ChemSearch Journal 14(2): 29 – 35, December, 2023
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 06/06/2023 Accepted: 24/08/2023
http://www.ajol.info/index.php/csj

Mechanical and Water sorption Properties of Untreated Footwear Leather Off-cuts (UFLO) Reinforced Waste High Density Polyethylene (wHDPE) Composites for the Production of Boot-last

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ABSTRACT
The utilization of waste polymers in footwear leather off-cuts fibre composites provides a useful material that is environmentally friendly. This work aimed at studying the mechanical and sorption properties of composites produced from wHDPE and UFLO. The matrix was waste high density polyethylene (wHDPE) and untreated footwear leather off-cut (UFLO) fibre as reinforcement. The composites were compounded using two roll melt mixing machine and compression moulding technique in the following weight percent of the fibre loading: 10%, 20%, 30%, 40% and 50% respectively. Subsequently, the mechanical and water sorption properties of the composites were analyzed. The results obtained indicated that, the tensile strength of the composites decreases as the fibre loads increases. The composites with 10 %wt fraction of the UFLO fibre recorded the highest strength of 19.11 MPa, while the lowest was obtained at 50 %wt fraction of the fibre. The highest impact energy of 4.5 J/mm^2 of the composites was recorded at 10 %wt fraction of the fibre. From the water sorption results, composite with 10 %wt fraction of UFLO fibre recorded the lowest water sorption properties of 0.78 % as compared to 20.27 % of the 50 %wt UFLO. Owing to the results obtained, these composites showed a promising mechanical and sorption properties for the production of boot-last as the tensile strength and water sorption of boot-last should not be less than 17.92 MPa 0.39 % and not more than 30.00 MPa and 11.57 % respectively.

Keywords: Composites, Fibre, Footwear, Leather, Weight fraction

INTRODUCTION
Footwear leather off-cuts are usually leather scraps of different sizes, colours, and shapes obtained in the process of leather production and processing (Chen and Chen, 2020). Leather cutting is a critical operation in the footwear industry through which the top part of the shoes or upper is made and mostly, cow leather. "Therefore, the footwear and leather goods manufacturing tend to generate large quantities of production wastes and scraps, especially during the leather cutting stages". There is need to investigate the recycling/reuse and conversion of these wastes into economically and environmentally friendly composites. UNIDO, (2000a) stated that about 152 kg of waste could be generated from an average hide of 225 kg. Couple to the issue of environmental impact of solid leather wastes, it is imperative to think about the technological measures to manage these solid wastes generated from leather processing activities. Basak *et al*. (2020) reported the potentiality of generating gas from solid leather wastes. Hang *et al*. (2021) studied the utilization of waste leather fiber (WLF) in polymer composite material based on nitrile butadiene rubber (NBR). The investigation indicated that, development of WLF/NBR composite can produce a temporary toluene for environmental protection. The leather wastes are also used in concrete for construction purpose as to reduce pollution and disposal problem resulting in less landfill pressures and reducing demand of extraction (Mushahary, 2017).Composite is a combination of two or more materials in the form of macroscopic structural unit, with one component as continuous matrix and other as fillers to form a new material different property with the constituent material (Widiastuti *et al*.,2022). Natural fiber reinforced polymer composites are materials that are in high demand in the automotive, aircraft, manufacturing and construction industries. Natural fiber reinforced polymer composites are significant over synthetic polymer composites, especially in low costs of manufacturing, high strength and stiffness, good heat resistance, low density and good energy absorption (Mathai and Mittal, 2018). Polymer

