STUDY ON THE ALKALINE-SILANE TREATED COCONUT SHELL POWDER MODIFIED HIGH DENSITY POLYETHYLENE FOR ROOFING APPLICATIONS

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Abstract
Modified thermoplastics, prepared with inorganic fillers, are used as an alternative to conventional roofing materials. The use of natural filler like coconut shell powder (CSP) will be an advantage as it is renewable, biodegradable and low cost. This study was carried out to develop CSP filled High Density Polyethylene (HDPE) composites to use as a roofing material. The objectives of this study were to develop composites with untreated and alkali-silane treated CSP at different loadings, to identify the optimum CSP loading, and to investigate the effect of treatment on mechanical properties and water absorption of composites. Of the properties studied, impact strength, tensile strength and water absorption, the major properties for roofing materials, dropped with incorporation of CSP into HDPE. However, properties were improved with the incorporation of treated-CSP and optimum loading was at 20%. Scanning electron microscopic images confirmed a better filler-matrix adhesion with CSP after alkaline-silane treatment.

Keywords: Alkaline-silane treatment, Natural filler, Modified thermoplastics, Morphology, Mechanical properties, Coconut shell powder

1. Introduction
Thermoplastic materials with superior properties are not cost effective compared to reinforced composites with conventional thermoplastics and therefore modified thermoplastics are developed for possible economic advantages. Thermoplastic modifications are done by incorporating fillers with and without reinforcement agents. Inorganic fillers such as calcium carbonate, silica, talc, kaolin and aluminum tri-hydrate, and organic fillers, both natural and synthetic, are used in developments of thermoplastic composites. Although a number of cellulosic fillers are available, organic natural fillers such as wood flour, shell flour and cellulose pulp are most often used (Ritchie et al., 1972). It was seen that treated coconut shell powder (CSP) enhanced mechanical properties such as tensile strength, hardness, impact strength etc. of polyester composites (Salmah et al., 2012). Low density polyethylene composite with CSP at 25% filler loading has shown tensile strength of 9 MPa (Olumuyiwa et al., 2012).

CSP, a agro-waste and lignocellulosic filler, compared to common mineral fillers exhibits some admirable advantages like low cost, renewable, high specific strength-to-weight ratio, minimal health hazard, low density, less abrasion to machine, biodegradability and environmental friendliness (Sarki et al., 2011; Udhayasankar & Karthikeyan, 2015). Further, adhesion property of CSP to polymer could be enhanced by surface modifications with silane treatment, alkaline treatment, and using a compatibilizer (Salmah et al., 2012). Combined effect of alkaline treatment prior to silane treatment has shown improved properties of a natural fiber named Henequen fiber filled high density polyethylene (HDPE) when peroxide was used as a catalyst for the reaction of fiber and polymer (Herrera-Franco & Valadez-González, 2005). Silane treatment alone will not restrict adverse effect like moisture absorption as amorphous structure of hemicellulose and lignin are also contribute to hydrophilic nature of natural fiber. Pre-alkaline treatment will contribute to reduction in non-cellulose and other impurities present in the fibre. Further, it exposes more cellulose on the surface of the fiber enhancing chemical bonding with the polymer matrix (Li et al., 2007). There are several silane treatment methods for natural fiber, which includes spraying method (Hill, 2006), pumping of silane and initiator into natural fillers and thermoplastic during extrusion (Bengtsson & Oksman, 2006) and impregnation process. Of them, impregnation process is the most efficient (Donathet et al., 2006).
Natural fibers and fillers are incorporated into thermoplastics to produce composites for roofing applications (Herrera-Franco, 2005). Coir-polyester composite is one example. In the construction sector of Sri Lanka, clay tiles, metal sheets, polycarbonate sheets, thatched sheets and asbestos are used as conventional roofing materials. Of them, asbestos is the most popular due to its strength, light weight and low cost. However it is reported as a carcinogen. Therefore, need of an alternative roofing material has been arisen as other conventional materials lacks cost benefits, availability and durability offered by asbestos.

