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Investigation of the Mechanical and Morphological Properties of High-Density Polyethylene (Hdpe)/Leather Waste Composites

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Abstract: *The potential of solid tannery waste as filler in high-density polyethylene (HDPE) was studied by examination of mechanical properties, morphology and thermal properties of the composites produced. The Composites were prepared by two roll melt mixing and compression moulding technique for varying fiber contents from 0% to 60%. The parameters tested were tensile, impact and hardness in accordance with ASTM specification. The morphology and thermal properties of the matrix and composites were studied by scanning electron microscopy and thermogravimetric analysis. The results of stress-strain behaviour of the composite was similar to those of thermoplastic polymer, the tensile strength and yield stress of the control (HDPE) was higher than that of the prepared samples by 8% and 5%. Hardness was better than HDPE by 12.86%. When 3.5g of Mg $(OH)_2$, 0.3g of Ti_2O, 10g of NR, 0.5g of trimethyl quinolene (TMQ), 2g of ethylene vinyl-acetate (EVA) copolymer and 2ml of Acrylic acid were incorporated into the formulation, 52.2%, 39.2% and 29.1% enhancement in yield stress, tensile and impact strength. SEM scan shows ductile tensile fractured surface of composites with better thermal stability than the control. Composite of HDPE90/fibers waste10 presents good mechanical performance with enhanced thermal stability.*

Keyword: *Leather waste; Mechanical properties; Thermal stability; Composite; Additives.*

I. Introduction

The growing environmental pressure such as increased pollution, increasing demand for biodegradable materials, material need for CO_2 neutrality and low greenhouse gas emissions, new environmental laws and regulations is making manufacturers and scientists keen to study novel environmental friendly materials (Jinchun *et al*., 2013; Muthuraj *et al*., 2015). Nowadays, the fibers resulting from wood, animals, leaves, grasses and other natural sources are commonly used as reinforcement in composites for various applications, like automotive (interior and exterior), building, ship, packaging etc., in addition, the unusual properties of natural fiber compared to other synthetic fibers had led to intensive research and development, in order to develop powerful composites using natural fibers that is capable of offering good bio-degradability and sustainability (Yong *et al.*, 2007). In many cases the source of natural fibers used as reinforcement is waste or residues from other industries, such as architectural, furniture, wood manufacturing, tannery waste etc., value has been added to waste and the reused of solid industrial and urban waste or residue Ambrósio *et al* (2011). The numerous advantages of natural fiber reinforced composites had become the reason of today's fastest growing industries (Souza *et al*., 2011).

The leather processing industry produces large amounts of solid organic waste in the form of un-tanned (trimmings, fleshing, splits) and tanned (trimmings, splits and shavings) waste from raw hides and skins including semi-processed leather (Ozgunay *et al*., 2007). The waste produced in leather industry far exceeds the quantum of finished leather (Zarfar *et al*., 2013 and 2014). Though a number of solutions for the utilization and/or safe disposal have been proffer, tested, practiced and applied at pilot and industrial scale (Yaohui *et al*., 2013); Pecha *et al*., 2012; Chrońska and Przepiórkowska, 2009 and 2011; Maria *et al*., 2011), but there is a huge leftover of these solid waste then can be managed by Tanners. This posed serious issue that most leather industry in the developing countries closed down for not being able to proffer safety disposal method nor meeting bio-chemical oxygen demand (BOD) and total dissolved solids (TDS) standards (Kanagaraj *et al*., 2006). The study is aimed at providing additional method of managing tannery solid waste generated in leather industry by dispersing solid leather waste (natural polymer) into thermoplastic polymer (HDPE) using compression molding technique, converting the solid waste into wealth. Despite the attractiveness of natural fiber reinforced polymer matrix composites, they suffer from lower modulus; lower strength and poor moisture resistance compare to the synthetic fiber reinforced composites (Moe, 200). They aged with time and are thermally unstable when exposure to ultra violet radiation (UV-light). When outdoor applications are necessary, stabilizers are added to the formulation to reduce the effects of ultraviolet radiations on the composite material. This will protect the mechanical properties, for long term service. Another limitation, is adhesion characteristic

of the fiber-matrix interface. Poor compatibility between hydrophilic fiber and hydrophobic thermoplastic matrix leads to poor dispersion of fibers in the matrix. This also influenced mechanical properties of fiber reinforced composites. Compatibilizers are used to improve the adhesion between the filler and the matrix (Mohammad *et al*., 2006). Physical or chemical method are also employed to improve the interaction between the fiber and the matrix of natural fiber reinforced composite (Jerzy and Elzbieta, 2012; Jinchun *et al*., 2013). There are many reports on the potential use and limitation of natural fibers as reinforcement in thermoplastics, available in literatures (Mohanty *et al.*, 2005).

II. Materials And Methods

Materials

Chrome tanned waste was collected locally from the tannery at the Nigerian Institute of Leather and Science Technology (NILEST), Zaria. High-density polyethylene (HDPE) commercial grade (EIPIN) was of Indorama Chemical Company Port-Harcourt, Nigeria. Magnesium hydroxide [Mg(OH)2], acrylic acid, sodium hydroxide (NaOH), titanium dioxide (TiO_2) and ethylene vinyl acetate (EVA) copolymer, were analytical-reagent grade of (M&B), GMS and Aldrich Chemical. Natural rubber (NR) was also locally obtained from Samaru market, Zaria.

