylene; Seashell waste; Calcinations; Thermo-mechanical properties; composite

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1 Introduction

The Seashell (SS) waste has gained a lot of attention worldwide because of the massive consumption of shellfish and dislodges from the ocean. Millions of seashells have been observed as waste on Clifton beach, Karachi, Pakistan, in the monsoon seasons, notably in 2010, 2011, and 2016. High wave action triggered by the onset of monsoon dislodges shellfish from the sea, and they landed on the beach in the shape of dead shells [1][2]. The phenomenon is very usual on Clifton beach and other countries' sandy beaches. Large seashell waste causes bad odor, injuries from broken seashells, and soil pollution [3]. In ambient conditions, microbes decompose organic matter in seashells and emit ammonia, hydrogen sulfide, and volatile hydrocarbon gases with a strong odor and toxicity that are dangerous to humans. Because of the leachate from seashells and moisture, the seashell stacking is a feeding ground for mosquitoes, rats, mice, and insects [4]. The seafood industries also generate millions of seashells, which are disposed of in landfills. The discarded seashells are a habitat for microbes which causes environmental and air pollution due to the emission of intensive odor, especially during microbial decomposition. Landfills also cause risks to water sources and public health [5]. Seashells

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are rich in calcium carbonate content, which can be used to boost the country's economic development. Most people in Pakistan only use seashells in poultry feed because of their proteins and minerals, while seashell is constantly thrown away as waste despite their useful economic minerals value. The seashell is made up of 95% Calcium carbonate ($CaCO_3$) and 5% organic matter (glycoprotein, polysaccharides, glycosaminoglycan, chitin, and other proteins) [4]. Calcium carbonate is used in process industries that as paper industries, poultry industries, food industries, polymer industries, Paint industries, etc [6][7]. Seashell wastes can be used to manufacture lime, with many advantages, such as the absence of environmental impacts related to the extraction of limestone from mine, lesser energy spent in the comminuting process, and avoidance of landfill disposal costs [5]. Seashell wastes may be used as a source of $CaCO_3$ filler widely used in polymer industries [8]. Li et al. [4] Compare the effect of Seashell and mineral-based calcium carbonate in polypropylene (PP) composite. The seashell / PP composites' mechanical properties were superior to mineral-based commercial calcium carbonate-filled PP composites. They reported higher yield strength, yield strain, tensile strength, and lower Elongation at the break for seashell / PP composites. Essabire et al. [9] also compared the thermo-mechanical properties of lower particle-size seashell $CaCO_3$ and mineral-based $CaCO_3$ / PP composites. The authors report increasing thermo-mechanical properties of both PP composites with little improved properties and with seashell $CaCO_3$. Their findings clearly show that composites prepared from SS particles perform similarly or better than those created from mineral-based $CaCO_3$. It is also reported that the thermomechanical properties of Low-density polyethylene (LDPE) composites are increased by adding cockle shell (CS) enriched in $CaCO_3$ [10]. The author's report improves crystallinity, young modulus, and tensile properties at 10-20 pphr CS loadings. Dweiri et al. [11] disclose the effect of adding eggshells as a bio-filler to HDPE with treated stearic acid on composite thermal, melt flow, and mechanical properties. The treated stearic acid composites have higher crystallinity values than the untreated ones, especially when comparing HDPE/eggshell composites compared to mineral-based $CaCO_3$ composites. The melting points of the composites showed no substantial changes in melting points compared to untreated HDPE/eggshell composites. However, a significant increase in mechanical properties is reported for treated stearic acid composites. In a very recent study [12] the importance of the removal of organic membranes present on eggshells and SS is reported. The PP/eggshell and fish bone powder composite have been determined. The increasing the addition of eggshell and fish bone powder into the PP composite the tensile strength, tensile modulus, flexural, and impact strength were increasing. However, the elongation at the break of the composites was decreasing with an increase in filler contents [13]. Melo et al. [14] HDPE and mollusk shell composite were prepared by melt and injection molding. It has been observed from the research that the crystallinity of the composite increased by 10% by adding 2% bio-based filler. The addition of 20% filler in HDPE composite base increased the 26 °C thermal degradation temperature. The tensile strength increased by 10% by adding 8% filler content.

