Pak. j. sci. ind. res. Ser. A: phy. sci. 2022 **65A**(3) 214-225

Effects of Cassava Peel and Eggshell on Some Properties of High-Density Polyethylene Composites

Joe Nwiyoronu, Chisom C. Umeileka, Remy U. Duru* and John O. E. Otaigbe
Department of Pure and Industrial Chemistry, University of Port Harcourt, Nigeria

(received July 6, 2020; revised March 25, 2021; accepted June 22, 2021)

Abstract. The need to produce biocomposites from agro-wastes materials with enhanced properties informed the basis of this investigation. Composites were prepared from cassava peel, eggshell and high-density polyethylene (HDPE) using an injection moulding machine. The study investigated the effects of eggshell powder (ESP) loadings of 30 wt.% and cassava peel powder (CPP) loadings of 10, 20, 30 wt.% on the mechanical, water absorption and biodegradable properties of HDPE composites. Results of the determined mechanical parameters showed a significant decrease in the tensile strength, tensile modulus, elongation-at-break, flexural strength, flexural modulus and impact strength as the CPP content increases. The water absorption behaviour of the composites increased as a function of the duration of exposure, while the biodegradable properties showed a steady decrease in the weights of the composites as a function of time of exposure in the soil and filler content. The results have shown that the incorporation of CPP and ESP into the polymer matrix provides significantly enhanced water absorption and bio-degradable properties with retarded mechanical properties.

Keywords: biocomposites, cassava peel powder, eggshell powder, biodegradable, mechanical properties

Introduction

The non-biodegradability of synthetic plastics and the reduction in fossil fuel production worldwide have stimulated a search for alternative sources of raw materials for the polymer industry. Synthetic plastics and agricultural wastes have contributed significantly to environmental pollution but the former contributes more to the accumulation of solid wastes that are not degraded. This has led to the search for new biodegradable materials with improved mechanical properties for both domestic and industrial applications. Furthermore, the demand for developing new polymeric materials with enhanced properties has been on the increase for the last few decades. This has led to the continuous rise of mixing different polymers among industries and researchers to meet these demands and explore the potentials of newly developed polymer products.

Polymer composites are formed from polymer resins (thermoplastic or thermosets) and filler materials (organic or inorganic) that are usually combined to produce a blend with either superior or inferior properties from that of the individual components as well to reduce the cost of the desired end product (Owuamanam and Cree, 2020). The properties of these composites formed are usually influenced by factors, such as the amount of filler, materials' characteristics and interfacial adhesion (Liang, 2006; Osman *et al*., 2004). Polyethylene (PE) is one of the most versatile and important polymeric materials used for different applications. Often, the materials are rarely applied as neat polymers due to the restriction resulting from the melting point and swelling of the hydrocarbon (Murugan *et al*., 2018). To fulfill the increasing demand for PE in polymer applications, various additives, such as fillers, antioxidants, plasticizers, flame retardants and stabilizers are added during the compounding of polyethylene in a bid to achieve the specifications and requirements of a particular application.

There has been a rapid growth in the utilization of natural fibre (e.g., wood and agro-wastes) as fillers when compared to synthetic fibre (e.g., glass) in the formation of composites. This is due to their renewability, low cost, density and thermal conductivity, high mechanical properties and nontoxicity (Boran, 2016; Ifuku and Yano, 2015; Zulkifli *et al*., 2015; Peng *et al*., 2014; Eichhorn *et al*., 2010). Apart from these properties, the need to apply a waste management approach by converting some agricultural wastes generated in our environment to value added products which aid the production of biodegradable products is very essential in the innovative concept of waste-to-wealth. Many

---

*Author for correspondence;
E-mail: remy.duru@uniport.edu.ng

studies have reported the preparation of composites with varying properties using fillers that are agricultural wastes such as, rice husk (Yap *et al*., 2020), palm kernel shell fiber (Oladele *et al*., 2020), corn husk fibre (Ibrahim *et al*., 2019), coconut husk (Ipilakyaa *et al*., 2019 and cassava cortex (Omah *et al*., 2018). Cassava (Manihot esculenta crantz), serves as a major staple food and source of energy in most developing countries. Africa remains the continent with the highest cassava production about 230 million tons in 2012 which corresponds to 53% of world production (Pondja *et al*., 2017). Large of wastes are generated daily by amount cassava processing industries and the impact on the environment could be alleviated through proper waste management. Cassava peel is an agro-industrial waste, obtained mechanically by peeling the tubers and it is very rich in carbohydrate. The chemical composition is cellulose (9.7%), hemicellulose (32-36%), protein (3.7%), lignin (16.89%) and ash (11.38%) which is subject to change or vary probably due to different climatic conditions, harvesting period, soil fertility and type (Nanssou *et al*., 2016). Annually, cassava peels production in Nigeria is about 450, 000 tons with a tendency to increase (Ajao *et al*., 2009). These peels (periderm and cortex) are usually discarded and allowed to rot and decay. Many studies have reported the use of cassava peels as feed, adsorbent, composites, briquettes and treatment of mine water (Waheed and Akogun, 2021; Akogun *et al*., 2020; Czaikoski *et al*., 2020; Oladele *et al*., 2020; Omah *et al*., 2018; Pondja *et al*., 2017; Edhirej *et al*., 2017; Schwantes *et al*., 2016; Simate and Ndlovu, 2015; Apata and Babalola, 2012).

Calcium carbonate is perhaps the most commonly used inorganic fillers for the production thermo plastics (Chan *et al*., 2002; Bartczak *et al*., 1999). Chicken eggshell, an agricultural by product obtained from chicken, predominantly contains about 94% calcium carbonate in the form of calcite (Karuppannan *et al*., 2021), a trace amount of other compounds and organic materials (Eletta *et al*., 2016; Hassan *et al*., 2012; Hussein *et al*., 2011). Many studies have reported the use of eggshell as a reinforcer in polymer matrixes, such as polypropylene, HDPE, Polyester, LDPE etc (Murugan *et al*., 2018; Hassan *et al*., 2012; Hussein *et al*., 2011; Shuhadah and Supri, 2009; Toro *et al*., 2007). There are other applications of eggshell composites such as in ceramic (Ramesh *et al*., 2016), particle board (Adediran *et al*., 2019) and cementpaper hybrid for ceiling boards (Adediran *et al*., 2020). Improved tensile modulus and increased crystallization temperature have been observed with eggshell-polypropylene composites (Ghabeer *et al*., 2013; Toro *et al*., 2007). On the other hand, cassava peels have shown to improve the crosslink density, tensile strength and tensile modulus of natural rubber latex (Harahap *et al*., 2016). The study investigates the concurrency and feasibility of eggshell and cassava peel in the same polymer matrix intending to produce more environmentally friendly plastic products. Thus, some mechanical properties (tensile, flexural, elongation at break and impact), water absorption and biodegradable behaviour of these composites were determined.

