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Mechanical and Chemical Resistance Properties of High Density Polyethylene Filled with Corncob and Coconut Fiber

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Authors' contributions

This work was carried out in collaboration between all authors. Author IOI designed the study and wrote the protocol. Author HOO performed the experimental, while the statistical analysis was carried out by both authors HOO and CME. Author CME managed the literature search and wrote the first draft of the manuscript with assistance from author HOO. All authors read and approved the final manuscript.

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ABSTRACT

The effects of incorporating coconut fibre and corncob fibre as fillers on the properties of high density polyethylene (HDPE) have been studied. The study also investigated the effects on tensile strength and hardness of the composites after immersion in different chemical media, and the long-term water uptake behavior of the composites were also investigated. Results showed that the incorporation of coconut, and corncob fibres into HDPE increased the tensile strength of HDPE. While coconut fibre increased the hardness of HDPE at all the fibre contents investigated, the hardness of all corncob fibre filled HDPE was lower than the unfilled HDPE. The specific gravity of

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HDPE composites was found to increase with increase in fibre content and at the fibre contents considered. The tensile strength and hardness of coconut, and corncob fibre filled HDPE were greatly reduced after immersion in 10% HCl, 13% bleach, and 10% NaOH. The 3% H₂O₂ and 1% soap solution had negligible effects and showed small reduction in composite properties. All the prepared composites absorbed more water than unfilled HDPE. The amount of water absorbed was found to depend on fibre type, fibre content, and immersion time. None of the prepared composites reached equilibrium water absorption after seven weeks immersion in water. The present study highlighted the benefits and limitations of coconut, and corncob fibres as fillers for HDPE for barrier applications. It is hoped that these fibres should be considered by the plastic/composite industries for their various applications.

Keywords: Polymer composites; mechanical properties; chemical resistance; coconut shell; corncob fibre; barrier properties; absorption.

1. INTRODUCTION

The utilization of fillers from various sources in thermoplastics has been an accepted route to achieving enhancement in materials' properties or cost saving possibilities. Calcium carbonate (CaCO₃), talc, and kaolin are examples of mineral fillers which are widely used in the plastic industry [1]. However, the mineral fillers require a lot of energy to produce since processing temperatures can exceed 1200°C [2]. This has the tendency to increase the cost of plastic products. Similarly, these fillers tend to abrade processing equipment, and also increase the density of the plastic system [2]. The use of natural fillers derived from agricultural sources, such as jute, oil palm empty fruit bunch, wood flour, rice husk, etc., in the preparation of polymer composites is gaining importance in recent years [2].

The use of natural fillers (bio-fillers) as reinforcing fibres both in thermoplastic and thermoset matrix composites provides positive environmental benefits with respect to ultimate disposability, and raw material utilization [3]. The advantages of natural fibres over traditional reinforcing materials such as glass fibres, talc, and mica are acceptable specific strength properties, low cost, low density, high toughness, good thermal properties, reduced tool wear, reduced thermal and respiratory irritation, ease of separation, enhanced energy recovery, and biodegradability. Thus, a broad range of bio-fibres are presently being utilized as the main structural components or as filler agents in polymer composite materials [4].

Recent advances on the use of natural fibres to fill polyolefin have been reported by several authors. The transport behaviour of n-hexane through carbonized oil palm empty fruit bunch

powder filled polypropylene/natural rubber has been studied [5]. The mechanical properties of high density polyethylene (HDPE) - oil palm empty fruit bunch (EFB) composites were studied by Rozman et al. [6]. The flexural, tensile, and impact strengths of the composites were found to increase with increase in the amount of EFB incorporated. Also, Rozman et al. [7] investigated the oil palm empty fruit bunch (EFB) - polyethylene composites produced using an internal mixer. The incorporation of EFB into the polymer matrix resulted in the reduction of flexural strength and tensile modulus of the prepared composites. The water absorption and thickness swelling of the composites were found to increase on the incorporation of EFB filler. This later observation was attributed to the presence of hydrophilic hydroxyl groups on the EFB filler. Nafaji et al. [8] prepared composite of sawdust and virgin and/or recycled high density polyethylene. The results showed that mechanical properties of samples containing recycled HDPE were statistically similar and comparable to those of composite made from virgin HDPE.