Preparation

Tannery waste collected were sorted out first according to chemical substance of tanning used, those tanned by chromium salt (Chrome tanned waste) were collected, cleaned, sun and oven dried at 50^0C, then ground to 0.5mm particle size in an Arthur Thomas Wiley laboratory Mill (model 4), Philadelphia, PA USA and was used as reinforcement in (HDPE) matrix while the HDPE was used as received. All composite measurements for tensile strength were in accordance with ASTM D638.

Table 1; gives the formulation of the composite variation of matrix and fiber used.

Table 1: Composite formulation

	Composite						
Samples (wt %)	PW01	PW02	PW03	PW04	PW05	PW06	PW07
HDPE	100	90	80	70	60	50	40
Chrome tanned waste	0	10	20	30	40	50	60

Compounding

The formulations on Table 1 were picked one after the other and compounded using a Carvers Two Roll Mill at a processing temperature of 180^0C within 7minutes. The method of Turu *et al* (2014) was used in compounding. The temperature, processing time was same for all formulations on Table 1.

Compression Moulding

A thin aluminum sheet was used as the mould through which film of composite were pressed. Each compounded formulation, 1.5g in weight, was measured out, and then wrapped in a cut foil-paper. The wrapped sample was then placed in the mould then placed on the moveable platens of the hot press. With the help of the hydraulic controlled ram, the lower platen containing the compounded sample moved up to the upper platen closing the mould and exerting moulding pressure (Musa *et al*., 2014). The films were compressed at a compression temperature and pressure of 180-185^{o}C and 3×10^3 N/m² within 3 minutes preheating and 5minutes pressed respectively. Each compounded formulation, 10 samples were pressed into thin film of 1.0 mm thick. All composite were produced in accordance with ASTM D638.

Impact test

Izod impact test was carried out according with ASTM D 256-05 at room condition using a Universal Pendulum Impact System (Ray-Ran, UK). The composite was clamped rigidly at one end of a Ceast Izod impact machine (model 957) and struck at the other end by pendulum weight. The kinetic energy of the pendulum is equivalent to the energy that breaks the composite. The impact (vertical) strength was calculated and recorded according to the equation given below.

Impact = Energy of pendulum/thickness composite (J/mm^2)

Hardness Test

The measure of deformation from indentation, scratching, cutting or bending was carried out in accordance with ASTM D2240 using Durometer Shore A hardness tester, manufactured by Zwick/Roell (Germany) model 3110 to 17, analogue type. The hardness value was determined by the penetration of the durometer indenter foot into the specimen. For every specimen, 3 readings were taken from which an average value was calculated as the hardness.

Density

The density of the composite sample was determined in accordance with ASTM D792-00 specification. The steps to calculate the density is as in the equation below.

$$\rho = \frac{\omega a \times 0.9975}{\omega a - (\omega w - \omega b)}$$

Where ρ = is the density of the composite material, in g/cm^3

W_a = is the weight of the specimen when hung in air

W_w = is the weight of the partly immersed wire holding the specimen.

W_b = is the weight of the specimen when immersed fully in distilled water, along with the partly immersed wire holding the specimen the density in g/cm^3 of the distilled water at 23^{o}C

The percentage water uptake

Water up-take by sample was done in accordance with ASTM D570 standard specification. The samples each were first weighed dry then immersed in distilled water in a transparent thermoplastic container with lid and left for 96 hrs at 27^{o}C. Excess water on sample surface was wiped off with a filter paper before reweighing. The percentage water absorption of the samples were then calculated and recorded as in the equation below.

$$\text{Increase in weight (\%)} = \frac{weight\ after\ 96hrs - initial\ weight\ at\ 0hr}{initial\ weight\ at\ 0hr} \times 100$$

Morphology

To study the morphological features of fiber-matrix interfaces in the composite samples, the tensile fractured surface was mounted on aluminium stubs, coated with gold using sputter coater. The gold coated samples were analyzed by a scanning electron microscope (SEM). The micrographs of the surface and cross section were obtained by operating SEM at an accelerating voltage of 12kV and at different magnifications.

Thermal Analysis

Thermogravimetric analysis (TGA) (ASTM E1131) differential scanning calorimeter (DSC) ASTM D3418 were used to determine thermal (performance) stability and the percent weight loss of composites. The loss in weight over specific temperature ranges provides an indication of the composition of the sample, including volatiles and inert filler.

III. Results And Discussions

The general tensile results obtained in Figures 1 and 2 shows that the strength and stiffness of leather waste reinforced HDPE composites are strongly dependent on waste content. Figure1, 2, 4 and 5 shows the tensile strength and impact strength of composites increases up to certain amount (optimum) then begin to decrease with further increased in filler content. Indicating that waste proportions below optimum value is able to distribute load to the fibers (waste). Implying that the filler were well bonded with matrix (HDPE), hence, better tensile and impact properties. When the waste proportion is above the optimum, matrix stress transfer to fibret is gradually reduced, resulting into lower tensile and impact strength because the available wetted area for bonding had decreased. Also, Figures 1 and 2, exhibit a wide variation of behavior featuring on a single stress-strain curve, showed hard, brittle to ductile region, including yield point similar to the profile of thermoplastic polymer when subjected to mechanical agitations (stresses) (Ebewele, 2000).

