ORIGINAL RESEARCH ARTICLE

Effect of Additives on the flexibility of High-Density Polyethylene Filled Cowhide Composite

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ABSTRACT

Fibre-filled high-density polyethylene composite was prepared by two roll melt mixing, and pressed into standard shapes using compression moulding technique for varying fibre contents from 10% by weight up to 60w% by weight. Tests were performed on composite specimens in accordance with ASTM D638. Additives have been incorporated into the design formulation of the composite to provide flexibility and intercalate (adhesion) between the fibre and the substrate. The results obtained were compared with specimens made of 100% weight of high-density polyethylene (HDPE). Results showed that waste loads in the range of 10-40% weight for un-treated hides (UH) and plant treated cowhide (*acacia nilotical*) (VT), represent good mechanical, physical, thermal and morphological properties, with improved intercalation between the fibre and interface substrate due to additives. 10-40 % weight (non-degradable) HDPE can be partially replaced with rawhide and processed shredded hide (both compostable), with the highest value at 10% by weight fibre content. The breaking strength of high-density polyethylene filled untreated hide with additive (HDPE/UHA) and high-density polyethylene filled plant treated hide with additives (HDPE/VTA) stretches longer under tension by 32.7% and 3.9% respectively, more than the control at 40% content by weight. The composites are suitable for producing composite-films, useful for manufacturing bags for packaging food goods, or in shoe soles, floor tiles and any material property requiring flexibility.

INTRODUCTION

On a daily basis, a large amount of solid waste, including finished leather shavings, shaving dust, animal hair, meat, hides and scraps, is produced by industries (Ali *et al.*, 2020). It is estimated that the processing of 1 ton of cowhide produces about 600 kg of solid waste and 50 cm³ of wastewater (Parisi *et al.*, 2021). Musa *et al.*, (2016) reported that out of 1000 kg of rawhide, only 150 kg of the raw material was converted into finished leather. Solid waste disposal is not profitable and is an economic burden for tanners (Clare, 2021). 80% of solid waste is generated during the pre-tanning process while 20% of the waste is due to the post-tanning process (Priebe and Gutterres, 2016; UNIDO, 2017; Elena *et al.*, 2019). As a result, the leather industry in developing countries faces many solid waste problems (Elena *et al.*, 2019; UNIDO, 2020). Researchers around the world are working on safer methods to reuse this waste in other diverse industrial applications due to environmental concerns and how to reduce large losses from tanners. Various methods have been proposed and documented in literature (Murali *et al.*, 2019; Ali *et al.*, 2020; Ramani *et al.*, 2020; Clare, 2021) on how these wastes are converted into valuable products. The plastics industry is another major sector in which manufacturers and scientists in the reinforced plastics industry have found a new eco-friendly way to create low-cost commercial materials that are biodegradable and molten (Mohanty *et al.*, 2005; Jinchun *et al.*, 2013; Rajendran *et al.*, 2016), but still such a large amount of waste.

Thanks to the development of composites, most polymers today can not only rival or even eclipse metals and light alloys in terms of stress sensitivity and safety in engineering applications, when modified or/and combine

with additives. Changing properties and processability of polymers by adding other substances is a large and growing field documented in literature (John and Richard, 2005; Parisi *et al.*, 2021). Similarly synthetic reinforced with natural fibres of plant and animal origins are today the most dynamic industry.

Composite design and fabrication is meeting the desired requirements of material technology. Thus finding an appropriate combination of materials would enable the development of composite with properties suitable for end-user applications. The ease of composite design and fabrication have thereby made composites versatile, valuable and important family of materials that have encompassed almost all material domains (Musa *et al.*, 2016). The matrix (which could be particulates, flakes, spheres or fibres) can range from cement through exotic, expensive polymeric chemical resins. In the case of the polymeric resins, the materials have to be cured in an autoclave which bind the fibres together in order to act as the medium through which an externally applied stress is transmitted and distributed. This, protect the individual fibres from surface damage as a result of mechanical abrasion or chemical reactions with its environment and separates the fibres by virtue of its relative softness and plasticity. The reinforced materials, give stiffness or rigidity, exhibit high tensile strength and undergo irreversible deformations in composites (Todd, 2015).

In the design and manufacture of composites, bond strength is an important consideration in selecting matrix fibre assemblies. The ultimate strength of the composite depends largely on this degree of bonding (Nahar *et al.*, 2014; Kilic *et al.*, 2021). Therefore, selecting compatible materials with sufficient cohesion is essential to maximize the stress transfer from the weak substrate (continuous phase) to the strong fibre (dispersed phase). The bond strength is related to the existing interface between the fibre and the matrix (Jerzy and Elzbieta, 2012; Jinchun *et al.*, 2013; Jefri *et al.*, 2017). Bond strength determines the mechanical, flexural, impact strength, physical properties, etc. of composites. Therefore, the link between the faces controls these properties (Musa *et al.*, 2022). This can be achieved by physical, mechanical or chemical treatment of the composite in order to improve the bond such that superior/reasonable surface strength and stiffness of composite generally increase with increasing fibres content up to a certain point (Ibe *et al.*, 2019; Hang *et al.*, 2021).