Majid et al. [9] investigated the effect of maleic anhydride -g- polyethylene on the properties of low density polyethylene /thermoplastic sago starch reinforced Kenaf fibre composites and found that water absorption for both compatibilized and uncompatibilized composites increased with increase in Kenaf fibre loading. The compatibilized composites were observed to show lower percentage of water uptakes as compared to the uncompatibilized composites. Kajaks and Reihmane [10] investigated the thermal and water sorption properties of polyethylene and linen yarn production waste composites. It was found that the modification of composites with diphenylmethane diisocyanate gave considerable increase of thermal stability and decrease water sorption in composites.

Natural fibre thermoplastic composites nowadays have a wide range of applications and can cost effectively replace wood and other construction materials in most applications. They are used in decking, cladding, automotive, building, and residential applications. The applications and end-uses of these composites and their exposure to atmosphere or contact with aqueous media (alkali, acid, and solvents) has made it necessary to evaluate the chemical resistance of natural fibre filled HDPE with the aim of improving the service life, and desirable properties for their specific end-uses.

The continued search for filler materials in compounding polyethylene is likely to grow with the introduction of improved compounding technology, and new coupling and compatibilizing agents that pursue the use of high filler contents. In this study is reported the utilization of coconut fibre and corncob fibres as fillers in high density polyethylene and the possibility of utilizing the composites for barrier applications. The effect of household chemicals like 10% sodium hydroxide (NaOH), bleach solution (NaOCl), 13% hydrochloric acid (HCl), 3% hydrogen peroxide (H₂O₂), and 1% soap solution on the mechanical properties of the composites will also be reported. The long term (7 weeks) water uptake behaviour of coconut and corncob fibre filled high density polyethylene will be investigated.

The effects of the natural waxy surface layer of the coconut fibre on fibre/low density polyethylene interfacial bonding and composite properties were studied by Brahmakumar et al. [11]. Similarly, Lebalanc et al. [12] prepared a series of polypropylene green coconut fibre (GCF) composites and studied their properties in the molten and solid states. Results showed that the complex modulus increased with GCF content but in such a manner that the observed reinforcement was at best of hydrodynamic origin. The PP-GCF composites were reported to be heterogeneous material and in the molten state, it was found to exhibit essentially a nonlinear viscoelastic character. Also, Igwe and Njoku [13] investigated the end-use properties of coconut fibre filled polypropylene and reported that the fibre increased the specific gravity, and hardness of polypropylene.

Water absorption is one of the important characteristics of natural fibre filled polymers that determine their end-use applications. It could lead to a decrease in some of the properties of

polymer composites, and therefore, needs to be considered when selecting applications. Water absorption in bio-fibre based composites could cause a build-up of moisture in the fibre cell wall, and also in the fibre-matrix interphase region. Moisture build-up in the cell wall could lead to fibre swelling, and concerns regarding dimensional stability of the composites. Coconut fibre and corncob fibre high density polyethylene composites are new materials, and being bio-based composites with tendencies to absorb water, it is necessary to study their water absorption properties for their optimum utilization.

Furthermore, Igwe and Njoku [13] investigated the end-use properties of corncob fibre, wood saw-dust, newspaper print fibre, and coconut fibre filled polypropylene at filler loadings of 0 to 30 wt.%. Among other results presented, the water absorption and flame retardant properties of corncob fibre were poor. The specific gravity and hardness of polypropylene were increased on incorporation of corn hub fibre. It is important to note that corncob is an agricultural waste obtained after extracting corn (or maize) from corn fruit. Presently, corncob has no industrial utilization, and can be found littering in dustbins and farm yards in the villages, and our towns. In some instances however, our rural women use corncob as a source of fuel. This fibre is readily available and biodegradable. The importance of corncob fibre as a filler in filling high density polyethylene will be borne out by the outcome of the present investigation.

2. MATERIALS AND METHODS

The high density polyethylene (HDPE) used was procured from a chemical store at Aba, Nigeria. The HDPE is a product of Exxon Mobil Chemicals, USA, and has melt flow index of 2.16 dg/min, and density of 0.965 g/cm³. The corncob and coconut fibers used were obtained locally. They were properly cleaned, dried, ground to fine powder, and sieved to 0.30 µm mesh size.

The chemical compositions of the coconut and corncob fibers were determined following the procedure of Iiyama and Wallis [14] for the acid-insoluble lignin content. The alpha cellulose content and ash content in the fibres were determined following standard methods. While the pentosan content of the coconut and corncob fibres were determined by colorimetric method using Orcinol and HCl [15].