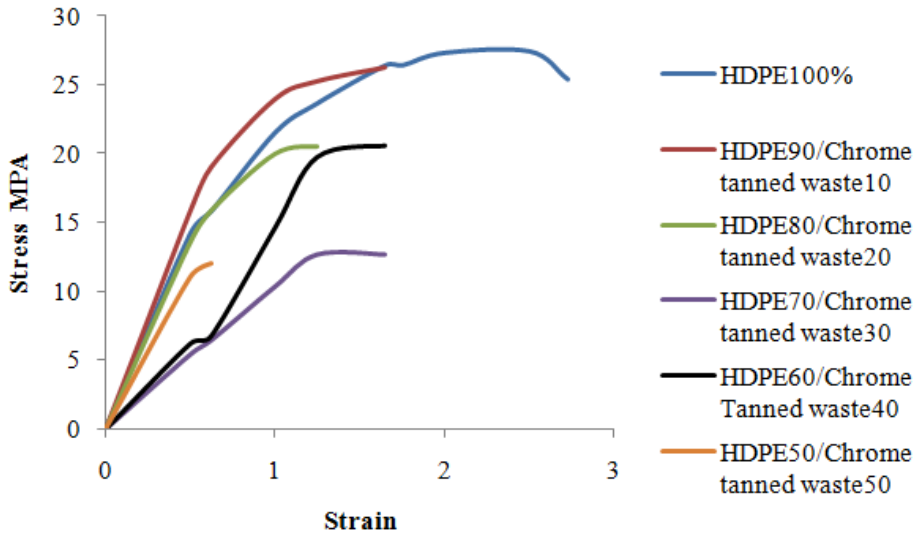

Figure 1: Stress-Strain behavior of HDPE/Chrome tanned waste composites without additives

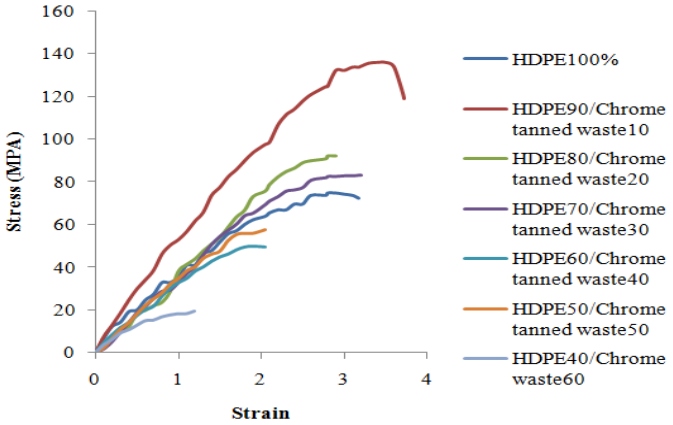

Figure 2: Stress-Strain behavior of HDPE/Chrome tanned waste composites with additives

The stress-strain curve is seen to be non-linear thus, agrees with the stress-strain profile of thermoplastic polymers. The strain of the control (HDPE) on Figure 1 was seen to be higher than its composites because the ductility had not be temper with by the filler, at minimum waste content (within 10-20wt% of fiber), the hardness and brittle nature of filler have imparted its rigidity to the most ductile matrix (HDPE), resulting in decreased strain. While on Figure 2 the composite formulation HDPE90/Chrome tanned waste 10 was seen to be higher in both stress and strain than the control (HDPE). The present of natural rubber, had influenced the strain (acting as an extender) and promoted dispersion of filler in the matrix. Thereby, stress of HDPE90/Chrome tanned waste10 was more ductile and tougher.

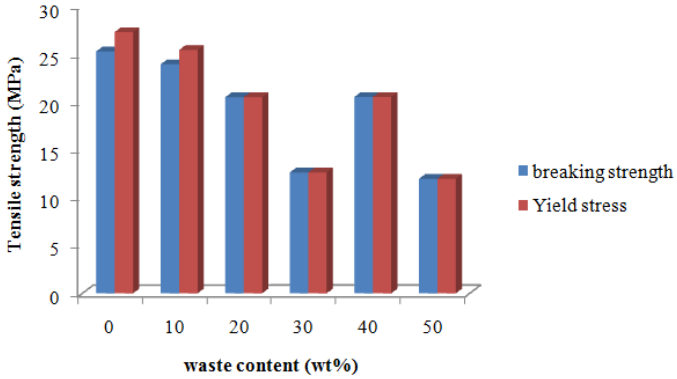

Figure 3: Effect of waste content on the tensile strength and Yield stress of HDPE/Chrome tanned waste composite.

From Figure 3, the yield stress and tensile strength of sample was shown to be lower than that of the control (HDPE) implying lower toughness, hence, limited usable properties.