This work was aimed at the preparation of cowhide (UH), vegetable-treated cowhide (VT)) and high-density

polyethylene (HDPE). Then study the flexibility of the composite mechanical, physical, thermal stability and morphological property of the processed sample for the production of packaging materials of various design that could be used for food products and other merchandise.

MATERIALS AND METHODS

Materials

Cow leather was collected from tannery, Nigerian Institute of Leather Science and Technology (NILEST), Zaria, Nigeria. Commercial high-density polyethene (EIPIN; melting index 0.488 g/min) came from Indorama Chemical Company Port-Harcourt, Nigeria. Magnesium hydroxide [$Mg(OH)_2$], acrylic acid, sodium hydroxide (NaOH), titanium dioxide (TiO_2) and ethylene-vinyl acetate copolymer (EVA) were quality analytes from (M and B), GMS and Aldrich Chemical. Natural rubber (NR) was sourced, Samaru market, Zaria, Nigeria.

Sample preparation

The cow leather was treated with hybrid acacia (Hausa: Bagaruwa), cleaned, sun-dried and oven-dried at 50 °C. The dried hide was then milled to a grain size of 0.5 mm using an Arthur Thomas Wiley Laboratory Grinder (Model 4), Philadelphia USA. The ground sample was stored in a clean, dry, covered thermoplastic transparent bucket. High-density polyethylene (HDPE) and additives were used as received. Tables 1 and 2 gives the formulation of the composite.

Mixing

The formulations in Table 1 (PW01-PW07) were mixed using a carver's double roll mill (model 5183) at a processing temperature of 180 °C for 9 min Musa *et al.*, (2014). Thus, treatment temperature and duration were the same for all the formulations in Table 1. The same procedure was performed on Table 2 to produce additive composites.

Compression casting

A thin aluminium plate was used as the mould through which the composite film was pressed. Each compound formulation, weighing 1.5 g, was measured and then wrapped in cut aluminium foil. The packed sample was then placed into the mould and then placed on the moving plates of the heat press machine. Using a hydraulically operated ram, the lower roller containing the mixed sample moves to the upper roller, closes the mould and pressurizes the casting (Musa *et al.*, 2019).

Table 1: Composite Formulation without Additives

Samples	Composite (%)						
	PW01	PW02	PW03	PW04	PW05	PW06	PW07
HDPE	100	90	80	70	60	50	40
Untreated hide waste (UH)	0	10	20	30	40	50	60
Treated hide waste (VT)	0	10	20	30	40	50	60

Table 2: Composite Formulation with additives

Samples	Composite (%)						
	PWA01	PWA02	PWA03	PWA04	PWA05	PWA06	PWA07
HDPE	100	90	80	70	60	50	40
untreated hide waste (UHA)	0	10	20	30	40	50	60
Treated hide waste (VTA)	0	10	20	30	40	50	60

Additives = (0.5 g trimethylquinoline (TMQ), 3.5 g $Mg(OH)_2$, 0.3 g TiO_2, 10 g natural rubber (NR), 2 g ethylene vinyl-acetate copolymer (EVA) and 2 ml acrylic acid).

Compression casting

A thin aluminium plate was used as the mould through which the composite film was pressed. Each compound formulation, weighing 1.5 g, was measured and then wrapped in cut aluminium foil. The packed sample was then placed into the mould and then placed on the moving plates of the heat press machine. Using a hydraulically operated ram, the lower roller containing the mixed sample moves to the upper roller, closes the mould and pressurizes the casting (Musa *et al.*, 2019). The films were compressed at compression temperature and pressure of 180-185 °C and 3×10^3 N/m² for 3 min of preheat and 5 min of pressing, respectively. Each sample was compound formulated and 10 samples were extruded into a 1.0 mm thick thin film.

In contrast, all other composite shapes were manufactured according to America Standard Testing Method (ASTM) D638. All analysis were carried out in accordance with standard testing procedures; Mechanical test, measures the force required to break the composite and the extent to which the composite stretches or elongates before breaking was with a universal testing machine having gauge length of 40mm, and width of 3mm. Izod impact test, was done using the Universal Pendulum Impact System "Ray-Ran, UK" each sample had dimension 90mm × 10mm × 3mm, clamped rigidly at one end of a Ceast Izod impact machine (Model 957) and struck at the other end by a pendulum-weight, to break the sample in accordance to ASTM D 256-05. The hardness of composites with dimension 50mm × 50mm × 3mm were determined by the penetration of the durometer indenter foot piercing into sample at its center