composite is an attractive potential in place of synthesised fibre reinforced polymer composites (Sathishkumar, 2013).Kamble and Behera (2020) studied the mechanical properties and water absorption characteristics of composites reinforced with cotton fibres recovered from textile waste. The equilibrium water content of the composites was observed to increase with increasing fibre loading. “The tensile strength of thermoplastics is the maximum amount tensile stress it can withstand before failure. The tensile test for HDPE and LDPE plastics is conducted by Standard Test Method for Tensile Properties of Plastics (ASTM D638) 2014. Typically, a dog bone shaped specimen was chosen for testing the plastic specimen”. Boot-last is the reproduction of the approximate shape of the human foot and also regarded as the heart and single most important element of the shoe (Majbaur, 2015). It is the most scientific and complex part of the whole shoe making process and it is the foundation upon which much of the shoe related foot health depends (Cheng and Pemg, 1999).The objective of this research is to utilize plastic and leather wastes in the production of an indigenous Military boot-last that represent the morphological shape of a typical Nigerian foot. Studying the mechanical and water sorption properties of footwear leather wastes reinforced HDPE composites becomes necessary for the production of the last.

MATERIALS AND METHODS

Materials

i. Footwear Leather Off-cuts (FLO)
ii. Waste High Density Polyethylene (wHDPE)

Methods

Elemental analysis using EDXRF

The X-ray Fluorescence analysis of the untreated footwear leather off-cuts (UFLO) was carried out using Thermo Fisher Scientific Energy Dispersive X-ray Fluorescence (EDXRF) model ARL.QUANT'X-9952120and the IAEA-155 biological sample method. The sample holders containing the sample were subjected to run in a vacuum or air for 10 minutes and afterward, they were inserted into the XRF Spectrometer for the Elemental analysis. The method was calibrated using biological calibration for elemental analysis. The samples were then allowed to run in the EDXRF spectrometer for 10 minutes each after which the results were obtained.

Composite Production

The wHDPE matrices and the fibres (FLO) were compounded on a Two Roll Mill (New Jersey, USA) at the Polymer recycling Laboratory, Department of Polymer Technology, Nigerian Institute of Leather and Science Technology (NILEST), Zaria. The composite samples were by the addition of the shredded waste HDPE while the rolls were in counter clockwise motion for a period of 10 minutes at a temperature of 180 ℃. Upon achieving a paste like matrix, the fillers material (FLO) was introduced by gently applying manually as the rolls rotate at a rate of 500 rpm. The percentage fibre loading was varied from 0 – 50% (0, 10, 20, 30, 40 and 50) respectively. The 0 % in this case is the control.

Curing

The compounded samples were cured under hydraulic machine with electrically heated platens. The temperature of the platens was set at 150℃ and on attaining the temperature the moulds was preheated to attain the platen temperature. The material was then cut to take the shape of the mould and placed in between the platen with a pressure of 2.5 MPa for 5 minutes. Finally, the cured samples were removed from the mould after cooling.

Plate I: Specimen cuts of the composites for analysis

Tensile Strength

To determine the tensile strength of the leather, the test samples were cut according to a total length of 100 mm and gage length of 47 mm. The testing of the samples was carried out at Department of Polymer and Textile Engineering, Ahmadu Bello University, Zaria-Kaduna State, Nigeria in accordance with ASTM D638 (2014) standard. The samples were machined to dumb bell shape and then placed in Tensile Strength Test Machine TM2101-T7 model and the tensile strength was evaluated. The tests were done in duplicate.

Plate II: Tensile Strength Test Machine TM2101-T7

Impact Energy test

The impact test on the developed composite samples was carried out using a fully instrumented Charpy impact testing; CAT NR412 model at the Department of Metallurgical and Materials Engineering, Ahmadu Bello University, Zaria according to an ASTM F2231-02 (2013) standard. The dimensions, gauge length and V-notch were chosen according to the standard. The specimen was placed between a sample holder with the notch oriented vertically and towards the origin of impact. The specimen was struck by a "tup" attached to a swinging pendulum. The specimen breaks at its notched cross-section upon impact, and the upward swing of the pendulum was used to determine the amount of energy absorbed in the process and the results was recorded in Joules (J).