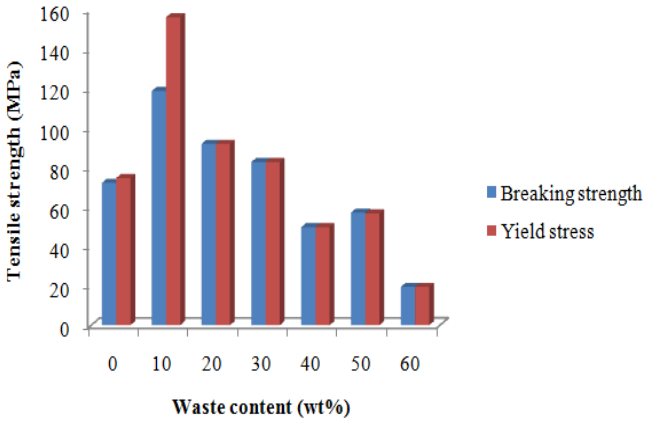

Figure 4: Tensile and Yield strength of HDPE/Chrome tanned waste composite with additives.

The incorporation of additives in Figure 4 improved dispersion of fibre in HDPE resulting in better interaction between the waste (fiber) and matrix as reported by Ambrósio *et al* (2011). The additives acted as a chemical group bonding the fiber surface and the matrix to form a bridge resulting in effective stress transfer. The reduction at higher waste contents could be attributed inadequate wetting surface leading to reduced stress transfer across the interface.

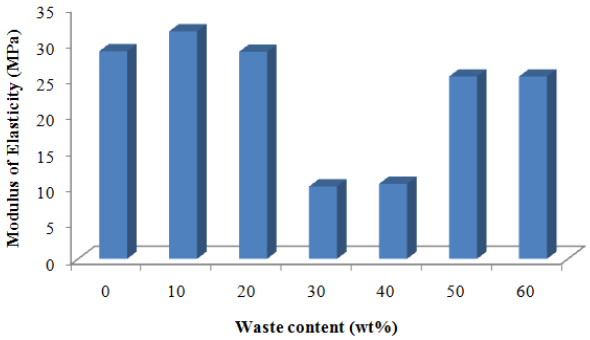

Figure 5: Modulus of elasticity of HDPE/Chrome tanned waste at different waste content of composite samples without additives.

Figure 5 shows HDPE90/Chrome tanned waste10 with higher modulus than the control (HDPE). The rigidity of reinforcement had successfully been transferred into the matrix. The amorphous structure of HDPE90/Chrome tanned waste10 when cool from melt after fabrication may be responsible for high modulus at 10 wt% waste content as reported by Covington (2009).

The result of Figure 6 shows a lower modulus than the fresh HDPE for all composites, meaning that the interaction between the matrix and fiber on Figure 5 had been broken by the addition of additives, thereby generating insufficient stress transfer at its interface.

The result of Figure 7 shows that the impact strength of composite HDPE90/Chrome tanned waste10 was higher to that of the control (HDPE). This result agrees with the result observed on Figure 4. The toughness of composites (Impact strength) is directly related to the tensile strength of the composites (Ebewele, 2000).

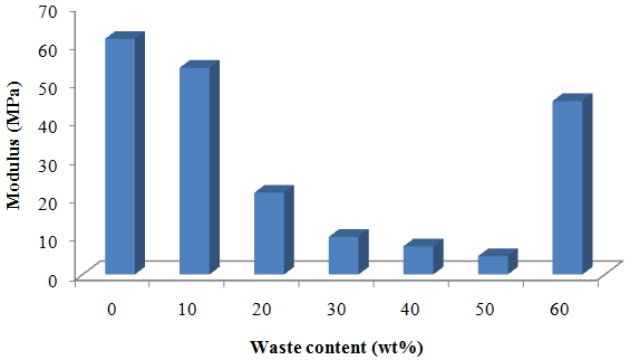

Figure 6: The effect of additives on the tensile modulus of HDPE/Chrome tanned waste composites at different waste content.

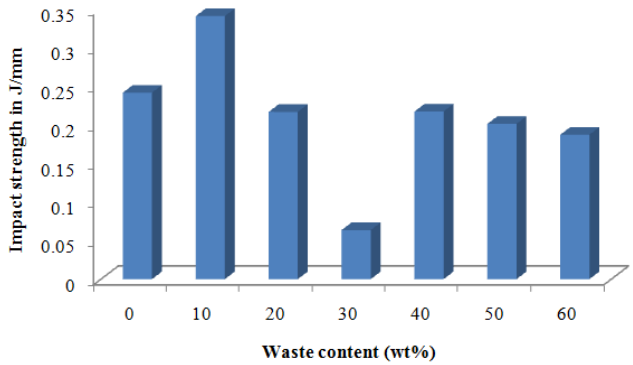

Figure 7: Impact strength of HDPE/Chrome tanned waste with additives:

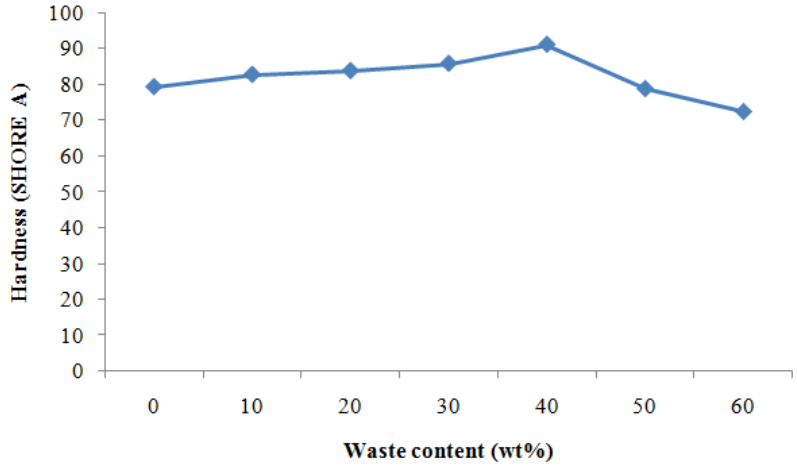

Figure 8: Effect of waste content on the hardness of HDPE/Chrome tanned waste composite

The resistance to elastic deformation on the surface of the composites was observed on Figure 8, hardness of composites increased with increasing chrome tanned waste from 0-40 (loading) before it later decreases with further increased in chrome tanned waste.

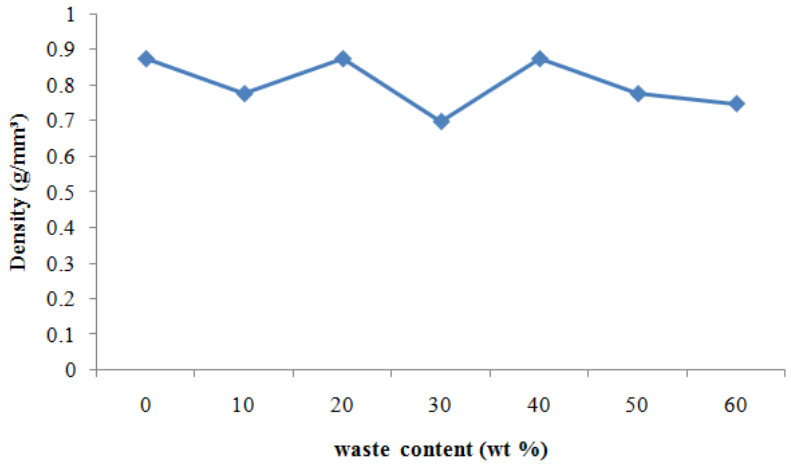

Figure 9: Effect of waste content on the density of HDPE/Chrome tanned waste composites.

From Figure 6, the density of composites varies within 0.9 and 0.7 g/cm³, this falls below the density of leather (0.86) and the density of HDPE (0.96).

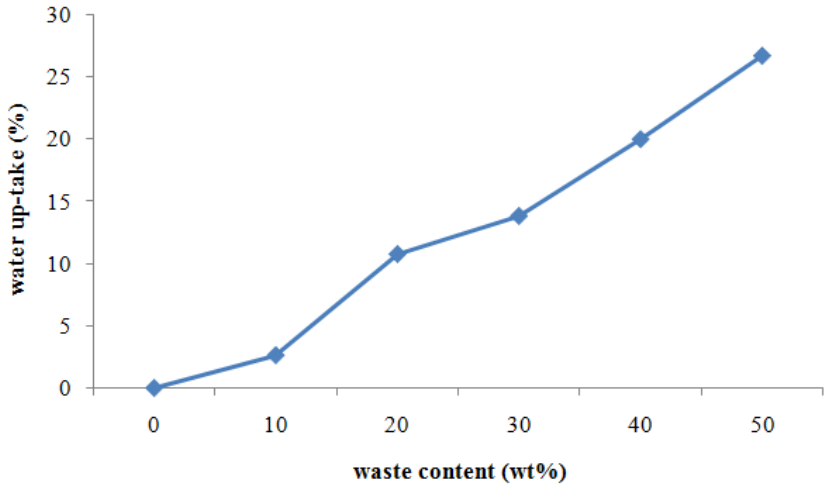

Figure 10: Percentage water up-takes of composites without additives

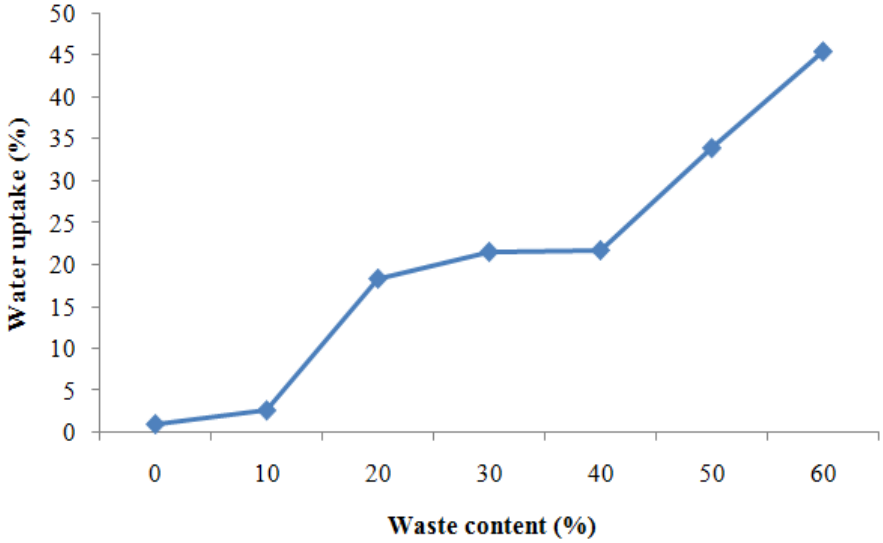

Figure 11: Effect of additives on the water uptake (%) of HDPE/Chrome tanned waste composites.