Material and Methods

The experimental procedure is schematically presented in Fig. 1.

The high-density polyethylene (HDPE) (density 0.956 g/cm^3, melt flow index 11 g/10 min) used for the study was supplied by Indorama Petrochemicals Company Ltd., Eleme, Nigeria. Cassava peels were obtained from a local farmer in Kabangha, Nigeria. They were carefully processed to obtain cassava peel powder (CPP) and the mesh size used was 90µm. Eggshells were also sourced from local eateries around Elelenwo area of Nigeria. The processed eggshell that was screened using the same mesh size as CPP was used for composite production.

Preparation of cassava peel and eggshell filled composites. All the materials were oven-dried at 110 °C to constant weight and then stored in air-tight containers. The moisture contents of the fillers were also determined, while the compounding and production of the composites were done at Ceeplast Industry, Ltd., Nigeria. The sieved eggshell powder ESP (30 wt.%),

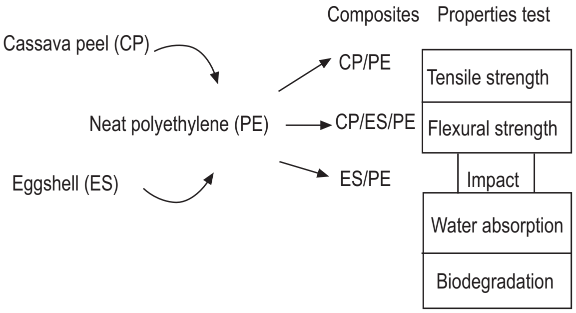

Fig. 1. Schematic representation of the experimental procedure.

cassava peel powder CPP (10, 20, 30 wt.%) and HDPE were mixed in different ratios to produce the final composite. All the processing parameters are presented in Table 1. They were introduced into the injection moulding machine (4.6 KW, 10 H, Taiwan) through the hopper at 200 °C. The mixture was melted into a paste in the barrel of the machine at 220 °C and moved under pressure at 60 rpm through the nozzle to the mould where flat sheets measuring 160 mm × 160 mm were ejected.

Mechanical properties. ***Tensile properties.*** Tensile test was performed using Universal Instron Testing Machine (model 3369). The composite samples were prepared according to ASTM D638 at 25 °C and a fixed cross head speed of 10 mm/min to obtain tensile strength, tensile modulus and elongation at break. The results presented are the average value of three runs for each of the samples.

Flexural properties. The flexural test was also determined using the same Universal Instron Tester per ASTM D790, at a crosshead speed of 3 mm/min by using three point bending geometry to evaluate the flexural strength and modulus. The test was carried out at room temperature and the average value obtained for three runs for each of the samples was recorded.

Impact test. Notched Izod Impact Tester was used on the samples per ASTM D256 to determine the impact strength of the composites. Different measurements arising from the three runs were obtained for each of the composites and the average value was computed.

Water absorption test. For the water absorption study, ASTM D750-95 standard was used. The samples were cut into dimensions measuring 4 cm × 4 cm, oven-dried at 50 °C for 24 h and weighed to get the initial dry weight (W_i). The weighed samples were then introduced into distilled water for 42 days. The weights of the samples were measured at intervals of 7 days to determine their weight gain. The percentage of water absorption Table 2 was computed using the equation below:

$$\text{Water absorption Wa (\%)} \frac{W_w - W_i}{W_i} = \times 100$$

where:

W_w = wet weight; W_i = initial dry weight.

Biodegradation test. The biodegradation was determined by the soil burial test. A modification of the method by Riyajan *et al*. (2012) was used for the study. The composite samples were cut into dimensions measuring 4 cm × 4 cm, oven-dried at 50 °C for 4 h and weighed to obtain the initial weight (W_i). The weighed samples were then buried differently in different holes of depth 20 cm for a period of 100 days. Each of the samples was carefully exhumed after 25 days regular interval and the exhumed samples were washed, oven-dried for 4 h at 50 °C and then weighed. The weight loss was recorded as weight after degradation time (W_d) and the percentage rate of biodegradation Table 3 was calculated using the equation below:

$$\text{Biodegradation Br (\%)} \frac{W_i - W_d}{W_i} = \times 100$$

where:

W_i = initial weight of the samples; W_d = weight of the samples after degradation time

Table 1. Composition of CPP and ESP filled polymer composites

Samples	Weight composition (%)		
	PE	CPP	ESP
NEAT HDPE	200	-	-
HDPE/CPP-10	190	10	-
HDPE/CPP-20	180	20	-
HDPE/CPP-30	170	30	-
HDPE/CPP-0/ESP-30	170	-	30
HDPE/CPP-10/ESP-30	160	10	30
HDPE/CPP-20/ESP-30	150	20	30
HDPE/CPP-30/ESP-30	140	30	30

HDPE = high density polyethylene; CPP = cassava peel powder; ESP = eggshell powder.

Results and Discussion

Mechanical properties. The mechanical properties, such as tensile strength and modulus, elongation at break, flexural strength and modulus and impact strength were affected by the incorporation of cassava peels powder (CPP) and eggshell powder (ESP).