Water Sorption

Water sorption test was carried out according to ASTM D570 (Klyovov, 2007) with oven dried specimen of dimension 76 x 25 x 5 mm immersed in water at ambient temperature for 24 h. After immersion for 24 h, the specimens were then removed and patted dry with a cloth (lint free) and then reweighed using a Sartorius Analytical balance ED 224S.To evaluate the long term moisture absorption of the composites, the process was repeated following 0 – 30 days exposure. The dried weight before immersion ($W_{initial}$) and the weight after immersion (W_{final}) were recorded. The water sorption was determined according to equation 1:

$$W = \frac{W_{final} - W_{initial}}{W_{final}} (\%) \quad (1)$$

RESULTS AND DISCUSSION

Table 1 present the elemental constituents of untreated footwear leather off-cuts. The results obtained showed Chromium representing the highest amount and sulphur followed. This could be due to the fact that chromium salts are basically used as tanning agents and sodium sulphide is use for unhairing. This chromium in the finished leather is existing as $Cr^{3+}$and not Cr^{6+}, therefore is environmentally friendly to human beings at the point of usage. These elements exist in their oxide forms.

Table 1:Result of the elemental constituents of footwear leather offcuts

Elements	Conc. (%)
Fe	0.031
Cu	0.003
Ni	0.002
Zn	0.001
Al	0.032
Mg	0.019
Na	0.262
S	0.971
P	0.059
Ca	0.233
K	0.033
Mn	0.000
Cl	0.890
Cr	2.755
Ba	0.011
Si	0.000

The tensile strength of the untreated FLO-wHDPE reinforced composites is shown in Figure 1. The results showed that, the tensile strength decreases as the weight fraction of the fibre increases. But at 40 % fibre loading, a sharp increase was observed. This could be as a result of uniform distribution of fibres in the matrix during compounding. A similar situation was reported by Hammajam *et al*. (2020). The untreated fibre at 10 wt % fraction indicated an improvement in tensile strength of 19.11 MPa as compared to the unreinforced (control) sample having a tensile strength of 17.92 MPa.

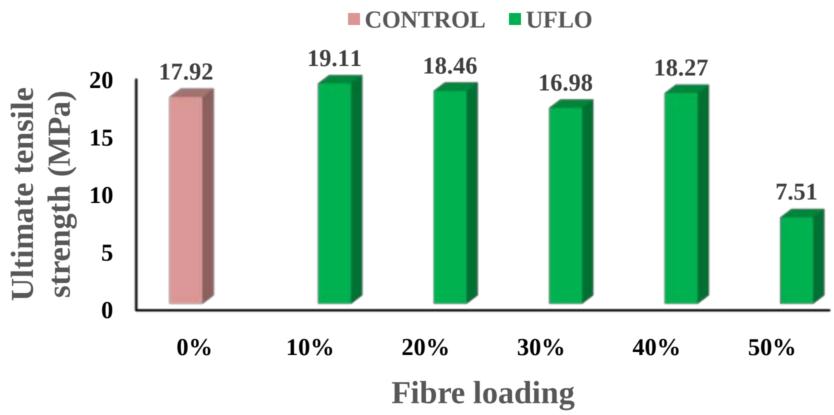

Figure 1: Effect of untreated footwear leather off-cuts on tensile strength of wHDPE composites

Figure 2 indicated the % elongation at break of untreated FLO-wHDPE composites. The results show a gradual decrease in elongation (%) at break of the composites with increase in fibre loading. Increase in untreated FLO loading in the wHDPE matrix resulted in the hardening and stiffening properties of the composites (Hang *et al*., 2021).

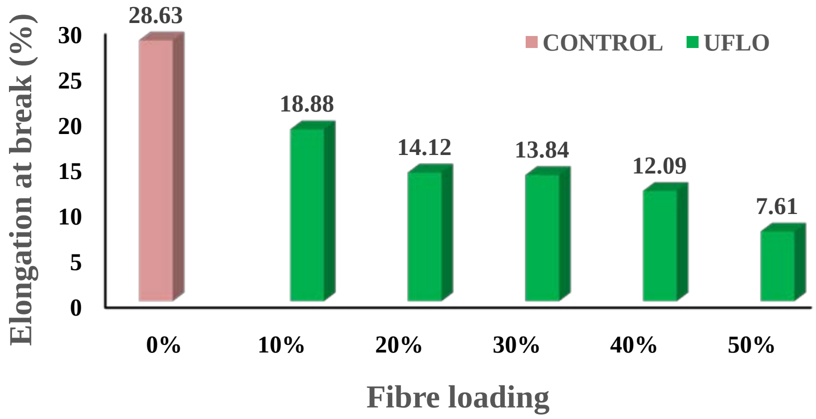

Figure 2: Effect of untreated footwear leather off-cuts on elongation at break of wHDPE composites