and its two edges, using a Durometer Shore A tester. Density was carried out according to ASTM D792-00 specification (the composites were cut into narrow rectangular strips of approximately uniform thickness of 80mm × 80 mm × 0.5 mm in dimension and used to determine the density of the composite). Water absorption of the composite was determined in accordance with ASTM D570. In this method, a circular shape of the prepared composites of diameter 20 mm and 2 mm in thickness were first weighed dry, then immersed in distilled water in a transparent thermoplastic container with its lid and left for 96 hrs at 27°C, excess water on each composite surface was wiped off with a filter paper before reweighing). Thermal analysis was performed according to ASTM D3418 and ASTM E1131, using DSC and TGA respectively. The heating rate was performed at 10°C/min; decomposition temperature in nitrogen atmosphere was 0 to 800°C. Sample mass was determined first by weighing the crucible before and after adding the accompanying mixture to the 160 μl aluminum crucible for testing (Musa *et al.*, 2019). Surface examination of sample morphology of treated and untreated cowhide and the composites fractured tensile surface using a JSM-5600 LV (Jeol, Tokyo, Japan) scanning electron microscope (SEM). Scanned images were taken at accelerating voltage of 2.0 and15.0 kV.

RESULTS AND DISCUSSION

Table 3 presents a summary of the mechanical and physical properties of untreated and treated cowhide prepared at 0 and 10 proportion of cowhide to a 100 and

Table 3: Shows the Mechanical and Physical Properties of Composite at 0% and 10% of UH and VT with and without additives.

S/N	Sample	Mechanical properties						Physical properties		
		BS (Nmm^{-2})	YS (Nmm^{-2})	E B	E Y	FS (Nmm^{-2})	Vertical impact (Jmm^{-2})	Hardness	Water uptake (%)	Density (gcm^{-3})
1	HDPE	25.33784	27.3649	2.7253	2.08333	-	-	79.3	0.01943	0.97
2	HDPE/A	72.27273	74.7273	3.175	2.45833	0.91837	0.24199	79.3	1.06906	0.872
3	HDPE90/UH10	38.4868	40.3618	2.125	1.9253	-	-	80.0	17.6534	-
4	HDPE90/VT10	21.16883	21.2987	2.2753	2.0147	-	-	74.5	8.31469	-
5	HDPE90/UHA10	53.5714	53.5714	1.9125	1.9125	1.17526	0.26683	80.0	7.7	0.798
6	HDPE90/VTA10	100.9709	100.971	2.0000	2.0000	0.84008	0.33495	74.5	2.0	0.855

HDPE = high-density polyethylene, A= additives, VT= treated cowhide, UH= cowhide, HDPE90/UH10 = 90: 10 ratio of HDPE to cowhide, BS = breaking strength; YS = yield strength; FS =flexural strength and E = elongation.

90 proportions of HDPE In Table 3, the values of yield strength, bending, impact, stiffness, water absorption and density of composites with and without additives at 10% by weight of cowhide and 90% of HDPE was higher than HDPE acting alone at 100%. This is an indication that an improved properties with cowhide loading of 10% by weigh was achieved. Hang *et al.*, (2021) and Mohammed *et al.*, (2006) in a similar research, observed a remarkable property in their study when fibre was embedded in polymer.

Tables 4, shows summary of the FT-IR Spectroscopic data of HDPE and composites. The FT-IR data in Table 4 confirms alkyl sp^3 C-H, disubstituted C=C stretching, at 2914cm^{-1} and 1461cm^{-1} HDPE. While typical signals of O-H, C=O, N-H and C-O stretching were the major strong and sharp vibrations at 3298, 1625, 1543 and 1080cm^{-1} for

UH and VT acting alone. In the case of composite, a combination of signals ascribes to O-H, N-H, CO and C-H stretching were seen. Implying a mixture of HDPE with cowhide without any reaction during the process, as shown in Appendix 2. The FT-IR was read as guided by Asep and Risti, (2019).

Table 5 shows the summary of TGA temperature and residual weight of HDPE and its composites. In the Table, the weight loss, residual weight, onset temperature and decomposition temperature of the composites are shown. The degradation of HDPE (Control) starts at about 293^{0}C with a weight loss of about 1.283%, and the maximum decomposition rate occurs with HDPE at about 440^{0}C with residual weight of about 15%. The HDPE90/UH10 mixture gained 0.298 percent in weight at 200^{0}C while the HDPE90/VT10 mixture gained 0.149% at 50^{0}C and increased in weight to 1.154% at 200^{0}C (Appendix 1). Meaning the mixed system is more thermally stable than the control sample. This may be because the interaction between the composites and the additives, limit the thermal movement of the composites and improved thermal stability. In addition, the addition of additives improved the thermal stability of the composites from 160^{0}C to 300^{0}C (Appendix 1). This result is similar with that of Zanaib (2012), who found that carbon black and titanium dioxide incorporated into high-density polyethylene composites, gave better thermal properties than pure HDPE.