Figures 2-3 illustrate the variation of tensile strength and tensile modulus with the filler loadings. The tensile strength of the composites decreases with increasing filler content. CPP-ESP filled composites exhibited much lower tensile strength when compared to CPP-filled composites and ESP-filled composite. This decrease may be attributed to two factors, the interactions

Table 2. Rate of water absorption by the composites

(a) after 7 days

Samples	Initial wt(g)	Initial thickness (mm)	Final wt(g)	Final thickness (mm)	Dwt	(%) increase
Neat HDPE	6.44	3.04	6.44	3.04	0	0
190 g HDPE/10 g CPP	7.46	3.15	7.49	3.16	0.03	0.4
180 g HDPE/ 20 g CPP	7.53	2.86	7.54	2.87	0.01	0.13
170 g HDPE/ 30 g CPP	5.80	2.95	5.81	2.96	0.01	0.17
170 g HDPE/ 30 g ESP	7.25	3.02	7.28	3.04	0.03	0.41
160 g HDPE/ 10 g CPP/ 30 g ESP	6.33	3.01	6.42	3.02	0.09	1.42
150 g HDPE/ 20 g CPP/ 30 g ESP	7.16	3.04	7.20	3.05	0.04	0.56
140 g HDPE/ 30 g CPP/ 30 g ESP	7.64	3.03	7.65	3.04	0.01	0.13

(b) after 14 days

Samples	Initial wt(g)	Initial thickness (mm)	Final wt(g)	Final thickness (mm)	Dwt	(%) increase
Neat HDPE	6.44	3.04	6.46	3.05	0.02	0.31
190 g HDPE/10 g CPP	7.46	3.16	7.50	3.17	0.04	0.54
180 g HDPE/ 20 g CPP	7.53	2.87	7.57	2.88	0.04	0.53
170 g HDPE/ 30 g CPP	5.80	2.96	5.83	2.97	0.03	0.52
170 g HDPE/ 30 g ESP	7.25	3.04	7.33	3.05	0.08	1.10
160 g HDPE/ 10 g CPP/ 30 g ESP	6.33	3.05	6.45	3.05	0.12	1.90
150 g HDPE/ 20 g CPP/ 30 g ESP	7.16	3.05	7.24	3.06	0.08	1.12
140 g HDPE/ 30 g CPP/ 30 g ESP	7.64	3.04	7.66	3.04	0.02	0.26

(c) after 21 days

Samples	Initial wt(g)	Initial thickness (mm)	Final wt(g)	Final thickness (mm)	Dwt	(%) increase
Neat HDPE	6.44	3.05	6.47	3.06	0.03	0.47
190 g HDPE/10 g CPP	7.46	3.16	7.53	3.17	0.07	0.94
180 g HDPE/ 20 g CPP	7.53	2.86	7.57	2.87	0.04	0.53
170 g HDPE/ 30 g CPP	5.80	2.95	5.87	2.97	0.09	1.55
170 g HDPE/ 30 g ESP	7.25	3.07	7.37	3.09	0.12	1.66
160 g HDPE/ 10 g CPP/ 30 g ESP	6.33	3.05	6.46	3.07	0.13	2.05
150 g HDPE/ 20 g CPP/ 30 g ESP	7.16	3.06	7.27	3.07	0.11	1.54
140 g HDPE/ 30 g CPP/ 30 g ESP	7.64	3.04	7.70	3.04	0.02	0.78

(d) after 28 days

Samples	Initial wt(g)	Initial thickness (mm)	Final wt(g)	Final thickness (mm)	Dwt	(%) increase
Neat HDPE	6.44	3.04	6.49	3.06	0.05	0.78
190 g HDPE/10 g CPP	7.46	3.17	7.58	3.18	0.12	1.61
180 g HDPE/ 20 g CPP	7.53	2.87	7.63	2.89	0.10	1.33
170 g HDPE/ 30 g CPP	5.80	2.97	5.88	2.98	0.08	1.4
170 g HDPE/ 30 g ESP	7.25	3.10	7.40	3.10	0.15	2.07
160 g HDPE/ 10 g CPP/ 30 g ESP	6.33	3.7	6.49	3.07	0.16	2.52
150 g HDPE/ 20 g CPP/ 30 g ESP	7.16	3.06	7.27	3.07	0.11	1.54
140 g HDPE/ 30 g CPP/ 30 g ESP	7.64	3.05	7.72	3.06	0.02	1.04

Continued ....

(e) after 35 days

Samples	Initial wt(g)	Initial thickness (mm)	Final wt(g)	Final thickness (mm)	Dwt	(%) increase
Neat HDPE	6.44	3.06	6.50	3.07	0.05	0.98
190 g HDPE/10 g CPP	7.46	3.18	7.54	3.19	0.08	1.07
180 g HDPE/ 20 g CPP	7.53	2.88	7.62	2.88	0.09	1.20
170 g HDPE/ 30 g CPP	5.80	2.98	5.87	2.91	0.11	1.20
170 g HDPE/ 30 g ESP	7.25	3.09	7.44	3.11	0.19	2.62
160 g HDPE/ 10 g CPP/ 30 g ESP	6.33	3.07	6.66	3.09	0.33	4.27
150 g HDPE/ 20 g CPP/ 30 g ESP	7.16	3.08	7.30	3.11	0.14	2.09
140 g HDPE/ 30 g CPP/ 30 g ESP	7.64	3.06	7.74	3.07	0.10	1.31

(f) after 42 days

Samples	Initial wt(g)	Initial thickness (mm)	Final wt(g)	Final thickness (mm)	Dwt	(%) decrease
Neat HDPE	6.44	3.07	6.51	3.07	0.09	1.09
190 g HDPE/10 g CPP	7.46	3.19	7.58	3.20	0.12	1.88
180 g HDPE/ 20 g CPP	7.53	2.88	7.63	2.89	0.10	1.33
170 g HDPE/ 30 g CPP	5.80	2.90	5.90	2.91	0.07	1.72
170 g HDPE/ 30 g ESP	7.25	3.11	7.58	3.13	0.33	4.55
160 g HDPE/ 10 g CPP/ 30 g ESP	6.33	3.09	6.67	3.13	0.34	5.37
150 g HDPE/ 20 g CPP/ 30 g ESP	7.16	3.11	7.46	3.12	0.24	3.35
140 g HDPE/ 30 g CPP/ 30 g ESP	7.64	3.07	7.65	3.09	0.15	1.96

between the filler-matrix and the filler-filler. The latter effect is more pronounced for the CPP-ESP filled composites which have an increased amount of the content of different fillers, having different surface features, thus resulting in a significant (HDPE/30 CPP/30ESP) decrease in their tensile strengths. Furthermore, the slightly higher tensile strength obtained for the same ratio of CPP-filled composites (HDPE/30CPP) when compared to the ESP filled composites (HDPE/30ESP) could be due to better interfacial adhesion of the filler-matrix which is dependent on the nature of the filler and polymer. According to previous studies

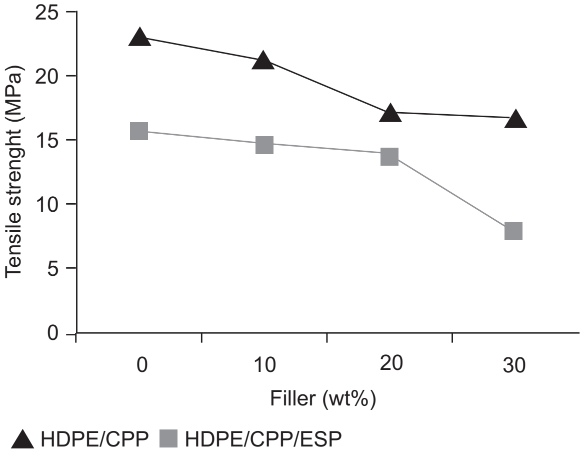

Fig. 2. Variation of the tensile strength of HDPE/CPP and HDPE/CPP/ESP composites at different filler loadings (P-value for both the CPP and ESP were less than 0.05).