Figure 3 depict the flexural strength of the untreated FLO-wHDPE composites. The result indicated an increase in flexural strength as the weight fraction of reinforcement increases. The increase could be as a result of good interfacial adhesion between the polymer matrix and the fibre, therefore, increasing the surface area for the matrix-fibre interaction leading stress transfer. This is in agreement with the work of Anosike-Francis *et al*. (2022) who deduced that sufficient amount of cowpea husk in the matrix facilitates effective stress transfer within the matrix due to intrinsic properties of cowpea.

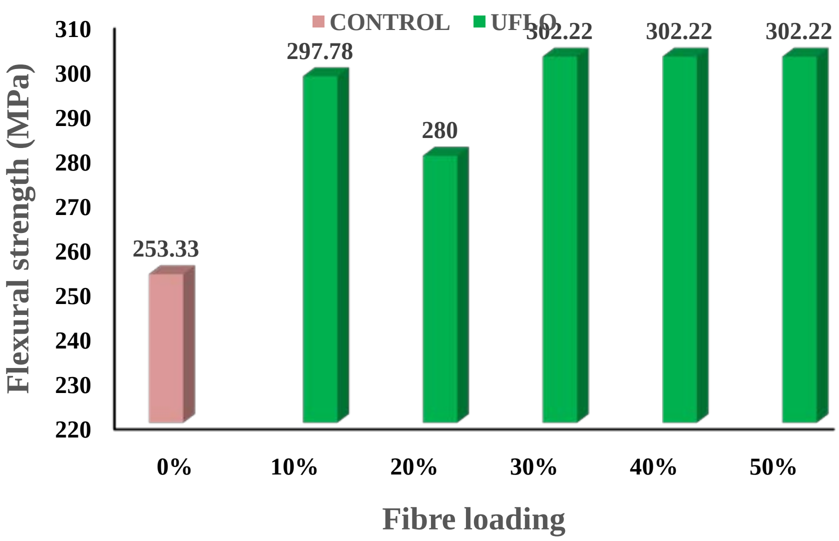

Figure 3: Effect of untreated footwear leather off-cuts on flexural strength of wHDPE composites

Figure 4 depicts the distinction of impact energy with fibre loading of untreated FLO. The results show a steady decrease in impact energy as the fibre loads or content increases, with a maximum value obtained as 4.5 Jmm^2 at 10 wt % FLO. Therefore, the decrease could be attributed to rigidity and deformation processes caused by the fibres imbedded in the matrix which restrict free chain movement during deformation. This deformation could be created through the reduction in ductility leading to the dynamic restrictions of the polymer matrix, therefore imposing mechanical constraints (Bartoli *et al*., 2022).