The percentage water up-take increases with increased in chrome tanned waste on both Figure 10 and 11, though, the result shows a higher percentage water up-take on Figure 11. This was indication that there were more micro gaps or flaws created in the composites with additives. This may be the reason for the poor tensile modulus seen of Figure 6.

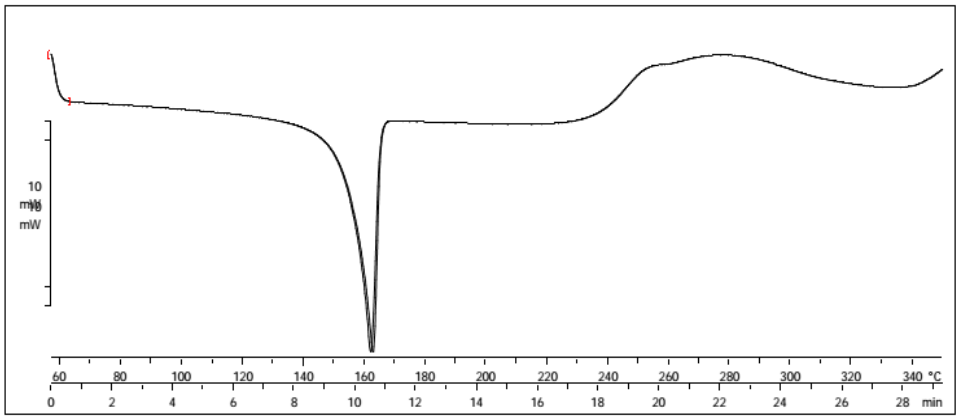

Figure 12: Differential scanning calorimeter (DSC) scan of control (HDPE)

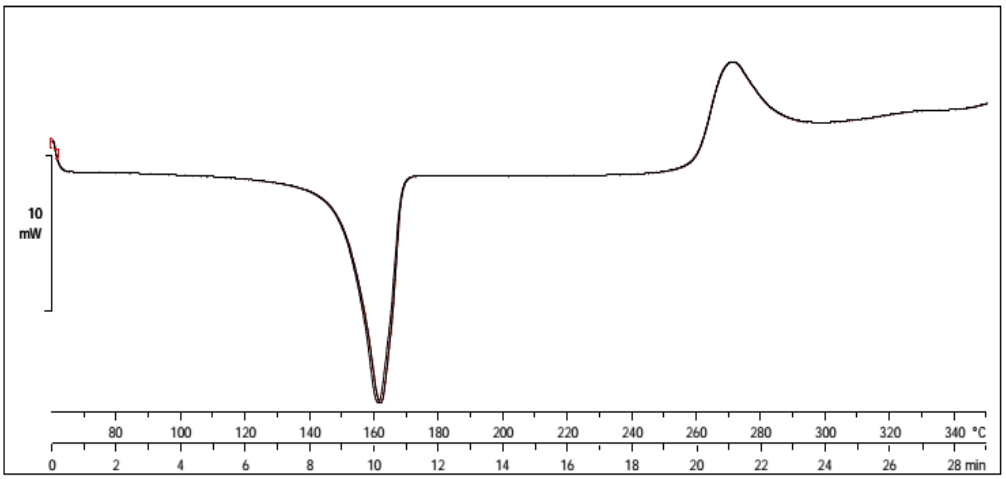

Figure 13: Effect of additives on the differential scanning calorimeter (DSC) scan of control.

Figure 13 shows broaden melting peak temperature than its fresh HDPE without additives in Figure 12.

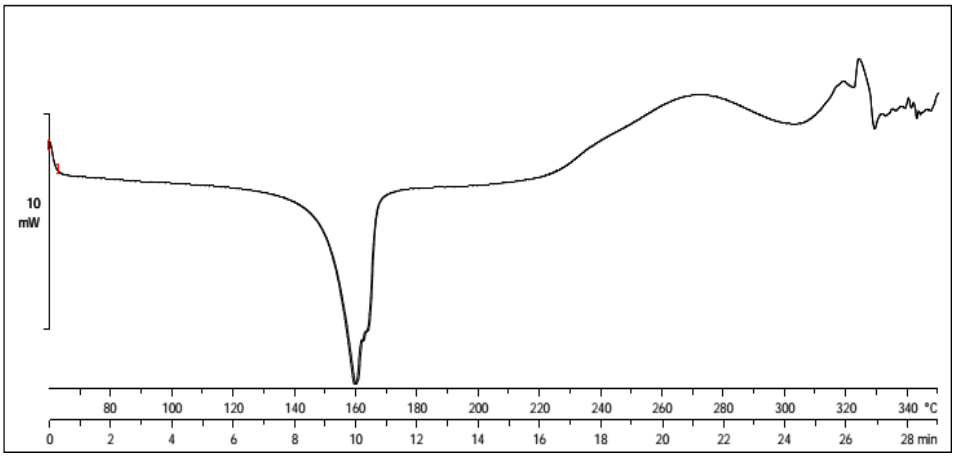

Figure 14: Differential scanning calorimeter (DSC) of HDPE90/chrome tanned10 composite,