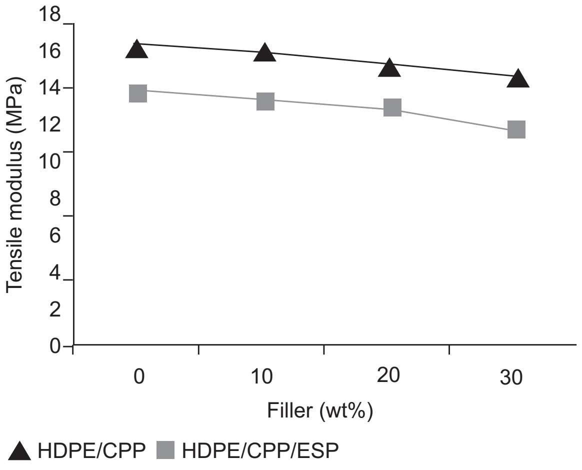

Fig. 3. Variation of tensile modulus of HDPE/CPP and HDPE/CPP/ESP composites at different filler loadings (P-value for both the CPP and ESP were less than 0.05).

Table 3. Rate of biodegradation of the composites

(a) after 25 days

Samples	Initial wt(g)	Initial thickness (mm)	Final wt(g)	Final thickness (mm)	Dwt	(%) increase
Neat HDPE	6.7	3.08	6.51	3.08	0.0	0
190 g HDPE/10 g CPP	8.12	3.19	8.10	3.18	0.02	0.25
180 g HDPE/ 20 g CPP	7.76	2.88	7.74	2.87	0.02	0.26
170 g HDPE/ 30 g CPP	5.92	2.90	5.88	2.88	0.04	0.68
170 g HDPE/ 30 g ESP	7.62	3.13	7.58	3.11	0.06	0.79
160 g HDPE/ 10 g CPP/ 30 g ESP	6.10	3.13	6.04	3.10	0.13	0.98
150 g HDPE/ 20 g CPP/ 30 g ESP	7.35	3.12	7.22	3.11	0.13	1.76
140 g HDPE/ 30 g CPP/ 30 g ESP	8.04	3.09	7.84	3.07	0.15	1.96

(b) after 50 days

Samples	Initial wt(g)	Initial thickness (mm)	Final wt(g)	Final thickness (mm)	Dwt	(%) decrease
Neat HDPE	6.72	3.07	6.71	3.07	0.01	0.15
190 g HDPE/10 g CPP	8.11	3.20	8.01	3.19	0.10	1.23
180 g HDPE/ 20 g CPP	7.74	2.89	7.64	2.88	0.10	1.29
170 g HDPE/ 30 g CPP	5.91	2.91	5.83	2.88	0.08	1.35
170 g HDPE/ 30 g ESP	7.60	3.13	7.48	3.11	0.12	1.58
160 g HDPE/ 10 g CPP/ 30 g ESP	6.10	3.13	5.97	3.09	0.13	2.13
150 g HDPE/ 20 g CPP/ 30 g ESP	7.33	3.12	7.15	3.11	0.24	2.45
140 g HDPE/ 30 g CPP/ 30 g ESP	8.03	3.09	7.81	3.07	0.15	2.74

(c) after 75 days

Samples	Initial wt(g)	Initial thickness (mm)	Final wt(g)	Final thickness (mm)	Dwt	(%) decrease
Neat HDPE	6.70	3.07	6.69	3.07	0.01	0.15
190 g HDPE/10 g CPP	8.11	3.19	8.00	3.17	0.11	1.36
180 g HDPE/ 20 g CPP	7.75	2.88	7.51	2.86	0.14	1.81
170 g HDPE/ 30 g CPP	5.91	2.92	5.79	2.89	0.18	2.09
170 g HDPE/ 30 g ESP	7.60	3.10	7.42	3.08	0.12	2.37
160 g HDPE/ 10 g CPP/ 30 g ESP	6.10	3.09	5.95	3.06	0.15	2.45
150 g HDPE/ 20 g CPP/ 30 g ESP	7.33	3.11	7.12	3.08	0.21	2.86
140g HDPE/ 30 g CPP/ 30 g ESP	8.04	3.09	7.78	3.06	0.26	3.23

(d) after 100 days

Samples	Initial wt(g)	Initial thickness (mm)	Final wt(g)	Final thickness (mm)	Dwt	(%) decrease
Neat HDPE	6.70	3.07	6.65	3.06	0.01	0.6
190 g HDPE/10 g CPP	8.11	3.19	7.78	3.17	0.11	1.99
180 g HDPE/ 20 g CPP	7.75	2.88	7.52	2.86	0.09	2.96
170 g HDPE/ 30 g CPP	5.90	2.98	5.71	2.91	0.11	3.22
170 g HDPE/ 30 g ESP	7.60	3.11	7.35	3.08	0.19	3.29
160 g HDPE/ 10 g CPP/ 30 g ESP	6.10	3.09	5.89	3.06	0.33	3.44
150 g HDPE/ 20 g CPP/ 30 g ESP	7.33	3.11	7.07	3.08	0.14	3.54
140 g HDPE/ 30 g CPP/ 30 g ESP	8.05	3.09	7.74	3.07	0.10	3.60

(Gomes *et al*., 2007; Pracella *et al*., 2006), the quality of interfacial adhesion is dependent on the method of processing and filler treatment, aspect ratio and nature of the filler and polymer components. Murugan *et al*. (2018) reported a decrease in the tensile strength, as the ESP filler loading increases above 20 phr filler loading, with optimum tensile strength obtained at 10 phr ESP loading. They stated that the agglomeration of ESP causes the interfacial adhesion between HDPE matrix and ESP filler to be weak. This implies that the adhesion of the polymer (HDPE) to the filler (ESP) is through a weaker bond, thus resulting to a significant decrease in their tensile strength with the incorporation of filler (CPP) at higher filler loadings for the CPP-ESP composites. Similar observations in the trend of tensile strengths have been reported in previous studies (Obasi, 2013; Mengeloglu and Karakus, 2008; Yang *et al*., 2004; Hussein *et al*., 2001).