A sheet extruder was used in preparing the high density polyethylene composites with the formulations shown in Table 1. The mechanical and end-use properties of the prepared HDPE composites were investigated before and after immersion in the following chemicals: 10% sodium hydroxide (NaOH), 13% bleach solution (NaOCl), 10% hydrochloric acid (HCl), 3% hydrogen peroxide (H₂O₂) and 1% soap solution. These investigations were carried out according to the following standard methods: specific gravity (ASTM D 792), tensile strength (ASTM D 638), shore D hardness (ASTM D2240), 7 weeks water absorption, and chemical resistance (ASTM D 543-95).

Table 1. Composition of prepared HDPE composites

S/N	Formulation code	HDPE content, %	Filler content, %
1	Pure HDPE	100	0
2	CCN-5	95	5
3	CCN-10	90	10
4	CCN-20	80	20
5	CCN-40	60	40
6	CC-5	95	5
7	CC-10	90	10
8	CC-20	80	20
9	CC-40	60	40

Abbreviations: CCN – Coconut fibre; CC – Corncob fibre

3. RESULTS AND DISCUSSION

3.1 Specific Gravity

Data on the specific gravity of coconut, and corncob fibre filled high density polyethylene are illustrated graphically in Fig. 1. The specific gravity of the composites was determined by the displacement technique in accordance to ASTM D792-08. Unfilled HDPE was found to have specific gravity of 1.01. Fig. 1 shows that there was a general increase in the specific gravity of the composites with increase in fibre content. Coconut fibre was observed to increase the specific gravity of high density polyethylene more than corncob fibre at any fibre content considered. This is to be expected since the specific gravity of coconut fibre is determined to be 1.13 while that of corncob fibre is 1.02. The increases in the specific gravity of thermoplastic composites on incorporation of natural fibres have been reported in the literature. For example, Sanadi et al. [2] gave the following

values of specific gravity for some natural fibre filled polypropylene: kenaf (1.02), and newspaper fibre (0.98). The specific gravity of unfilled polypropylene was given as 0.9. Similarly, Ewulonu and Igwe [16] who studied oil palm empty fruit bunch fibre (OPEFB) filled high density polyethylene reported general increases in the specific gravity of high density polyethylene on the incorporation of OPEFB into high density polyethylene.

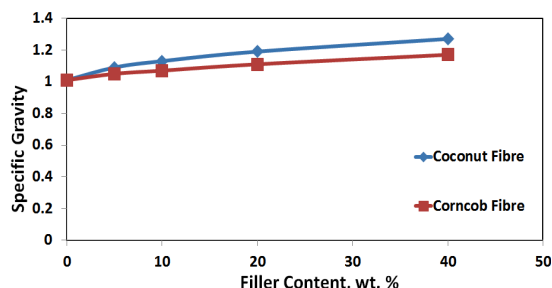


Figure 1: Effect of Filler Content on Specific Gravity of Filled High Density Polyethylene Composites

The specific gravity of lignocellulosic-based composites is much lower than the mineral-filled thermoplastic systems. For example, the specific gravity of a 50 % (w/w) kenaf-PP composite is about 1.07, while that of a 40 % (w/w) glass-PP composite is 1.23 [17]. Since materials are bought in terms of weight, and pieces or articles are in general sold by the number, more pieces can be made with lignocellulosic fibres such as coconut, and corncob fibres as compared to the same weight of mineral fibres. This could lead to significant material cost savings in the high-volume, and low-cost commodity plastics market.

3.2 Tensile Strength

The tensile strength of high density polyethylene is 77.17 MPa. Data on the incorporation of coconut, and corncob fibres on the tensile strength of HDPE are illustrated graphically in Figs. 2 and 3. Also, the effects of immersion of pure HDPE and its composites on different chemical media (3% H₂O₂, 1% soap solution, 10% NaOH, 13% bleach, and 10% HCl) are illustrated in Figs. 2 and 3. These figures show that the incorporation of coconut and corncob fibres into HDPE increased the tensile strength of high density polyethylene; the increase being dependent on the amount of these fibres incorporated. The increase in tensile strength of a polymer on the incorporation of filler has been reported in the literature. For example, Martzinov et al. [18] who studied low density polyethylene –

starch composites reported that the tensile strength of the composites increased with increase in starch content, passed through a maximum, and fell significantly thereafter. However, Rozman et al. [6] and Thakore et al. [19] who studied polypropylene, and low density polyethylene composites respectively reported decreases in the tensile strength of these composites with increase in filler contents. The increase in the tensile strength of HDPE composites with increase in coconut, and corncob fibres is attributed to the ability of these fibres to support stress transferred from the matrix. The ability of these fibres to support transferred stress could likely come about when there is better compatibility or improved adhesion between the fibres and the polymer matrix (HDPE).