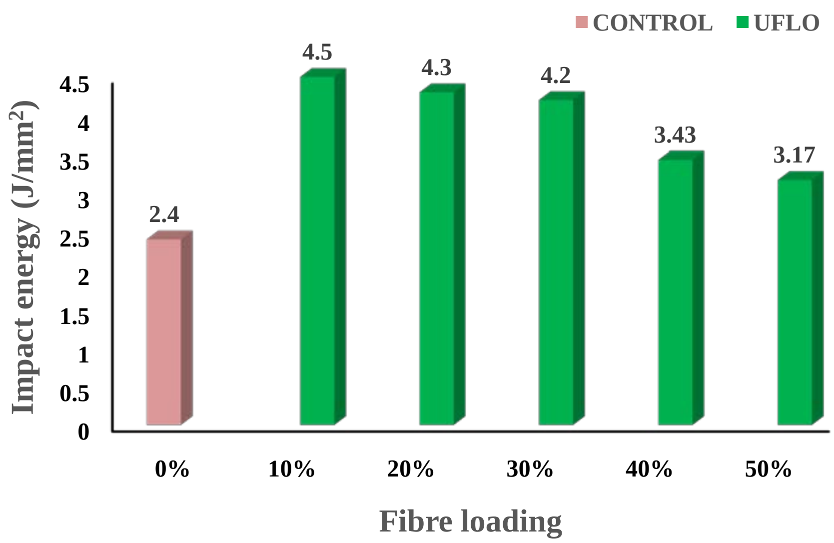

Figure 4: Effect of untreated footwear leather off-cuts on impact energy of wHDPE composites

Figure 5 represent the water absorption of untreated FLO-wHDPE composites. It could be seen from the results that, the trend indicated an increase in moisture absorption with weight percentage of untreated FLO fibres and time. The highest water absorption recorded was 20.27 % at 50 wt % of FLO. This could be due to the fact that natural fibres are hydrophilic in nature with many hydroxyl groups (- OH) in the fibre structure leading to the formation of hydrogen bond between the macromolecules of the fibres and polymer (Polyethylene) (Jacob and Mamza, 2020). Generally, the amount of water absorption is greatly affected by the void contents and density of composites as a result of higher fibre loading (Tezara *et al.*, 2021).

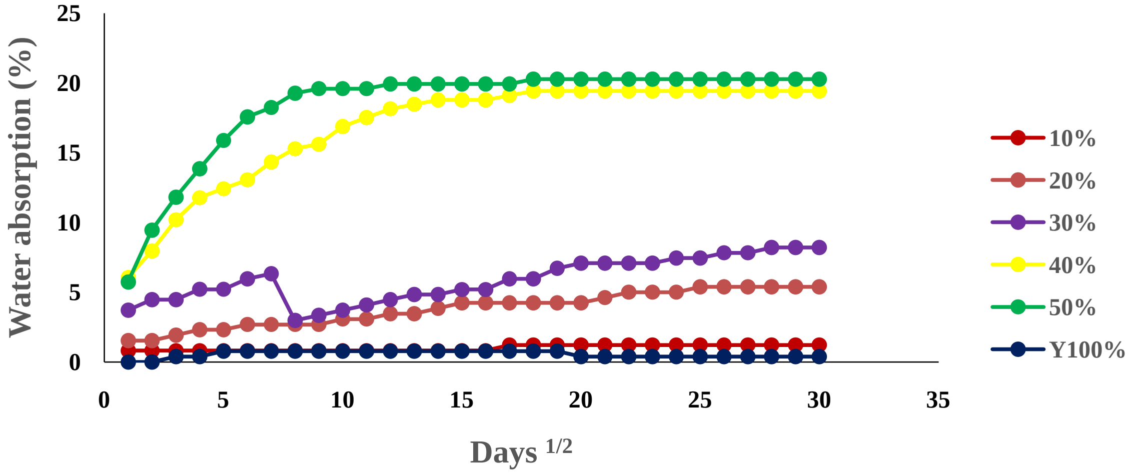

Figure 5: Effect of untreated footwear leather off-cuts on water sorption of wHDPE composites

CONCLUSION

From the results of the characterization of the composites, the following conclusions were drawn:

- At 10 %wt fraction of 4.5 Jmm^2 impact energy, the composite has the ability to absorb the impact stress due to the even distribution of stress between the polymer matrix and fibres. The ultimate tensile strength of the UFLO-wHDPE composites at 10 %wt is 19.11 MPa which is higher than 17.92 MPa tensile strength of the unreinforced (control) sample.
- Thus, considering the mechanical properties of the composites obtained, 10 %wt fraction shows a promising result suitable for the production of Boot-last, owing to the fact that, the minimum tensile strength of 19.00 MPa of pure HDPE is required for the production of last.

ACKNOWLEDGEMENT

The authors would like to appreciate Nigerian Institute of Leather and Science Technology (NILEST), Zaria, Kaduna State for the award of NILEST-Grant to make this research work come to reality.

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