The tensile modulus for the composites also had same trend as the tensile strength. Tensile modulus is a measure of stiffness and resistance to stress, which often depends on the orientation of a material. The reduction in the tensile modulus with addition or increase in the fillers infers weak and poor interfacial bonding resulting from non-uniform interactions between the surface characteristics of the filler particles and the HDPE matrix. Due to the poor interfacial bonding, voids can open up at the polymer-filler interface under tension and the resultant cavitations can dramatically reduce the tensile modulus of the composites. (Yang *et al*., 2004) reported that the decrease in the tensile strength and modulus is due to the agglomeration that limits the load transfer from the matrix to the fillers as well as the poor interfacial bonding between filler and matrix polymer, thus causing cracks to initiate and propagate easily. The resultant cracks reduced the strength of the filled composites. This afore mentioned effect is much more pronounced for the CPP-ESP filled composites, with higher reductions for higher filler fractions.

Figure 4 shows the reduction in the elongation-at-break as a result of the increase in the filler loadings. Incorporation or addition of the fillers increased the hardness and toughness of the composites which led to lower elongation at break. The lower filler loadings for CPP-filled composites showed higher values for elongation at the break because of its better dispersions in the matrix, which decreases as the filler loadings increase. CPP-ESP filled composites have a much lower elongation at break when compared to CPP-filled composites, as the filler fractions increases. This reduc-tion may be due to interaction and interference of both fillers (ESP and CPP) in controlling the mobility of the polymer matrix there by resulting to a discontinuous morphology and extended surface area, thus leading to a reduction in the elongation at break. Again, the incapability of the filler to support the stress transfer from the polymer matrix can result to a shorter elongation at break. Again, weak interfacial bonds resulting from poor adhesion of the fillers/HDPE interactions, facilitate crack propagation, thus composites fracture at the lower value of elon-gation which was obtained with increasing filler content.

Figures 5a-b illustrate the variation of the flexural strength and modulus of the composites. The flexural strength and modulus decrease with the increasing amount of filler fractions. The neat HDPE polymer showed flexural strength of 18.44 MPa which decreased on the addition of cassava peel powder (CPP) for the CPP-filled composites and a more pronounced decrease on the addition of both fillers (CPP and ESP) at different filler loadings for the CPP-ESP filled composites. This reduction may be attributed to the weak interfacial bonding resulting from the uneven dispersion and distribution of the fillers in the polymer matrix which inefficiently hinders chain movement during deformation. Another factor may be related to the non-wettability of the fibre by the resin. The inability of resin to wet fibre properly can lead to a reduction in

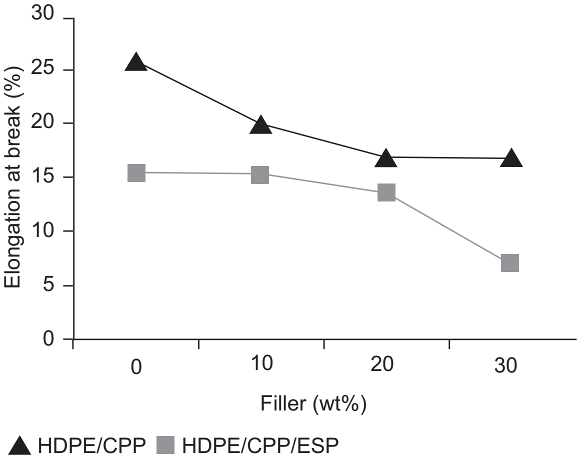

Fig. 4. Variation of elongation at break of HDPE/CPP and HDPE/CPP/ESP composites at different filler loadings (P-value for both the CPP and ESP were less than 0.05).

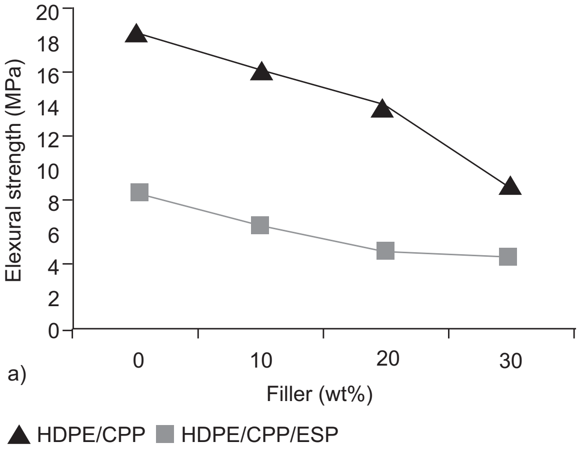

Fig. 5a. Variation of flexural strength of HDPE/CPP and HDPE/CPP/ESP composites at different filler loadings (P-value for both the CPP and ESP were less than 0.05).

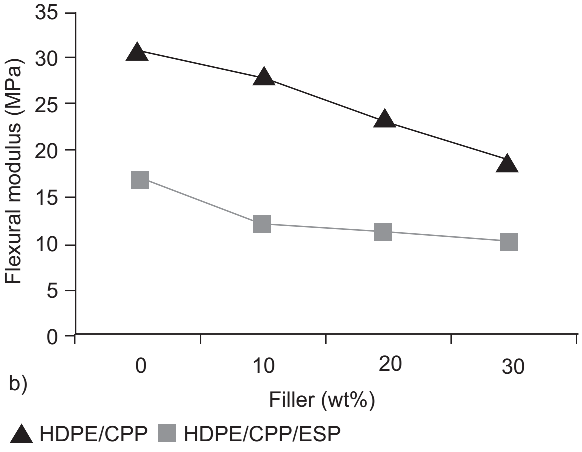

Fig. 5b. Variation of flexural modulus of HDPE/CPP and HDPE/CPP/ESP composites at different filler loadings (P-value for both the CPP and ESP were less than 0.05).

the strength of materials under flexural loading (Daramola *et al*., 2017).