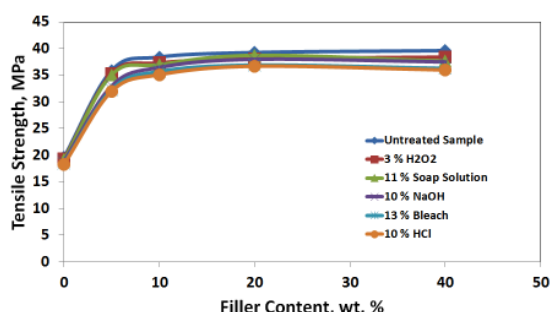


Figure 2: Plot of Tensile Strength versus Coconut Fiber Content for High Density Polyethylene Composites Immersed in Different Household Chemicals

It is important to point out that the incorporation of small amount of coconut fibre (5 wt. %) into HDPE significantly increased its tensile strength by 83.21% (35.91 MPa), a value which was far above the tensile strength of HDPE obtained after the incorporation of 40 wt. % of corncob fibre (35.85 MPa). From the results obtained in this study, it is reasonable to suggest that 10 wt. % of CCN, and 20wt. % of CC fibres should represent the optimum doses of these fibres to be used in filling HDPE. This study has also shown that coconut fibre is superior to corncob fibre in filling HDPE since at each fibre content considered, coconut fibre gave much higher tensile strength value in the composite than that obtained with corncob fibre.

3.3 Hardness (Shore D)

The effects of coconut and corncob fibres on the high density polyethylene hardness studied using shore D tire durometer tester in accordance to ASTM D2240 are illustrated in Figs. 4 and 5. The hardness of unfilled high density polyethylene is

77.17 showing that the hardness of all coconut fibre filled HDPE increased with increase in the amount of coconut fibre incorporated into the polymer matrix. This result indicates enhancement of abrasion and impact strength of the composites. For reinforcing filler, the composite becomes stiffer and harder with increasing filler content, and which results to increase in the composite hardness. Such increase in composite hardness with increasing filler content had been reported by Chakraborty et al. [20]. The increases in the hardness of fibre filled HDPE was less than that obtained for the increase of tensile strength of these composites. For example, when 5 wt. % of coconut fibre was incorporated into HDPE, a 5.13% increase in the hardness of the composite was obtained, whereas for the tensile strength, the increase was 83.21%. Similarly, the incorporation of 40 wt. % of coconut fibre into HDPE increased the hardness by 13.01%, whereas for the tensile strength, the increase was 102.19%. The hardness of all corncob filled high density polyethylene was found to be lower than the unfilled HDPE at all the fibre contents studied. However, the hardness was found to increase with increase in corncob contents.

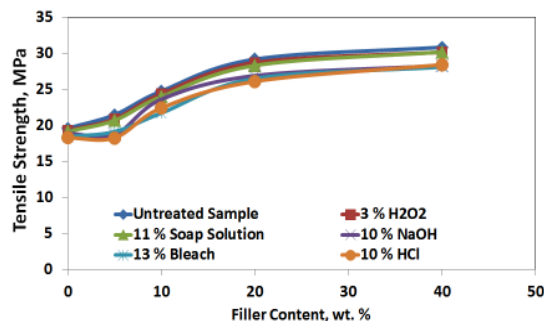


Figure 3: Plot of Tensile Strength versus Corncob Fiber Content for High Density Polyethylene Composites Immersed in Different Household Chemicals

Generally, the addition of filler is expected to increase the hardness of polymer matrix. Chakraborty et al. [20] who studied short-jute fibre reinforced carboxylated nitrile rubber found that the hardness of the composite increased with increase in jute fibre content. However, Machiadikwe [21] who studied domestic waste filled polypropylene system found that the hardness of the composites decreased with increase in the particle sizes of the fillers used. The reported decrease was attributed to decreases in the degree of polymer-filler interaction associated with large filler particle size. However, Karimi et al. [22] who studied the effects of delignification of wood fibre on the

properties of wood fibre – polypropylene composites reported that the hardness of the composites was unaffected by delignification, whereas Ewulonu and Igwe [16] who studied the oil palm empty fruit bunch fibre filled HDPE found that the hardness of the composites increased with increase in the fibre content.