HDPE is also used in roofing applications (European Patent No. EP 2687646 (A1), 2014), (Anon., n.d.). However, HDPE alone cannot be used due it’s to low impact properties and low rigidity. Addition of natural filler like CSP will enhance such mechanical properties of HDPE, and especially will promote biodegradation. More importantly, development of roofing material made of HDPE with CSP as filler is not yet been carried out. Due to composite’s thermoplastic behavior, reprocessing can be done in case of a production defects or damage caused during the usage, and after use. Sri Lanka is a coconut cultivation country, and widely exports CSP as charcoal without giving a value addition for CSP. Therefore, the aim of this study was to develop a CSP filled HDPE composites which can be used as a roofing material. Drawbacks displayed by current roofing products will be addressed through this product. The objectives of this study are to develop CSP filled HDPE composites, and to identify the optimum CSP loading before and after surface treatment of CSP on mechanical properties and water absorption of the composites.

2. Materials and Methods
HDPE of extrusion grade (SABIC- HDPE CC254, MFR - 6.3 g/10 min) was used as the base polymer. CSP was obtained from Silver Mills, Girulla, Sri Lanka and was sieved to 35-45 micron size. For the surface modification of CSP, Silane (triethoxyvinyl Silane) was used. Sodium hydroxide (NaOH) aqueous solution (10% w/v) was used to perform alkaline treatment. Silane acted as the coupling agent. Dicumyl peroxide performed as an initiator to the reaction between the Silane and HDPE. All chemicals were of industrial grade and were used without further purification.

For the Silane treatment, 1 w% silane and 0.5 w% dicumyl peroxide were dissolved for their hydrolysis in a mixture of methanol–water (90/10 w/w) at 30 °C. Treated CSP was then washed with distilled water until all NaOH was eliminated. This was repeated until washed water no longer indicates any alkalinity reaction. pH of the solution was adjusted to 3.5 with acetic acid under continuous stirring for 10 min. CSP was then immersed in the solution and left for 1 hour under agitation. The treated CSP was then dried at 70 °C for 24 hours (Balan, et al., 2017).

Composite compounds with CSP were prepared by varying the CSP loading from 10% to 50% by weight at 10 % intervals. Selected composite compounds with treated-CSP were prepared at CSP loading of 10%, 20% and 30%. HDPE and CSP were mixed using plasticorder operating at a speed of 75 rpm and at a temperature of 140 °C for 8 minutes. Composite compounds were compression moulded at a temperature of 150°C under 30 MPa pressure for 8 minutes to prepare test specimens required for property testing.

Tensile and tear tests were performed using Hounsfield Universal tensile tester according to ASTM D751 standard, where dumbbell and crescent test specimens were used, respectively. Crosshead displacement was
taken as the displacement, while maintaining the strain rate at 50 mm/min. Flexural testing was performed using specimens having dimensions of 250×25×5 mm using three point bending test. Support span was maintained at 120 mm length. Izod impact test was performed as per BS EN ISO 180:2001 standard, using test specimens having dimensions of 80×10×5 mm. Shore Durometer of type D, was used to perform hardness test according to ASTM D2240. For water adsorption, moulded specimens having dimensions of 50×10×4 mm were immersed in water for 24 hours, and the weight difference before and after immersing was considered. Tensile fracture surfaces of the composites with and without treated CSP were gold sputtered and observed under Scanning Electron Microscope.

3. Results and discussion

3.1 Mechanical Properties

Roofing materials must withstand to weight and other external stresses and therefore tensile strength is considered as an important property for a roofing material. Tensile strength and tear strength of the CSP filled HDPE composites are given in Figure 1 and Figure 2, respectively. HDPE has a tensile strength of 37 MPa. With addition of CSP to HDPE, tensile strength drops drastically to 22 MPa at 10% CSP loading, and further decreases with increase in CSP loading. This drop will be due to disturbance of crystalline structure of HDPE by CSP filler, and to poor interfacial adhesion between the two phases. However, composites with the alkaline-silane treated-CSP showed greater strength at every CSP loading studied. Tear strength is also showed similar pattern of property variation. Composite with treated-CSP at 20% loading shows the best tensile and tear strengths. Further, composites with treated-CSP and untreated-CSP do not show significant variations at CSP loading greater than 20%.

Impact strength is an important property for roofing products, as they must be able to bear the impact of hails. Impact strength is related to the energy absorbed by a material during fracture and is indicated toughness of the material. Impact strength of the composites are given in Figure 3. Impact strength of composites decreases with increase in CSP loading. At similar CSP loadings, composites with treated-CSP exhibits higher strength (increased by 40%) compared to those with untreated-CSP. This is associated with the greater interfacial adhesions between CSP and HDPE created through silane coupling agent.