Figure 14 shows more broadened melting peak than Figure 12

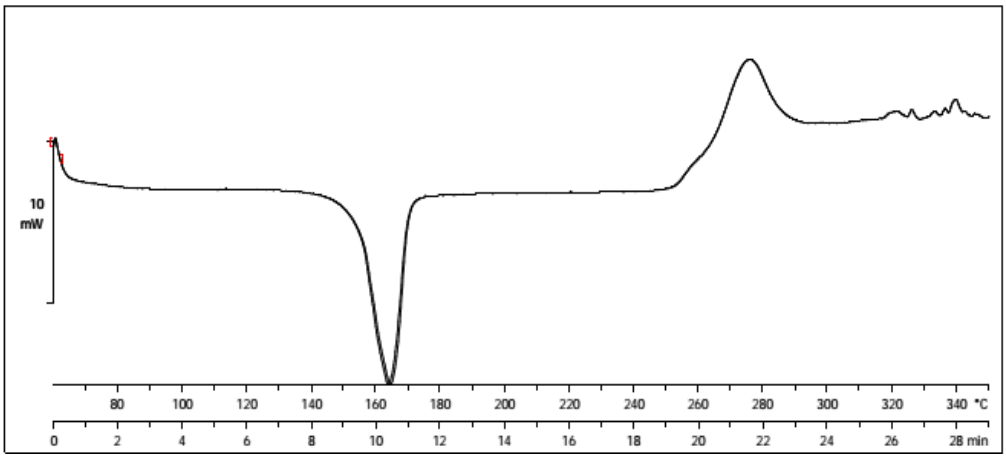

Figure 15: Effect of additives on the differential scanning calorimeter (DSC) scan of HDPE90/chrome tanned10 composite.

Figure 15 shows much more broadening melting peak and degradation peaks to that on Figure 12.

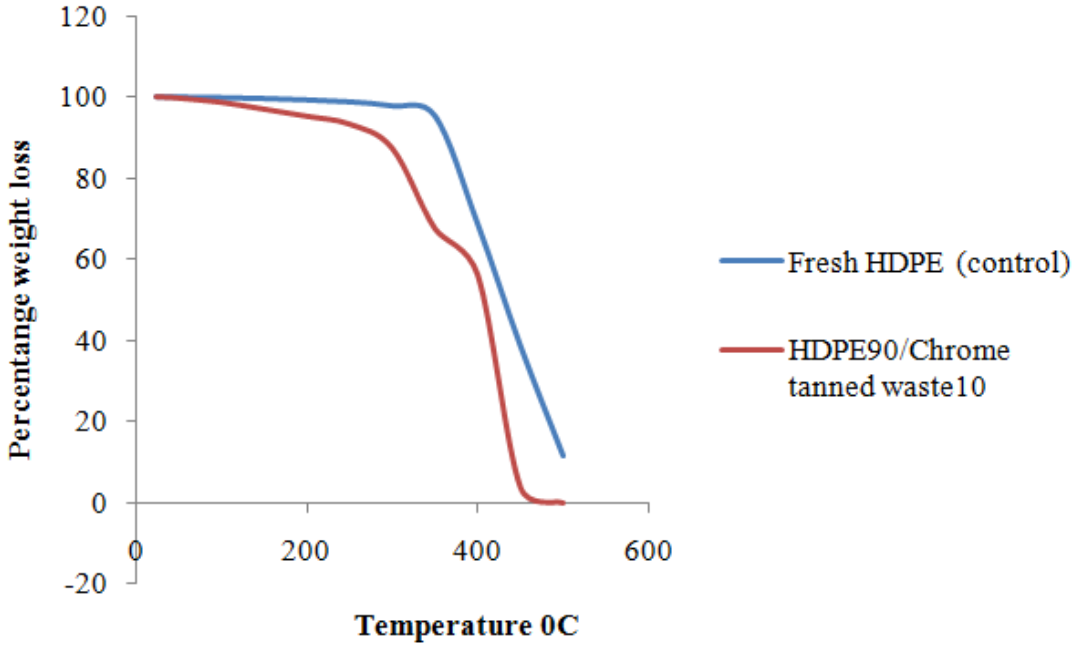

Figure 16: TGA of fresh HDPE and HDPE90/Chrome tanned waste10 without additives

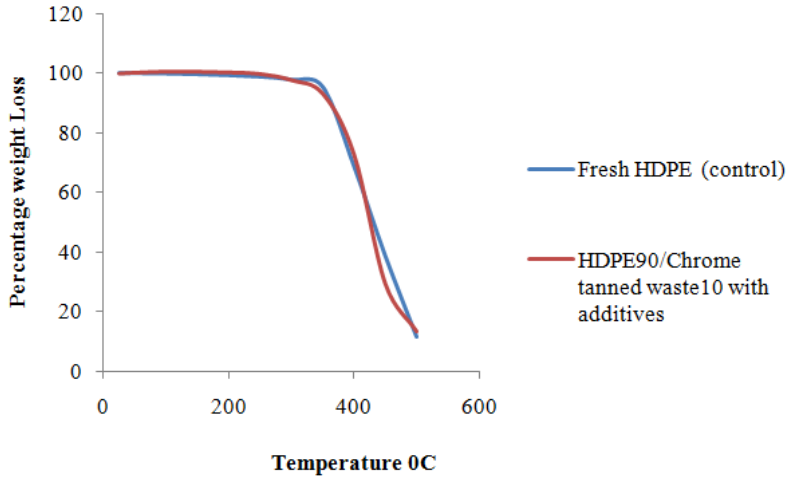

Figure 17: TGA of Fresh HDPE and HDPE90/Chrome tanned waste10 with additives

Table 3 TGA temperatures and residue weight of HDPE and its composites.