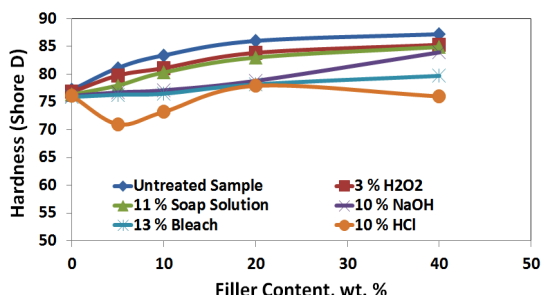


Figure 4: Plot of Hardness versus Coconut Fiber Content for High Density Polyethylene Composites Immersed in Different Household Chemicals

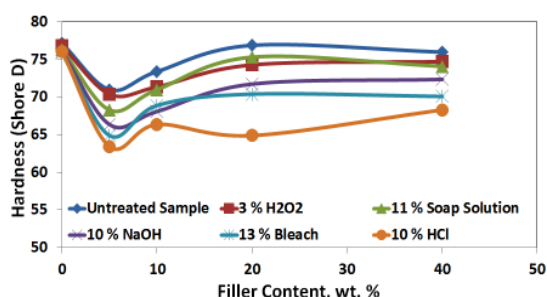


Figure 5: Plot of Hardness versus Corncob Fiber Content for High Density Polyethylene Composites Immersed in Different Household Chemicals

3.4 Effects of Household Chemicals on the Properties of HDPE Composites

The composites of high density polyethylene immersed in the different solvents investigated in this study exhibited differing degrees of percentage weight loss which depended on the type of chemical used. The percentage of weight losses are illustrated in Figs 6 and 7. The order in the percentage of weight losses in the different chemicals is as follows: 10% HCl > 13% Bleach solution > 10% NaOH > 1% soap solution > 3% H₂O₂. The weight losses suffered by the composites in the chemicals investigated affected their tensile strength, and hardness which are also discussed and illustrated graphically in Figs. 2 and 3. The tensile strengths of coconut, and corncob filled HDPE were adversely affected on treatment with HCl, followed by bleach, and then 10% NaOH solution. The other chemicals 3% H₂O₂ and 1% soap solution exhibited small decreases in the

tensile strength of the composites. In other words the studied composites were mildly on immersion in hydrogen peroxide, and soap solution. The effects of HCl, bleach, and NaOH solution on the tensile strength of the composites could be explained as follows. Celluloses are of low acid resistance [23], and coconut and corncob fibres are rich in cellulose as shown in Table 2. Therefore, the considerable decrease in the tensile strength of the coconut, and corncob fibre filled HDPE can be attributed to the degradation of cellulose.

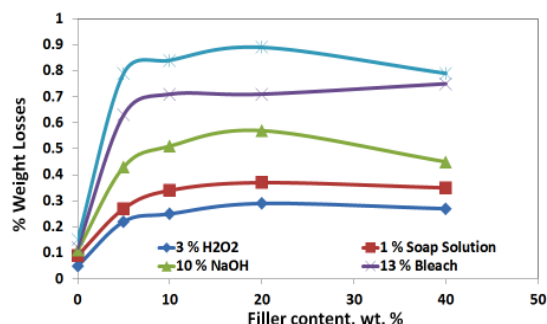


Figure 6: Effects of Household Chemicals on the Percentage Weight Losses of Coconut Fibre Filled HDPE Composites

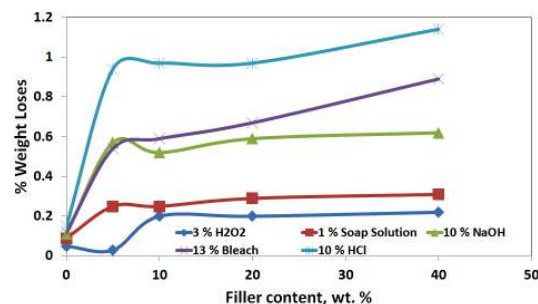


Figure 7: Effects of Household Chemicals on the Percentage Weight Losses of Corncob Fibre Filled HDPE Composites