As far as the authors' knowledge is concerned, modification of seashells, collected from Seaview Clifton Karachi, via calcinations at 800 °C of $bio - CaCO_3$ is not reported in the literature as a bio-filler in polymer matrix composites. The study aims to synthesize $bio - CaCO_3$ from a seashell, use $bio - CaCO_3$ as filler in polymer matrix composite, and explore the effect of modified seashell at 10% and 20% by weight loadings on the thermo-mechanical properties of high-density polyethylene (HDPE). Moreover, this study aims to keep the environment sustainable and insight into different directions for utilizing seashell waste in process industries in the future.

2 Experimental Materials and Method

2.1 Materials

Commercial grade HDPE SABIC (M200056) with a melt flow index of 20g/10min at $190°C$. Seashells (Figure 1) were collected from the seashore of Seaview Clifton, Karachi, Pakistan. Analytical grade hydrogen chloride (HCl) and sodium carbonate (Na_2CO_3) were purchased from Merck.

2.2 Synthesis of Bio-Calcium Carbonate ($bio - CaCO_3$) From Seashell Waste

Small size seashells were collected from the seashore of Seaview Clifton, Karachi, Pakistan. Seashells were washed 3-4 times with distilled water. Seashells were mashed and powdered in a ball mill at room temperature. Thoroughly washed powder with distilled water was dried in a vacuum oven at $60°C$. The dried powdered seashells were calcined into calcium oxide (CaO) after heating in a muffle furnace at $800°C$ for 4 hours [15]. 2 M HCl was added to the CaO powder and stirred overnight at room temperature. The resultant mixture was filtered through Whatman No.1. to

Fig. 1: Seashells wash up on the Seaview Clifton beach in Karachi, Pakistan

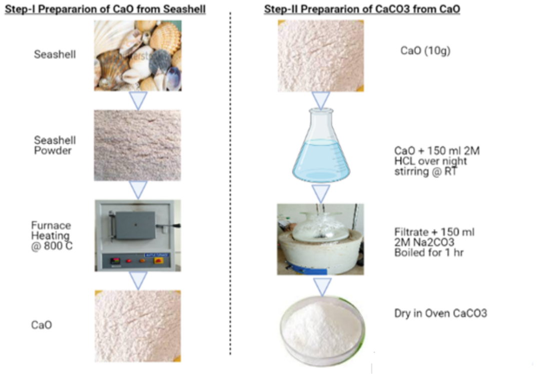


Fig. 2: Synthesis of $bio-CaCO_3$ via a two-step process namely calcinations and chemical treatment. [15]

separate CaCl2 from the mixture. 2 M Na_2CO_3 solutions were added to the filtrated CaCl2. The mixture solution was boiled for 1 hour at $80°C - 100°C$ with continuous stirring. The resultant $bio-CaCO_3$ was dried in a vacuum oven for further use.

2.3 Preparation of HDPE Composites

Oven-dried HDPE and $bio-CaCO_3$ were tumble mixed and melt blended at $190°C$ in a counter-rotating twin-screw extruder (L:D = 40:1. LABTECH Engineering, Thailand). The $bio-CaCO_3$ was mixed in 10% and 20% by weight in HDPE composite samples that will be read as composite samples hereafter. Virgin HDPE was also processed at $190°C$ for comparison purposes. The samples are named HDPE00 (virgin HDPE without filler), HDPE10 (containing 10% by weight $bio-CaCO_3$, and HDPE20 (containing 20% by weight $bio-CaCO_3$). Table 1 shows the composition compositions. The extrudates were crushed into small resins and compression-molded in dumbbell-shaped samples in accordance with ASTM D638 at $190°C$ under the pressure of 10 MPa for mechanical testing.

TABLE 1: Composition of Composites

Sample Name	HDPE (%)	Shell Powder (%)
HDPE00	100	00
HDPE10	90	10
HDPE20	80	20

3 Characterization

3.1 Thermal Gravimetric Analysis (TGA)

Synthesized $bio-CaCO_3$ and composite samples were subjected to TGA analysis on TGA/DSC+3, Mettler Toledo. The $bio-CaCO_3$ sample was heated from room temperature to 900°C at the rate of $10°C$/min under the dry nitrogen (99.99%) with a 30 mL/min flow rate to confirm its purity. Composite samples were heated from room temperature to $600°C$ at $10°C$/min under the dry nitrogen (99.99%) with a 30 mL/min flow rate to determine the thermal stability effect of $bio-CaCO_3$ content on the HDPE composites.