Table 4: FT-IR Spectroscopic Data

S/N	Sample	Stretching Frequency (cm^{-3})	Bond Type	Shape
1	HDPE	2847, 2914, 1461	C-H	Strong and sharp peaks of alkyl and alkene
2	UH	3298, 2937 1625, 1543, 1080 and 663	O-H and N-H, C-O, N-O and sp^2 C-H	Strong, sharp and broad peaks with finger print alcohol and amide bond
3	VT	3280, 2922, 2191, 1628, 1543, 1080 and 1448	O-H, N-H,sp^{3}C-H, C-O, C=O, nitro and alkyne	
4	HDPE90/UHA10	3697, 2914, 1893, 1461, 1738 and1021	O-H, sp^{3}C-H, C=O, sp^{2}C-H, N-O and C-O (aldehyde and alkoxy)	All strong and shape peaks were in the prepared sample,
5	HDPE90/VTA10	3701, 3675, 2918, 2847, 1461, 1038 and 719	O-H, N-H,sp^{3}C-H, C-O, C=O sp^{2}C-H and N-O	

Table 5: TGA Data of Samples.

Sample	T_o Onset tempt. (T^0C)	T_d Max decomposition tempts. (T^0C)	% Weight loss T_o	% Weight loss T_d	% Residual weight
HDPE	293	440	2.01	49.744	15
HDPE90/UH10	265	417	0.148	14.661	12
HDPE90/VT10	263	395	1.977	98.948	0
HDPE90/UHA10	237	421	1.982	87.723	11
HDPE90/VTA10	262	414	0.991	69.26	30.7

Table 6 shows, the melting temperature, peak height and peak area of composites. The melting temperature of control and its composites on Table 6 varies within 162.21 to 160.68^{0}C indicating that the T$_m$ of composite

was on average 161.59^{0}C. HDPE has the highest peak at 17.7, suggesting that it is easier to crystalize the HDPE than composite. The composite are likely to be amorphous as Benzler (2013) explains, distinguishing

between crystalline and amorphous organic samples. The rate of thermo-oxidation process corresponds to the maximum of the thermo-oxidation peak. High peak relate to an advanced deterioration (Elena *et al.,* 2019) the results obtained have an oxidation rate reduction effect (Appendix 3).

Table 6: DSC Data Samples.

S/No	Composite Name	Peak height mw	Melting temperature (°C)	Peak Area JK/(mg)s
1	HDPE	17.7	162.21	26.58105
2	HDPE(A)	17.57	161.12	33.54034
3	HDPE90/VT10	16.31	160.68	30.63222
4	HDPE90/UH10	12.25	162.02	28.25667
5	HDPE90/UHA10	10.64	161.3	29.24996

(a) Cowhide (UH)   (b)Treated hide (VT)   (c) HDPE

Figure 1 (a, b and c): shows the physical state of cowhide, treated hide (0.5mm particle size) and high-density polyethylene respectively before compounding.