Bleach solution (NaOCl) on the other hand contains OCl⁻ ion which is found in chemicals widely used for bleaching pulp and paper [23]. OCl⁻ is highly reactive, and is able to degrade the structure of lignin through breakage of chemical bonds. This breakage will manifest in weight losses on exposure to bleach solution with the resultant decrease in the tensile strength of the composites. The quantitative effect of NaOH on the other hand may be associated to its reaction with cellulose present in the fibres the product which has the tendency to undergo oxidative degradation with the resultant decrease in tensile strength of the composites. The present study shows that all composites of HDPE manifested much reduction in tensile strength when compared to pure HDPE on immersion in the different chemicals investigated.

Table 2. Determined chemical composition of coconut and corncob fibres

Fibre	Composition %			
	α -cellulose	Lignin	Pentosans	Ash
Coconut	29.0	14.5	24.0	1.90
Corn cob	43.0	16.6	31.0	1.0

Similarly, all HDPE composites immersed in HCl showed much reduction in tensile strength when compared to those immersed in bleach, and NaOH solutions. This may be due to the quantitative effects of these chemicals on the constituents of the fibres investigated. No relationship between the fibre contents and the reduction in tensile strength on immersion of the composites in chemical media was observed in this study.

The HDPE composites of corncob fibre were generally observed to show much reduction in tensile strength when compared to those of coconut fibre on immersion in HCl, and bleach solution at fibre contents, 0 to 20 wt. %. This may be due to the higher amount of cellulose and lignin present in corncob fibres since there are the components of fibres attacked by HCl, and bleach solution respectively. The present study has shown that HCl, bleach solution, and NaOH are the chemicals that have resulted in considerable tensile strength reduction in the composites.

The effects of the chemicals investigated on the hardness of pure and filled HDPE are illustrated in Figs. 4 and 5. Small decreases in the hardness of pure HDPE was observed with 10% HCl, and 13% bleach solution having higher effects. All the coconut and corncob fibre filled HDPE showed reduction in hardness on treatment with the chemicals investigated in this study. As was noted on the effects of the chemicals on the tensile strength of the composites, 10% HCl, followed by 13% bleach solution, and then 10% NaOH solution had more pronounced effects on the hardness of the composites. The reason adduced for the effect of HCl, bleach and NaOH solution on the tensile strength of the composites also apply for their effects on the hardness of the composites. Generally, the reduction in the hardness of the composites on treatment with chemicals did not bear any relationship with the amount of the fillers incorporated into HDPE.

3.5 Water Absorption Properties

The values of water absorbed by the pure high density polyethylene (HDPE), and its composites

over a period of seven (7) weeks are presented in Figs. 8 and 9. From these figures, it is evidence that pure HDPE absorbed a negligible amount of water after 7 weeks immersion in water. This is attributed to the hydrophobic nature of HDPE. Figs. 8 and 9 show that all the prepared HDPE composites absorbed more water than the unfilled high density polyethylene and the difference in water absorption increases with increase in the amount of fibre incorporated into HDPE. This higher amount of water absorbed by the composite is attributed to the hydrophilic nature of the fibres since the matrix (HDPE) is hydrophobic in nature. The more amounts of fibres in the high density polyethylene, the more the amount of water absorbed by the composite.

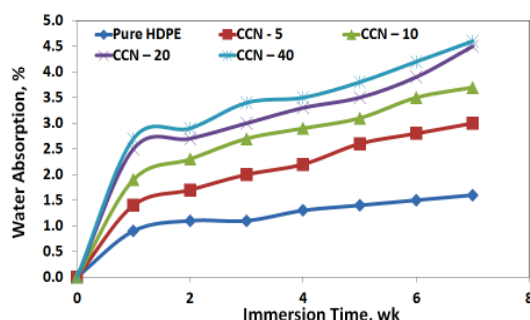


Figure 8: Plot of Percentage Water Absorption versus Immersion Time for Coconut Fibre Filled HDPE Composites

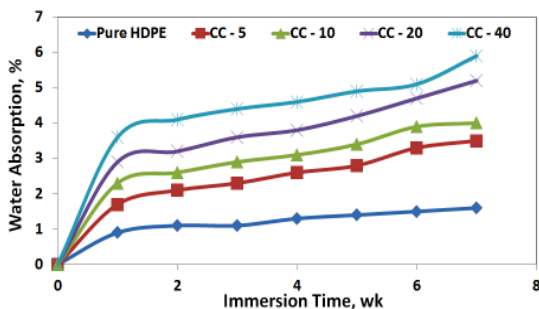


Figure 9: Plot of Percentage Water Absorption versus Immersion Time for Corncob Fibre Filled HDPE Composites