Flexural strength provides bending capabilities of a roofing material. Flexural strength is increased with the addition of CSP as filler, however, no significant changes are shown with increase in the CSP loading. Flexural strength is reduced drastically after alkaline-silane treatment. Silane treatment remove hydrophilic components of CSP and initial alkaline treatment promotes the partial removal of the hemicelluloses, waxes present on the surface of the fiber. This leads to reduction in stiffness, which eventually lower the flexural strength.
3.2 Hardness
Hardness is resistance of material to plastic deformation caused by indentation. Hardness is considered to be one of the important factors in composites for determination of wear rate. To qualify as roofing material, composite must possess a recommended hardness. Figure 5 illustrates increase of hardness with the addition of CSP, as similar to incorporation any filler into thermoplastics. However, the addition of treated-CSP decreases hardness to a greater extent and is due to increase of flexibility of the composite. These results are in line with the impact properties, and confirm that the incorporation of treated-CSP into HDPE reduces rigidity of HDPE and makes it tough and more suitable for roofing applications.

3.1 Water Absorption
Water absorption of HDPE and composites with treated- and untreated-CSP is given in Figure 6. It can be found that the water absorption of HDPE is dropped with incorporation of CSP. CSP consists of high lignin content (Mohanty et al., 2001), which is hydrophobic in nature and therefore, CSP has contributed to decrease in water adsorption of the composites. Alkaline-silane treatment reduces the hydrophilic nature of CSP, as silane reacts with hydroxyl groups of CSP, and further reduces the water absorption property when incorporated treated-CSP into HDPE.

3.2 Morphology
The microstructural characterization is an important step in understanding practical engineering properties of a material. For composites, the microstructural characterization is even more critical, as many possible arrangements that can exist between the reinforcing phase and the matrix. SEM images of tensile fracture surfaces of HDPE-CSP composites with treated- and untreated-CSP at 20% and 30% loadings are illustrated in Figure 7. The composites with untreated–CSP (Figure 7 (a) and (b) ) show discontinuous phases between CSP and HDPE matrix, and is mainly caused by the poor wetting of hydrophilic filler by hydrophobic polymeric matrix. In addition, there are numerous of holes caused by CSP filler pull out. All of this indicate that the incompatibility and poor filler-matrix interfacial adhesion. SEM images for the composites with treated-CSP given in Figure 7 (c) and (d) show rough fracture surfaces, suggesting better filler–matrix adhesions in the composites. The treated-CSP particles are embedded tightly in the HDPE matrix. This morphology developed through silane coupling is the reason for the enhancement of mechanical properties of HDPE-CSP composites discussed above.

4. Conclusions and Recommendations
Tensile, tear and impact strengths of composites with untreated-CSP decreased with the CSP loading from 10% to 50%, with a drastic decrease from 40%, suggesting that the incorporation of CSP loading was limited to 30%. Flexural strength and hardness dropped due to partial removal of CSP constituents during treatment. In overall context, water absorption, impact strength, tear strength and tensile strength of composites with treated-CSP were improved, when compared to composites with untreated CSP. This clearly showed the coupling effect of silane for HDPE and CSP. SME analysis was evident to good phase adhesion between CSP and HDPE after alkaline-silane treatment of CSP. Under the given treatment and processing parameters, composite with CSP loading of 20% generates most favorable properties, and it will be suitable for production of roofing tile/sheet. Further investigation could be focused to determine weather ability, biodegradability of
the composites and the process ability of the composite compounds to confirm its applicability as eco-
freindly roofing material.

5. Tables and Figures

![Figure 1-Tensile Strength of HDPE-CSP composites](image1)

![Figure 2- Tear Strength of HDPE-CSP composites](image2)
Figure 2 - Impact Strength of HDPE-CSP composites

Figure 3 – Flexural Strength of HDPE-CSP composites
Figure 4 – Hardness of HDPE-CSP composites

Figure 6 – Water absorption of HDPE-CSP composites
Figure 5 – SEM images of tensile fracture surfaces of HDPE-CSP composites with

(a) 20% untreated CS   (b) 30% untreated CSP
(c) 20% treated CSP(d) 30% untreated CSP
6. References