Figure1 (a, b and c) shows the physical state of the sample of untreated cowhide, treated and HDPE as used for the research.
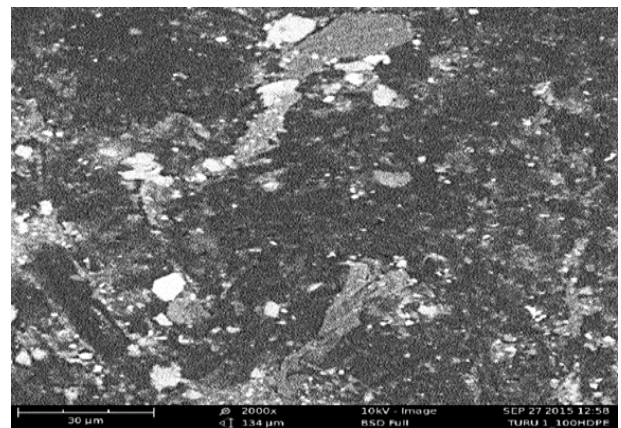
Figure 2 (a, b, c and d) shows SEM micrographs of composite surfaces without and with additives. The optical fibre dispersion mode in the matrix is clearly shown in each image. In Figure 2 a), it's seen that the treated hide stick together like a bud (plug together) at a distance from the HDPE, the two are not attracted to each other, that is, the bond between fibre-fibre may be stronger than the fibre-polymer bond (mixing rule) (España *et al.,* 2013) or it may be because the surface is poorly wetted for mixing. In the case of Figure 2 b), the fibre adhesion in the fibre shoot is reduced, allowing some fibre-polymer interaction to occur. This observation may be due to the presence of gelatin in cowhide which reduces fibre-fibre interaction by creating a wet surface for mixing. In contrast, the gelatin of vegetable-treated hides Figure 2 a) can be modified during tanning process. However, on Figure 2 (c and d), the fibres are seen dispersed in the substrate. The additives had successfully broke the fibre-fibre bond and improve the fibre-polymer bond, thereby promoting dispersion, as observed by uniform distribution of fibres in the substrate; that is, the additives help in separating the fibre bundles into single fibre and bridge the gap by creating surfaces for bonding.
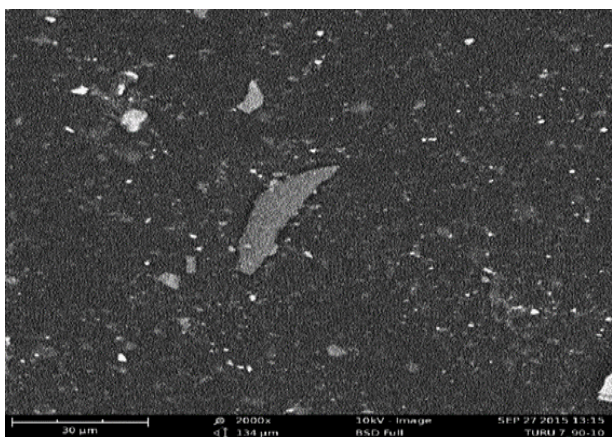
Figure 3 (a, b, c and d) shows SEM micrographs of tensile fracture surfaces of HDPE90/UH10, HDPE90/VT10, HDPE/VTA and HDPE/A composites. The tensile fracture surface in Figure 3 shows a degraded pattern, stress reduction and elongation (plasticity) before failure. Failure modes in Figure 3 (a, b and c) included tearing, fracture at focus points (i.e. at the point of fibre agglomeration) and an anti-deformation lines network. The observed rupture mode is similar to that of Hang *et al.,* (2021). On the other hand, the observed ductile failure surface of composite is a form of tensile strain, seen by the bonding networks in Figure 3 (a, c and d), illustrating a good fibre-matrix overlap, respectively, with high characteristic of Table 3. This finding agrees with Mohit (2015) and Rajendran *et al.,* (2016) results. They describe affiliate network as a powerful force.
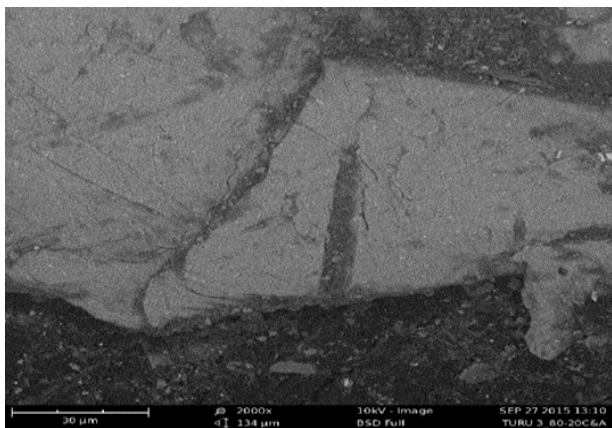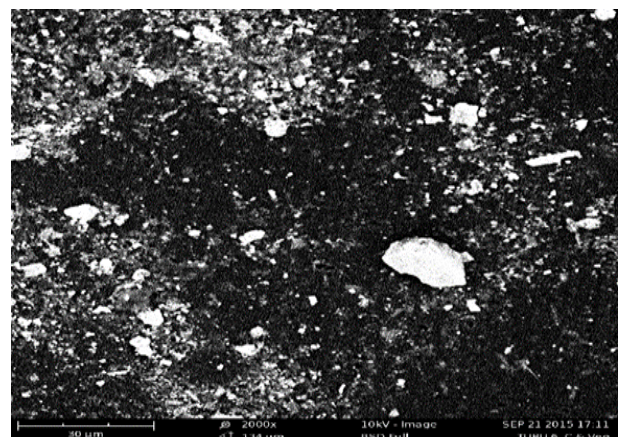
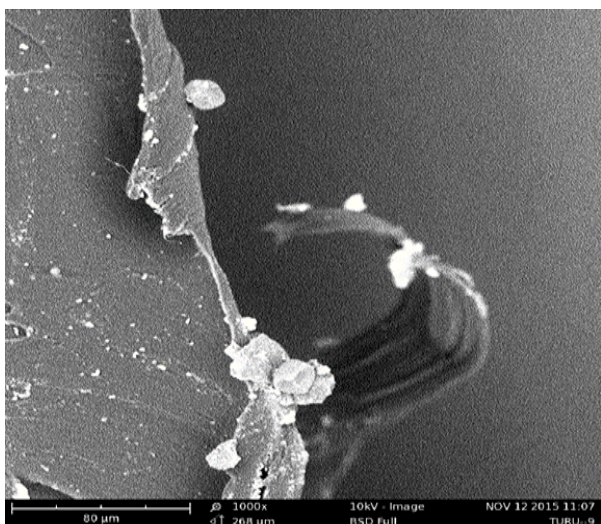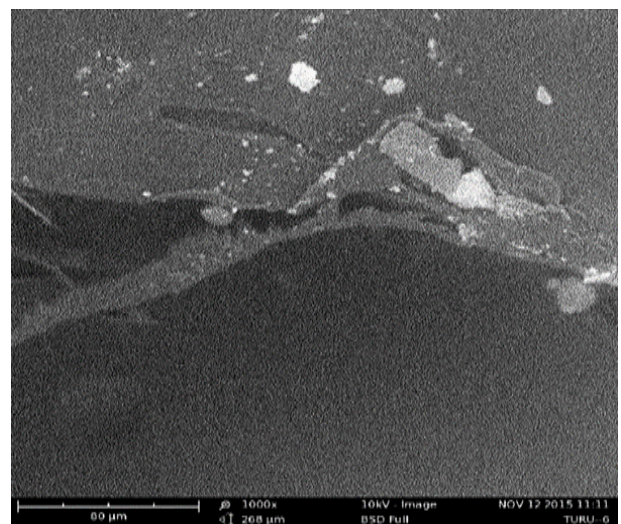(a) HDPE 90/VT10