The figures also shows that at any particular period of immersion of HDPE composites in water and fibre content considered, corncob fibre filled high density polyethylene adsorbed more water than coconut fibre filled high density polyethylene. The chemical composition of the

natural fibre in Table 2 can explain the differences observed in their water uptake behaviour. The higher amount of water absorbed by corncob fibre filled high density polyethylene compared to coconut fibre filled high density polyethylene can be attributed to the hydrophilic nature of corncob fibre having higher amounts of cellulose and lignin containing free hydroxyl groups. These groups absorb water easily, and take water molecules easily through hydrogen bonding in the fibre cell wall. Therefore, the higher the corncob fibre content in the composites, the higher the hydroxyl content, and the higher the water absorption. It is important to note that of all the constituents making up the composition of natural fibres, cellulose and hemi-celluloses are the one with the highest water absorption properties [17].

These figures further show that the addition of natural fibres up to 40 wt. % resulted in the higher value of water absorption. In addition to this phenomenon, the increased absorption by composite at higher amount of natural fibre can be attributed to the poor adhesion/compatibility between the fibres and high density polyethylene. As the amount of natural fibre increases, the micro-level processing of the composite become difficult, and may cause the fibre layering out this creates micro-void and cracks within composites. This has a tendency to cause the flow of water molecules along the fibre matrix interface, thereby leading to diffusion of water from the interface to the matrix and fibres [24]. Figs. 8 and 9 also show that the water absorption by HDPE, and the composites gradually increased with increase in immersion time. The water absorbed by HDPE, and its composites after 24 hours immersion in very similar to the water absorbed after one week immersion in water. Thereafter, the difference in water absorbed increased with increase in time of immersion. Figs. 8 and 9 also show that none of the composites reached equilibrium water absorption after 7-weeks immersion in water. Such a phenomenon has also been reported by Stark et al. [25] who reported that injection-moulded specimen continued to absorb water even after 12-weeks immersion. This was attributed to the fact that injection moulded specimens have a thin plastic coating all around them, which results in lower water absorption at a slower pace. It has also been reported that corncob restrict the swelling of elastomer composites in aromatic solvents [26].

4. CONCLUSIONS

Coconut and corncob fibres have been found to increase the tensile strength of high density polyethylene at the filler contents studied. However, while coconut fibre increased the hardness of HDPE, the hardness of all corncob fibre filled HDPE was found to be lower than the unfilled HDPE at the fibre contents investigated in this study; although increases in hardness of composites with increase in corncob content was observed.

The specific gravity of HDPE was increased on addition of coconut or corncob fibre, and at any fibre content considered; coconut fibre increased the specific gravity of HDPE more than corncob fibre. The present study has shown that chemicals can strongly affect natural fibre-high density polyethylene composites in terms of weight loss, and reduction in tensile strength and hardness. HCl, bleach and NaOH solutions greatly affected the tensile strength and hardness of coconut, and corncob fibre filled HDPE whereas 1% soap solution and 3% H₂O₂ had negligible effects, and showed very small weight changes. The effects of HCl and bleach solution on the mechanical properties of the composites can be critical, and necessitates further study on the chemical resistance of natural fibre thermoplastic composites because of their wide range of applications, and exposure to different chemicals. All the filled HDPE composites absorbed more water than unfilled HDPE in a 7-week water absorption test, and the difference in water absorption was found to increase with increase in the amount of coconut, and corncob fibre incorporated into HDPE. Equilibrium water absorption was not reached in this study after a 7-week water immersion test.

By understanding the limitations and benefits of coconut, and corncob fibre filled HDPE, it is reasonable to conclude that these fibres have great potentials in the composite industry. The fibres are relatively of low cost, and have the advantage of being non-abrasive to the mixing and moulding equipment. They are of lower specific gravity when compared to the mineral-based fillers, and which would give these fillers a definite weight advantage for these composites. This will have implications in the automotive and other transportation applications. The utilization of these fibres as sources of thermoplastic composites fillers would not only provide a renewable resource, but would also generate a

non-food source of economic development for the farming rural areas.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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