3.2 Differential Scanning Calorimetric (DSC) Analysis

The composite samples' melting point and percent crystallinity were determined using DSC, Mettler Toledo. The samples were heated from room temperature to $300°C$ at $10°C$/min under the dry nitrogen (99.99%) atmosphere with a 30 mL/min flow rate. The crystallinity of virgin HDPE and composite samples was calculated using the following formula, and the enthalpy of melting for 100% crystalline HDPE used was 290 J/g [16]. The amount of filler was corrected for crystallinity determination.

$$Crystallinity(\%) = \frac{\Delta H_m}{\Delta H_{100\%}} \times 100$$

3.3 Mechanical Properties of Specimen

Mechanical properties of the composite samples were determined using a universal testing machine (Zwick DO-FB010 TN, Germany) following ASTM D638M at a crosshead speed of 50 mm/min.

4 Results and Discussion

4.1 Thermal Gravimetric Analysis (TGA)

The TGA thermograms are shown in figure 3 for $bio-CaCO_3$ powder, virgin HDPE, and composite samples. The presence of $bio-CaCO_3$ was confirmed in composite samples as 18% (HDPE20) and 8% (HDPE10), respectively. The amount is slightly

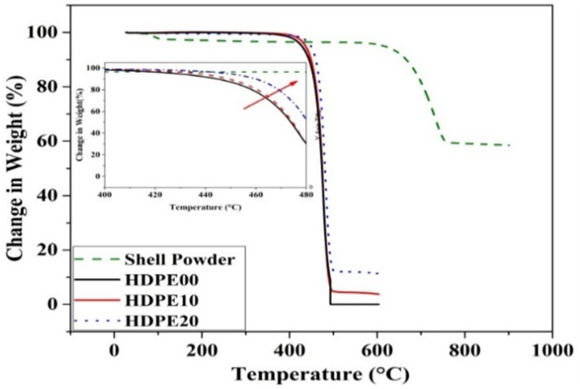


Fig. 3: TGA Thermograms: Thermal stability of $bio - CaCO_3$ and composites, the arrow in the inset graph shows the increase in thermal stability

less than the added amount of $bio - CaCO_3$ in the composite samples. A similar difference in the added amount of filler in composites is reported in the literature [17][18][19]. Both the composite samples show higher thermal stability as compared to virgin HDPE, see inset in figure 3. The arrow direction shows the increase in the thermal stability of the composite samples. To further elaborate on the difference between virgin HDPE and composites' thermal behavior the first derivative (DTG) of the TGA thermogram was plotted in figure 4. For clarity reasons, the virgin HDPE sample thermogram is omitted in figure 4. The DTG curve shows a small peak in $bio - CaCO_3$ at $89^{\circ}C$. This lower peak is attributed to the moisture in the sample. The higher peak at $734^{\circ}C$ of the $bio - CaCO_3$ shows the thermal decomposition of $CaCO_3$ which leads to the formation of CO_2 and CaO as reported in the literature [20][21]. HDPE10 and HDPE20 show thermal degradation temperatures of $477^{\circ}C$ and $480^{\circ}C$ when compared to the virgin HDPE for which the thermal stability temperature is $443^{\circ}C$. It is evident that the composite sample with 20% $bio - CaCO_3$ shows $37^{\circ}C$ higher thermal stability when compared to virgin HDPE. The higher thermal stability of composite samples is attributed to the presence of $bio - CaCO_3$ which might be due to strong interactions between the polymer chain and the filler. A similar increase in thermal stability trends is also reported for other polymer matrix composites [22][9].

4.2 Differential Scanning Calorimetric (DSC) Analysis

Figure 5 shows the DSC thermograms of virgin HDPE and composite samples. The melting temperature of $134.8^{\circ}C$, $89^{\circ}C132.8$ and $134.3^{\circ}C$ were observed for HDPE00, HDPE10 HDPE20, respectively. It is evident that the melting point is not much affected by the addition of $bio - CaCO_3$. Other researchers reported a similar trend in $bio - CaCO_3$ composite samples [23][24]. It is also interesting to note that the onset of melting, marked with the arrow of composite samples is less than the virgin HDPE. This might be due to the nucleation effect of $bio - CaCO_3$ in the composite samples, which leads to smaller crys-