(b) HDPE 90/UH 10

(c) HDPE90/VTA10

HDPE90/UHA10

Figure 2: (a, b, c and d): Shows SEM microgram surfaces of VT, UH mixed HDPE (composites) with and without additives.
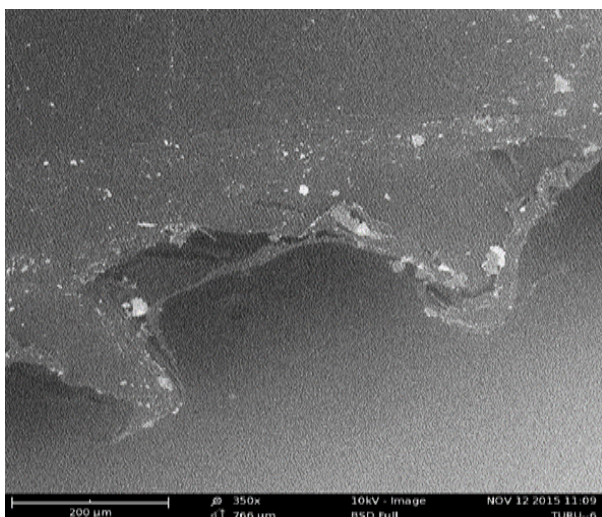

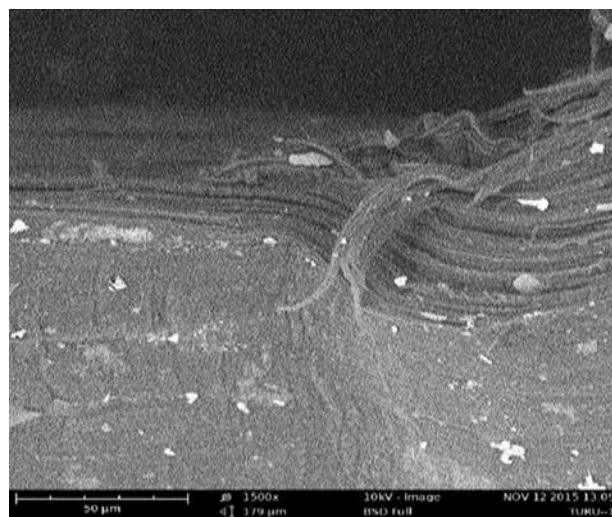(a) HDPE90/UH10 (tear and focus point)

(b) HDPE90/VT10 (poor dispersion)

Figure 3 (a and b): SEM micrograph of tensile fracture surfaces of HDPE90/UH10 and HDPE90/VT10

(c) HDPE90/VTA10 (Good wettability)

(d) HDPE100/A (link next work)

Figure 3 (c and d): SEM micrograph of tensile fracture surfaces of HDPE90/VTA10 and HDPE

Figure 4 shows the ultimate stress of composites prepared at different loads for HDPE/UH, HDPE/UHA, HDPE/VT and HDPE/VTA from 0w% to 60w% of fibres content when encountered tensile stress at break. The figure, clearly shows the influence of filler content, filler type and additive on the tensile properties of the composite. In the case of HDPE/UH, it can be seen that the ultimate stress, decreased with increasing UH content. While HDPE/UHA, HDPE/VT and HDPE/VTA first decreased at 10% filler content before it increased with increasing cowhide content to a certain maximum point differently, then decreased with further increased in filler content. This means, HDPE/UH, HDPE/UHA, HDPE/VT and HDPE/VTA at 10% filler content are less resilient to HDPE with or without additives. The decrease in ultimate stress may be due to the stiffness of the collagen fibre in HDPE, which impedes the free flow of the substrate and reduces its ductility.
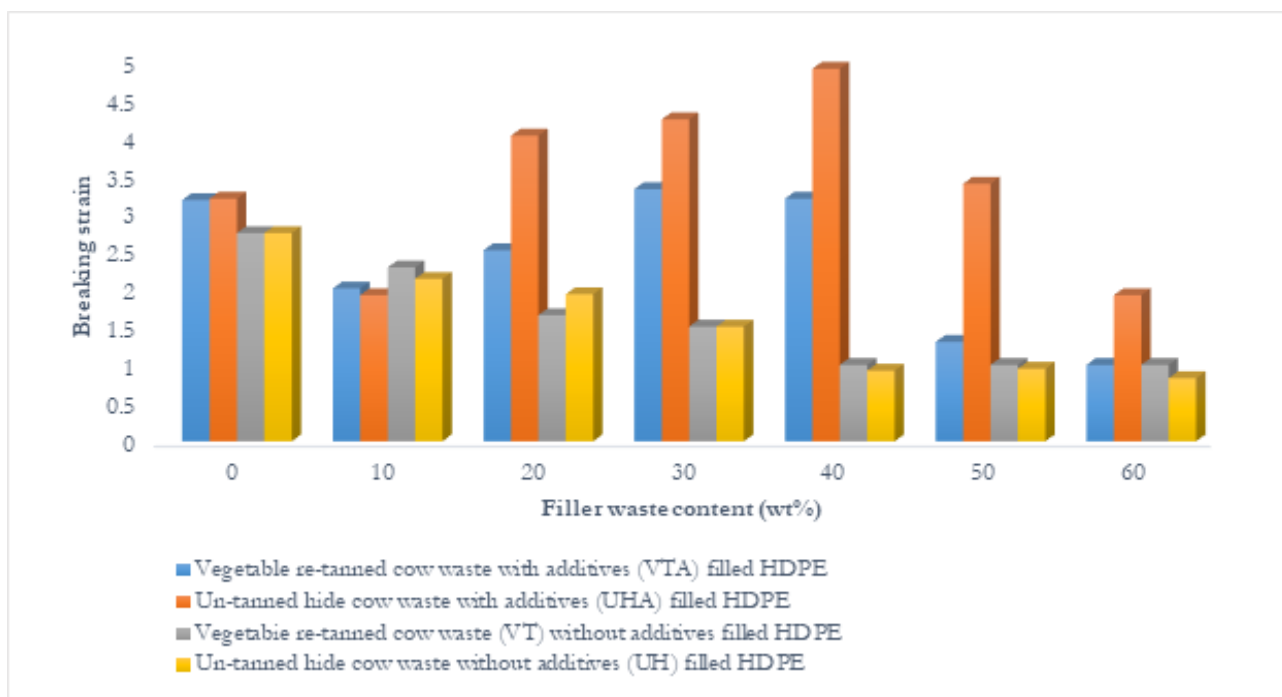