Figure 6 showed the impact strength as a function of the filler content. The addition of the ESP and CPP decreased the stiffness of the HDPE gradually with increasing filler fractions. The impact strength values of the CPP-filled composites were higher than those of the CPP-ESP filled composites except for the neat HDPE. The significant reduction in their impact strength may be attributed to fibre agglomeration resulting from the nature and higher amount of two different fillers (CPP and ESP) and poor interfacial bonding resulting from filler-matrix interactions. At lower filler loadings, the composites absorb higher impact energy, which decreases as the filler loadings increase. This is because the fibre particles at lower filler loadings enhance better interfacial bonding between the matrix and the fillers and can distribute the energy within the particles. The ability of the composites to absorb impact energy decreases as the CPP and ESP filler loadings increase. This reduction is more pronounced for the CPP-ESP filled composites when compared to the CPP-filled composites and ESP-filled composite. Furthermore, it has also been reported that an increase in the number of filler particles increases the chances of fibre agglomeration, resulting in regions of stress concentration and thus requiring less energy for crack propagation (Sreekala, 2007). According to Tawakkal *et al*. (2012), the amount of matrix is another factor, which may probably be insufficient or capable of transferring the stress effectively during sudden impact together with the filler's lower absorption features.

From the water absorption study, Fig. 7 showed that the rate of water absorption in the composites increased proportionately to their duration or exposure in water. It can be seen that the CPP-ESP filled composite with the composition ratio 16:1:3 showed the highest water absorption when compared to the other composites. This may be due to more pores, cracks or cavities arising from its surface as observed by Sreekala *et al*. (2000)

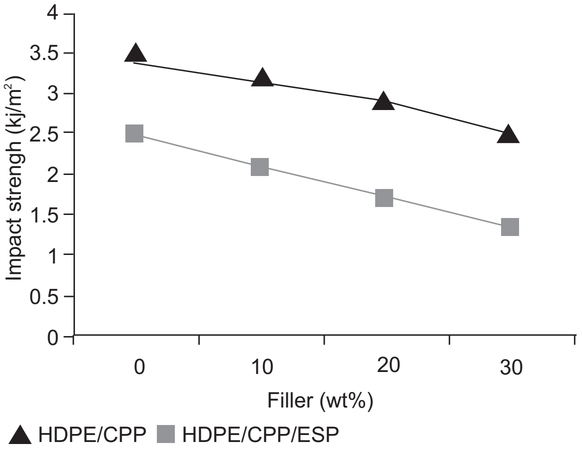

Fig. 6. Variation of impact strength of HDPE/CPP and HDPE/CPP/ESP composites at different filler loadings (P-value for both the CPP and ESP were less than 0.05).

who stated that water absorption is a measure of the material's porosity. Also, Farahana *et al*. (2015) reported that water absorption in a composite is facilitated by the presence of agglomeration caused by in homogeneous dispersion of the fillers within the polymer matrix. Again, the rate of water absorption in 30% wt ESP-filled composite was higher when compared to the CPP-filled composite of the same ratio. This may be due to better interfacial bonding as can be seen from their discussed tensile and flexural properties. Obasi (2015) stated that the better the compatibility of the polymer composites, the greater the reduction of the penetrant molecules into the composites.

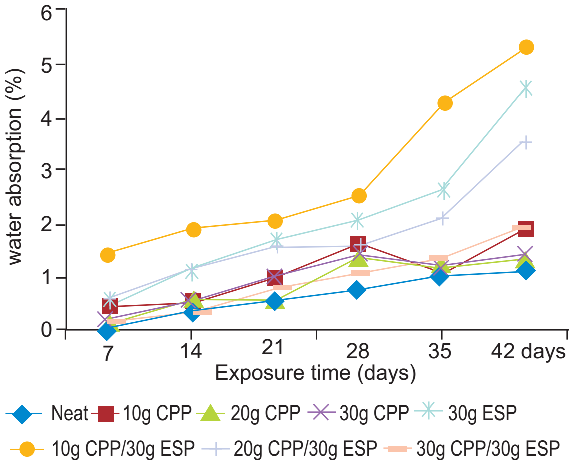

Fig. 7. Effect of exposure time on the rate of water absorption of the composites (P-value for both the CPP and ESP were less than 0.05).

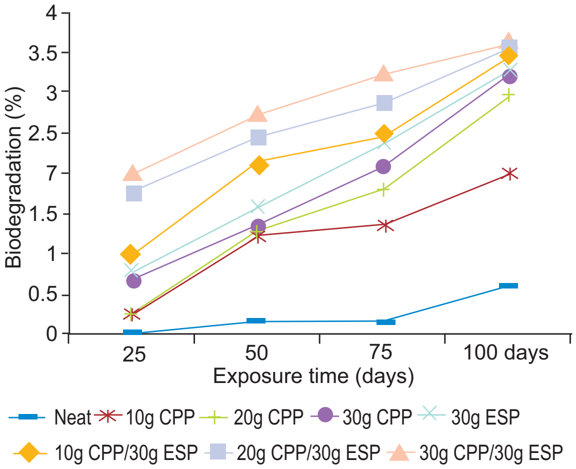

Fig. 8. Effect of exposure time on the rate of biodegradation of the composites (P-value for both the CPP and ESP were less than 0.05).

From Fig. 8, it was found that the composites responded to microbial attack after the first 25 days in the soil. This could be attributed to the water uptake of the composites when compared to the neat high density polyethylene. It was also observed that the rate of biodegradation was a function of exposure time in the soil as there was a steady decrease in weights of the composites as they remained in the soil. All the composites showed linear degradation within the period except for neat HDPE whose degradation was very insignificant. Furthermore, the rate of biodegradation of the composites increased with increasing filler contents. For CPP-filled and CPP-ESP filled composites, the samples with the ratios 17:3 and 14:3:3 have a greater rate of biodegradation when compared to their composites respectively. However, the CPP-ESP filled composites showed the highest rate of biodegradation to the amount of filler content when compared to all the composites. This may be attributed to the reduction in the volume of HDPE in the interstice of the matrix caused by the agglomeration of the fillers. This made the composites to be more susceptible to biodegradation as a result of the increasing number of agglomerates with increasing filler contents. Again, ESP-filled composite (30%wt) showed a higher rate of biodegradation when compared to the CPP-filled composite of the same ratio. This may be attributed to poor interfacial adhesion when compared to CPP-filled composites of the same ratio.