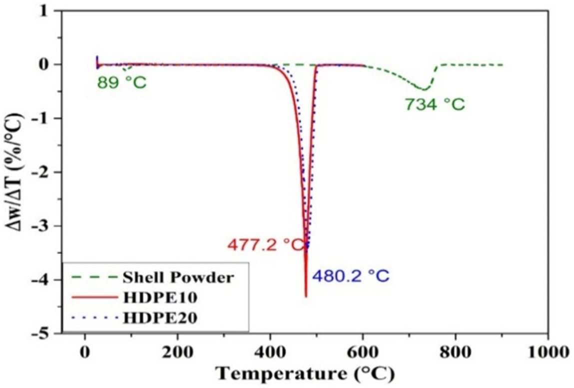


Fig. 4: DTG Graph for $bio - CaCO_3$ and composite

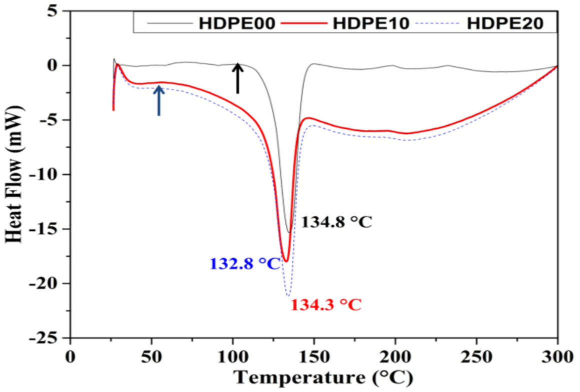


Fig. 5: DSC thermogram for virgin HDPE and composite samples.

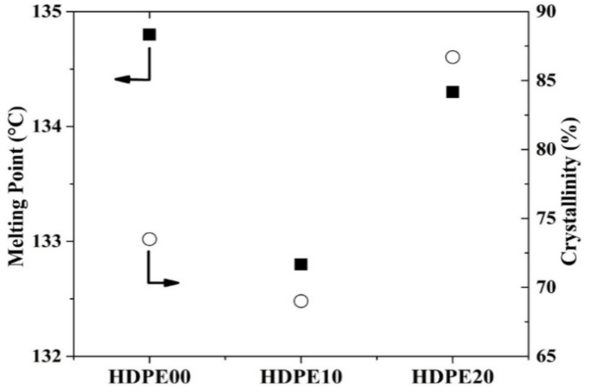
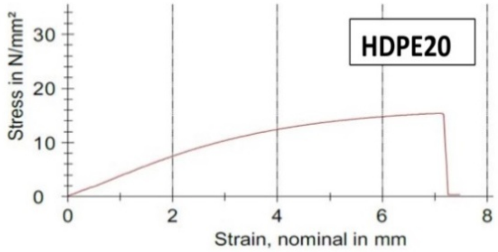


Fig. 6: Melting point and percent crystallinity of virgin HDPE and composites

(a) Stress versus Strain curve for virgin HDPE

(b) Stress versus Strain curve for virgin HDPE10



(c) Stress versus Strain curve for virgin HDPE20

Fig. 7: Stress versus Strain curve

tallites and hence lowers the onset of melting. The nucleation effect of $bio - CaCO_3$ is obvious from the higher percent crystallinity in the HDPE20 sample, see figure 6. The similar nucleation effect of $CaCO_3$ is also reported by other researchers [23][24][25]. The earlier nucleation of composite samples leads to a higher degree of crystallinity notably in HDPE20. The degree of crystallinity is found 73%, 69%, and 87% for HDPE00, HDPE10, and HDPE20 samples, respectively. The HDPE20 sample shows a substantial increase in crystallinity that is about 14% higher than the virgin HDPE.

4.3 Mechanical Properties

4.3.1 Tensile Properties of the Composite and Virgin HDPE

Figure 7 shows the tensile curve of virgin HDPE and composite samples. It is evident that both the composite samples show higher tensile strength when compared to virgin HDPE. Figure 8 (Bar Graph) shows the comparison of tensile strength for the prepared samples namely HDPE00, HDPE10, and HDPE20. Tensile strength was found to be 12.18, 12.86, and 15.08 N/mm2 for virgin HDPE and composite samples containing 10% and 20% by weight $bio - CaCO_3$. The increase in tensile strength is reported by the addition of $CaCO_3$ in the literature [26][27]. A substantial increase in tensile strength is observed for HDPE20 which is 23% higher than virgin HDPE.