Figure 4: Effect of filler content on the breaking-strain of UH and VT cowhide dispersed HDPE at different proportions of HDPE/UH and HDPE/VT composite with and without additives, respectively.

On the other hand, HDPE/UHA composite showed an increased in ultimate stress with increasing filler content at 20% to 40% then decreased as filler content increases, HDPE/VTA was seen to increase at 30% to 40% VTA

content then decreased with increasing VTA content, indicating that the cowhide is a non-reinforcing filler. William, (2007); Musa *et al.*, (2016); Hang *et al.*, (2021); Musa *et al.*, (2022) observed similar result. The 30-60%, reduction in breaking stress with increased cowhide for HDPE/VTA and 40-60% for HDPE/UHA can be attributed to reduced wetting ability of the substrate for the number of fibres. When this occurs, the fibrous nature of collagen make homogenization difficult to maintain, thereby, results in fibre agglomeration (Eze *et al.*, 2016; Jefri *et al.*, 2017; Ibe *et al.*, 2019; Kilic *et al.*, 2021). This is evidenced by the results of SEM images presented in Figure 2 (a, b) and the tensile fracture surface in Figure 3 b). The increased in elongation of HDPE/VTA with increasing filler content before the critical point (20% and 30% by weight of HDPE/UHA and HDPE/VTA, respectively) compared with control (HDPE), could be attributed to the additives used (España *et al.*, 2013). The exceptional elongation observed for HDPE/UHA in Figure 4 can be attributed to the elastic nature of natural rubber and ethylene vinyl-acetate copolymer (EVA) that acts as the elongating hardening agent in the formulation of Table 2.

CONCLUSION

In conclusion, composites' ultimate stress (flexibility) was observed to depend on filler-type, the amount of filler content and the additives. HDPE/UHA and HDPE/VTA stretches higher by 32.7% and 3.9% respectively, more than the control at 40% weight of fibre content, while the elongation at yield for HDPE/UHA was 9.15% and 8.90% at 20% and 40% weight of fibre content, respectively. Acrylic acid, EVA copolymer and natural rubber was used as extender to improved the flexibility, in contrast making the composite possess properties of elastomeric materials. The additives had an advantageous property on the prepared composites and made cowhide in HDPE a viable alternative for producing new materials for used in many new applications where HDPE is applicable.

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Appendix 1: Summary of TGA data of composites with additives