Conclusion

The study has shown that the mechanical properties of polyethylene decreased with the incorporation of CPP and ESP. However, CPP-filled composites had better mechanical properties when compared to CPP-ESP filled composites. Also, the biodegradation and water absorption studies showed that the incorporation of CPP and ESP into PE synergistically improved their biodegradation and water absorption properties, with the CPP-ESP filled composites higher than the CPP-filled composites. Therefore, the use of natural polymers to blend polyethylene can trigger water absorption and biodegradation. Summarily, the presence of eggshell in CPP blended HDPE proved significant improvement in the water absorption and biodegradation properties with a decline in the mechanical properties. However, due to the improved biodegradable properties of the composites formed, they have the potential to be used in applications with low mechanical strength requirements, such as packaging films for food items and pharmaceutical products. Furthermore, studies are recommended in this area using coupling agent (polyethylene graft maleic anhydride), chemical modification of the fillers for improved mechanical properties or using other natural fibres or materials.

Conflict of Interest. The authors declare no conflict of interest.

References

Adediran, A.A., Balogun, O.A., Akinwande, A.A., Adesina, O.S., Olasoju, O.S. 2020. Influence of chemical treatment on the properties of cement-paper hybrid composites for ceiling board application. *Heliyon*, **6:** e04512.

Adediran, A.A., Olawale, O., Ojediran, J., Aladegboye, S., Atoyebi, O.D., Akinlabi, E.T., Olayanju, T.M. A. 2019. Properties of agro-based hybrid particleboards. *Procedia Manufacturing*, **35:** 442-446.

Ajao, A.T., Abdullahi, H.J.I., Atere, T.G., Kolawole, O.M. 2009. Studies on the biodegradation and utilization of selected tuber wastes by penicillium expansum. *Bioscience Biotechnology Research Communications*, **21:** 221-227.

Akogun, O.A., Waheed, M.A., Ismaila, S.O., Dairo, O.U. 2020. Co-briquetting characteristics of cassava peel with sawdust at different torrefaction pretreatment conditions. *Energy Sources, Part-A: Recovery, Utilization and Environmental Effects*, 1-19.

Apata, D.F., Babalola, T.O. 2012. The use of cassava, sweet potato and cocoyam, and their by-products by non-ruminants. *International Journal of Food Science and Nutrition Engineering*, **2:** 54-62.

Bartczak, Z., Argon, A.S., Cohen, R.E., Weinberg, M. 1999. Toughness mechanism in semi-crystalline polymer blends: II. High-density polyethylene toughened with calcium carbonate filler particles. *Polymer*, **40:** 2347-2365.

Boran, S. 2016. Mechanical, morphological and thermal properties of nutshell and microcrystalline cellulose filled high density polyethylene composites. *Bio-Resources*, **11:** 1741-1752.

Chan, C.M., Wu, J., Li, J.X., Cheung, Y.K. 2002. Polypropylene/calcium carbonate nanocomposites. *Polymer*, **43:** 2981-2992.

Czaikoski, A., da Cunha, R.L., Menegalli, F.C. 2020. Rheological behaviour of cellulose nanofibres from cassava peel obtained by combination of chemical and physical processes. *Carbohydrate Polymers*, **248:** 116744.

Daramola, O.O., Akintayo, O.S., Adewole, T.A., Talabi, H.K. 2017. Mechanical properties and water absorption behaviour of polyester/soil-retted banana fibre (SRBF) composites. *Annals of the Faculty of Engineering Hunedoara*, **15:** 183.

Edhirej, A., Sapuan, S.M., Jawaid, M., Zahari, N.I. 2017. Cassava: its polymer, fibre, composite and application. *Polymer Composites*, **38:** 555-570.

Eichhorn, S.J., Dufresne, A., Aranguren, M., Marcovich, N.E., Capadona, J.R., Rowan, S.J., Gindl, W. 2010. Current international research into cellulose nanofibres and nanocomposites. *Journal of Materials Science*, **45:** 1-33.

Eletta, O.A.A., Ajayi, O.A., Ogunleye, O.O., Akpan, I.C., 2016. Adsorption of cyanide from aqueous solution using calcinated eggshells: equilibrium and optimisation studies. *Journal of Environmetal Chemical Engineering*, **4:** 1367-1375.

Farahana, R.N., Suprib, A.G., Tehc, P.L. 2015. Effect of PVC-MA coupling agent on tensile, water absorption and morphological properties of recycled high density polyethylene/ethylene vinyl acetate/eggshell powder composites. *Journal of Advanced Research in Materials Science*, **10:** 1-11.

Ghabeer, T., Dweiri, R., Al-Khateeb, S. 2013. Thermal and mechanical characterization of polypropylene/eggshell biocomposites. *Journal of Reinforced Plastics and Composites*, **32:** 402-409

Gomes, A., Matsuo, T., Goda, K., Ohgi, J. 2007. Development and effect of alkali treatment on tensile properties of curaua fiber green composites. *Composites Part A: Applied Science and Manufacturing*, **38:** 1811-1820.

Harahap, H., Rusli, A., Surya, I. 2016. Effect of microcrystalline cellulose from cassava peel waste filler loading on natural rubber latex products. *Journal of Polymer Materials*, **33:** 213.

Hassan, S.B., Aigbodion, V.S., Patrick, S.N. 2012. Development of polyester/eggshell particulate composites. *Tribology in Industry*, **34:** 217-225.

Hussein, A.A., Salim, R.D., Sultan, A.A. 2011. Water absorption and mechanical properties of high-density polyethylene/egg shell composite. *Journal of Basrah Researches (Sciences)*, **37:** 36-42.

Ibrahim, M.I.J., Sapuam, S.M., Zainudin, M., Zuhri, Y.M. 2019. Potential of using multiscale corn husk fibre as reinforcing filler in corn starch-based biocomposites. *International Journal of Biological Macromolecule*, **139:** 596-604.

Ifuku, S., Yano, H. 2015. Effect of a silane coupling agent on the mechanical properties of a microfibrillated cellulose composite. *International Journal of Biological Macromolecules*, **74:** 428-432.

Ipilakyaa, T.D., Tuleun, L.T., Sule, J.T. 2019. Evaluation of physical and dynamics mechanical properties of coconut husk ash (CHA) reinforced polyester composites. *European Journal of Materials Science and Engineering*, **4:** 212-220.