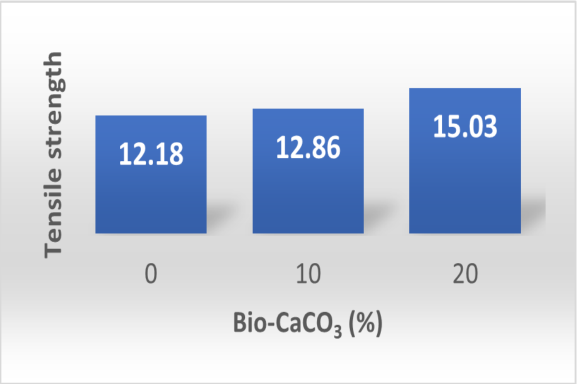


Fig. 8: Effect of $bio - CaCO_3$ on the tensile strength (MPa) of virgin HDPE and composite samples

4.3.2 Elongation at Break of the Composite

Figure 9 shows the comparison of elongation at break, which measures the ductility of material for the samples prepared in this study. Elongation at break was observed at 230%, 64%, and 72% for virgin HDPE, HDPE10, and HDPE20, respectively. It is evident that the ductility of composite samples is decreased with the addition of $bio - CaCO_3$. The decrease in elongation at break with the increasing content of

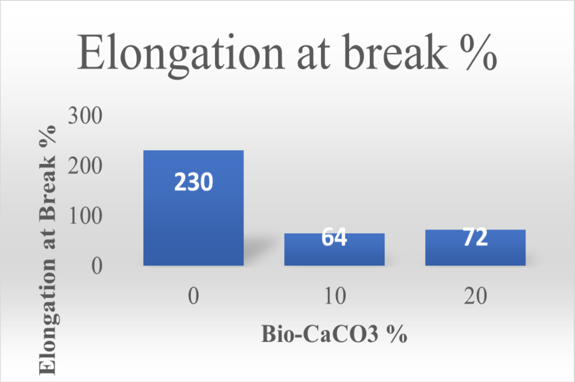


Fig. 9: Effect of $bio-CaCO_3$ on the Elongation at break of virgin HDPE and composite samples

$bio-CaCO_3$ is also reported by other research groups [28]. The decrease in elongation at break is attributed to the adhesion of polymer chains on the surface of $bio-CaCO_3$ particles, which restricts their mobility [28]. However, the HDPE20 sample shows an 8% increase in elongation at break compared to HDPE10. The effect might be due to the better dispersion of $bio-CaCO_3$ in the former composite.

5 Conclusion

The successful synthesis of $bio-CaCO_3$ was carried out using calcinations techniques from seashells that will reduce the hazards of a seashell to the environment and landfills. $bio-CaCO_3$ filler is a cost-efficient filler that will apply in process industries. Composite samples with 10% and 20% by weight loadings of $bio-CaCO_3$ were prepared via the industrially preferred melt route. The purity and composition of $bio-CaCO_3$ were carried out with TGA analysis. The two distinct thermal degradation peaks were observed in the range of $443°C$ and $734°C$. The first and second degradation peaks are attributed to the virgin HDPE and $bio-CaCO_3$ respectively. The content of $bio-CaCO_3$ was found to be 8% in HDPE10 and 18% in HDPE20. The thermogram showed a similar decomposition phenomenon of the mineral $CaCO_3$ as reported in the literature. The thermal stability of HDPE was enhanced with the addition of $bio-CaCO_3$. The higher content of $bio-CaCO_3$ leads to higher thermal stability. The increase in the thermal stability of HDPE20 was found to be $37°C$ higher than virgin HDPE. The melting temperature $134.8°C$, $132.8°C$ and $134.3°C$ of HDPE00, HDPE10 and HDPE20 respectively. The melting point of virgin HDPE ($134.8°C$) and composite samples were comparable which might be due to the same morphological structure. The degree of crystallinity was comparable or increased by 14% notably in HDPE20 when compared to virgin HDPE. The increase in percent crystallinity is attributed to the nucleation effect of $bio-CaCO_3$. The tensile strength was also increased by 23% for composite samples, compared to virgin HDPE, containing 20% by weight $bio-CaCO_3$. However, the elongation at break is decreased for composite samples as expected. It is interesting to note that the HDPE20 sample showed higher elongation at break than HDPE10. The study will not only help in the reduction of landfilling resulting from seashells but will also provide a cost-effective bio-based filler for process industries.

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