Temperature ^{0}C	Control Sample	Composites (%)	
	HDPE	HDPE/UHA	HDPE/VTA
		Percentage weight loss (g)	
24	99.976	99.985	100.023
50	99.895	100.052	100.412
100	99.753	99.899	101.128
150	99.532	99.154	100.936
200	99.202	98.712	101.154
250	98.717	97.32	99.828
300	97.731	92.914	95.478
350	95.269	69.216	77.859
400	68.58	36.141	45.66
450	38.466	-	0.035
500	11.328	-	-
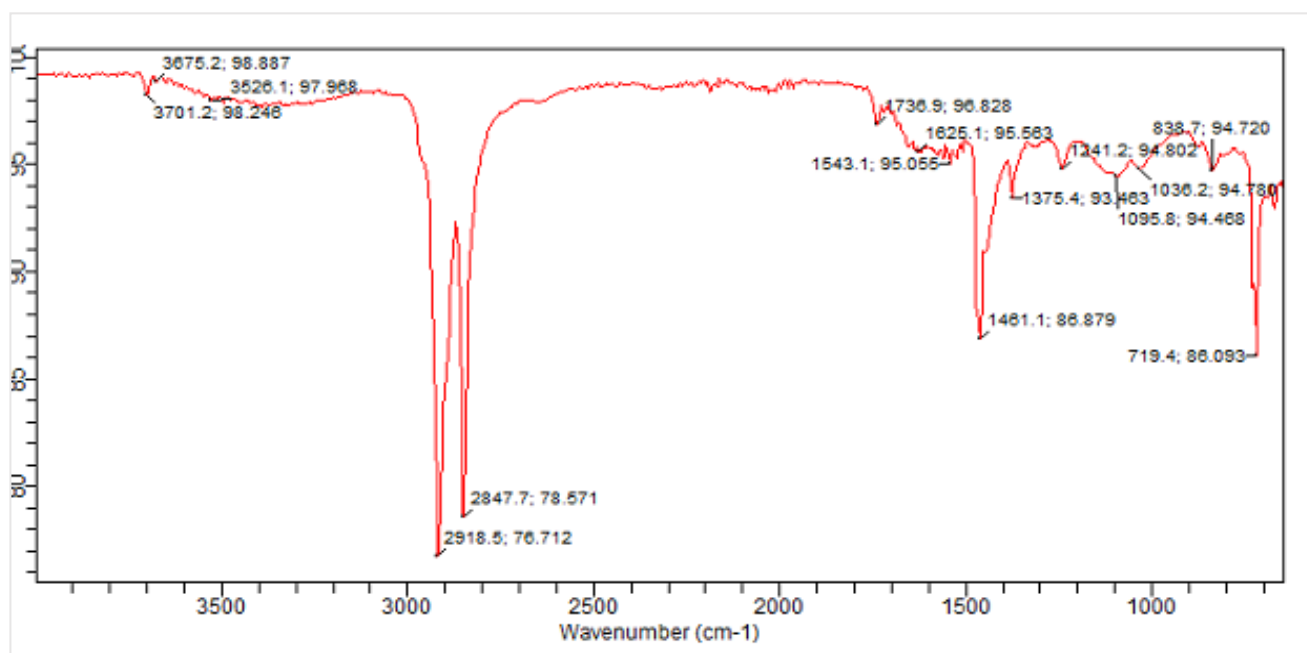
Appendix 2: FT-IR for HDPE/VTA composite
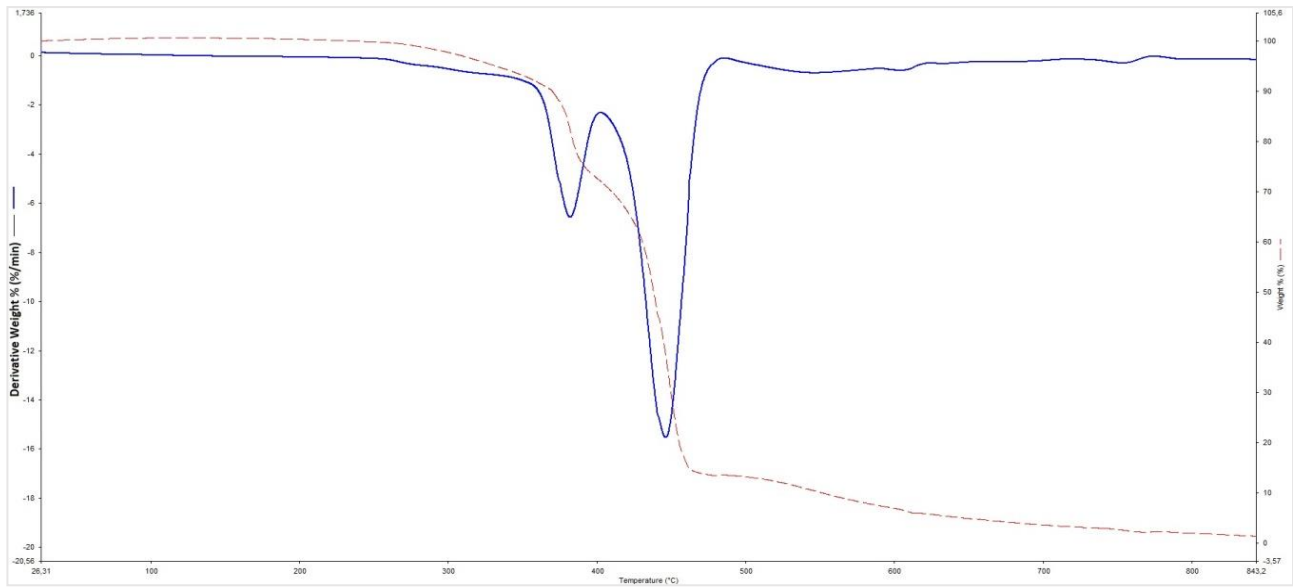
Appendix 3: **Thermogravimetric and Differential Thermal analysis for UH composite with additives.**