Kiziltas, A., Nazari, B., Gardner, D.J., Bousfield, D.W. 2014. Polyamide 6-cellulose composites: effect of cellulose composition on melt rheology and crystallization behaviour. *Polymer Engineering and Science*, **54:** 739-746.

Karuppannan, S.K., Dowlath, M.J.H., Raiyaan, G.D., Rajadesingu, S., Arunachalam, K.D. 2021. Application of poultry industry waste in producing value-added products - a review. *Concepts of Advanced Zero Waste Tools*, 91-121.

Liang, J.Z. 2006. Effects of particle size on melt viscoelastic properties during capillary extrusion of glass bead-filled LDPE composites. *Journal of Thermoplastic Composite Materials*, **19:** 703-713.

Mengeloglu, F., Karakus, K. 2008. Thermal degradation, mechanical properties and morphology of wheat straw flour filled recycled thermoplastic composites. *Sensors*, **8:** 500-519.

Murugan, S., Munusamy, Y., Muniandy, M., Ismail, H. 2018. Development of HDPE-modified eggshell composite. *Polymer Composites*, **39:** 1630-1637.

Nanssou, P.A.K., Nono, Y.J., Kapseu, C. 2016. Pretreatment of cassava stems and peelings by thermohydrolysis to enhance hydrolysis yield of cellulose in bioethanol production process. *Renewable Energy*, **97:** 252-265.

Obasi, H.C. 2015. Peanut husk filled polyethylene composites: effects of filler content and compatibilizer on properties. *Journal of Polymers*, **2015,** Article ID 189289.

Obasi, H.C. 2013. Properties of Raphia palm interspersed fibre filled high density polyethylene. *Advances in Materials Science and Engineering*, **2013,** Article ID 932143.

Oladele, I.O., Ibrahim, I.O., Adediran, A.A., Akinwekomi, A.D., Adetula, Y.V., Olayanju, T.M.A. 2020. Modified palm kernel shell fibre/particulate cassava peel hybrid reinforced epoxy composites. *Results in Materials*, **5:** 100053.

Omah, A.D., Omah, E.C., Offor, P.O., Mgbemene, C.A., Eke, M.N. 2018. Feasibility study on the use of carbonized cassava cortex as reinforcement in polymer-matrix composites. *Cogent Engineering*, **5:** 1545-1557.

Osman, M.A., Atallah, A., Suter, U.W. 2004. Influence of excessive filler coating on the tensile properties of LDPE-calcium carbonate composites. *Polymer*, **45:** 1177-1183.

Owuamanam, S., Cree, D. 2020. Progress of bio-calcium carbonate waste eggshell and seashell fillers in polymer composites: a review. *Journal of Composites Science*, **4:** 70.

Peng, Y., Liu, R., Cao, J., Chen, Y. 2014. Effects of UV weathering on surface properties of polypropylene composites reinforced with wood flour, lignin and cellulose. *Applied Surface Science*, **317:** 385-392.

Pondja Jr., E.A., Persson, K.M., Matsinhe, N.P. 2017. The potential use of cassava peel for treatment of mine water in Mozambique. *Journal of Environmental Protection*, **8:** 277-289

Pracella, M., Chionna, D., Anguillesi, I., Kulinski, Z., Piorkowska, E. 2006. Functionalization, compatibilization and properties of polypropylene composites with hemp fibres. *Composite Science and Technology*, **66:** 2218-2230.

Ramesh, S., Natasha, A.N., Tan, C.Y., Bang, L.T., Ching, C.Y., Chandran, H. 2016. Direct conversion of eggshell to hydroxyapatite ceramic by a sintering method. *Ceramics International*, **42:** 7824-78290.

Riyajan, S., Sasithornsonti, Y., Phinyocheep, P. 2012. Green natural rubberg-modified starch for controlling urea release. *Carbohydrate Polymers*, **89:** 251-258.

Schwantes, D., Gonçalves, A.C., Coelho, G.F., Campagnolo, M.A., Dragunski, D.C., Tarley, C.R.T., Leismann, E.A.V. 2016. Chemical modifications of cassava peel as adsorbent material for metals ions from wastewater. *Journal of Chemistry*, **2016,** Article ID 3694174.

Shuhadah, S., Supri, A.G. 2009. LDPE-Isophthalic acid modified eggshell powder composites (LDPE/ESPI). *Journal of Physical Science*, **20:** 87-98.

Simate, G.S., Ndlovu, S. 2015. The removal of heavy metals in a packed bed column using immobilized cassava peel waste biomass. *Journal of Industrial and Engineering Chemistry*, **21:** 635-643.

Sreekala, M.S., Kumaran, M.G., Joseph, S., Jacob, M., Thomas, S. 2000. Oil palm fibre reinforced phenol formaldehyde composites: influence of fibre surface modifications on the mechanical performance. *Applied Composite Materials*, **7:** 295-329.

Sreekumar, P.A., Joseph, K., Unnikrishnan, G., Thomas, S. 2007. A comparative study on mechanical properties of sisal-leaf fibre-reinforced polyester composites prepared by resin transfer and compression moulding techniques. *Composites Science and Technology*, **67:** 453-461.

Tawakkal, I.S.M., Talib, R.A., Abdan, K., Ling, C.N. 2012. Mechanical and physical properties of kenaf-derived cellulose (KDC)-filled polylactic acid (PLA) composites. *Bio-Resources*, **7:** 1643-1655.

Toro, P., Quijada, R., Yazdani-Pedram, M., Arias, J.L. 2007. Eggshell, a new bio-filler for polypropylene composites. *Materials Letters*, **61:** 4347-4350.

Waheed, M.A., Akogun, O.A. 2021. Quality enhancement of fuel briquette from cornhusk and cassava peel blends for co-firing in coal thermal plant. *International Journal of Energy Research*, **45:** 1867-1878.

Yang, H.S., Kim, H.J., Son, J., Park, H.J., Lee, B.J., Hwang, T.S. 2004. Rice-husk flour filled polypropylene composites; mechanical and morphological study. *Composite Structures*, **63:** 305-312.

Yap, S.Y., Sreekantan, S., Hassan, M., Ong, M.T., Sudesh, K. 2020. Characterization and biodegradability of rice husk-filled polymer composites. *Polymers*, **13:** 104.

Zulkifli, N.I., Samat, N., Anuar, H., Zainuddin, N. 2015. Mechanical properties and failure modes of recycled polypropylene/microcrystalline cellulose composites. *Materials and Design*, **69:** 114-123.