S/No	Composites	T_o onset temperature (^{0}C)	T_d Max. decomposition temperature (^{0}C)	Residual weight (%)	Weight loss (%)
1	Virgin HDPE	293	440	15	1.283
2	HDPE90/Chrome tanned waste10	290	453	44	12.758
3	HDPE90/Chrome tanned waste10 with additives	297	452	25	2.205

From the results in Figures 13 to 15, the dips of the melting peaks were seen to broaden with the incorporation of wastes and additives as compare to that of Figure 12. The summary of the DSC results for the various curves is presented in Table 4.The observed result of TGA/DTA curves on Figures 16 and 17, shows that the degradation of fresh HDPE began at about 293 ^{0}C with a weight loss of 1.283%, the maximum decomposition rate appeared at 440 ^{0}C (T_d) with residual weight of 15%. The summary of the TGA results for the other composites is presented in Table 3. The results in Table 3 and on Figures 16 and 17 imply that the composites system was more thermally stable than the fresh HDPE.

Table 4: DSC Analysis results for fresh HDPE and its composites.

compositions	T_m ^{0}C	Mass (mg)	Width of peak	Height of peak (Wm)	Area Tm peak	Area (JK/smg)
Fresh HDPE	162.21	5.7	8.56	17.7	151.512	26.58105
Fresh HDPE plus Additives	161.12	6.7	12.79	17.57	224.7203	33.54034
HDPE90/Chrome tanned waste10 without additives	159.51	5.1	13.28	12.02	159.6256	31.29914
HDPE90/Chrome tanned waste10 with additives	163.89	4.8	11.46	15.43	176.8278	36.83913

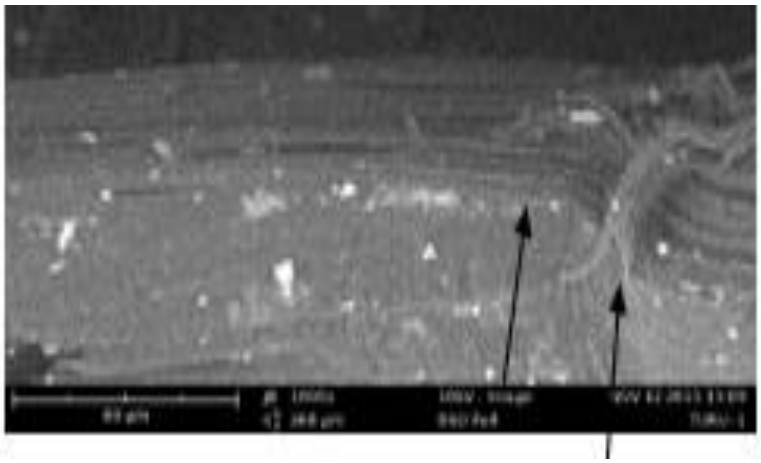

Plate 1 SEM micrographs of the tensile fracture surface of fresh HDPE with additives

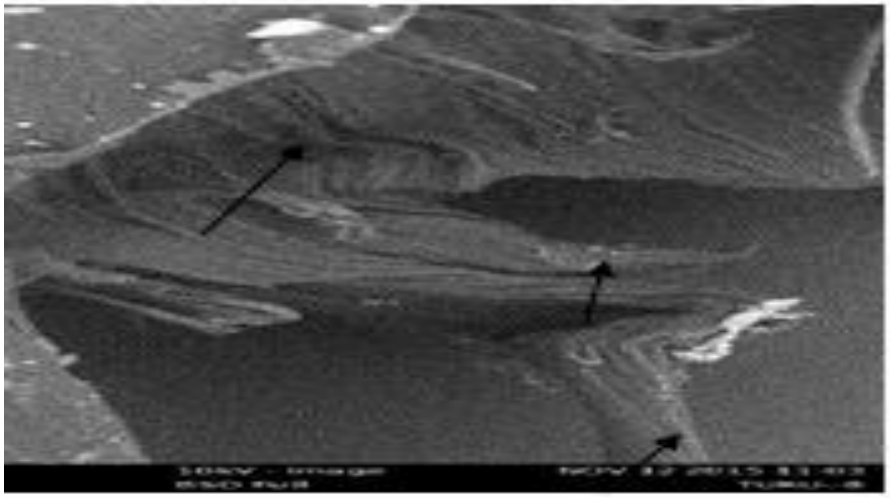

Plate 2: SEM micrograph of the tensile fracture surface of HDPE/Chrome tanned waste without additives

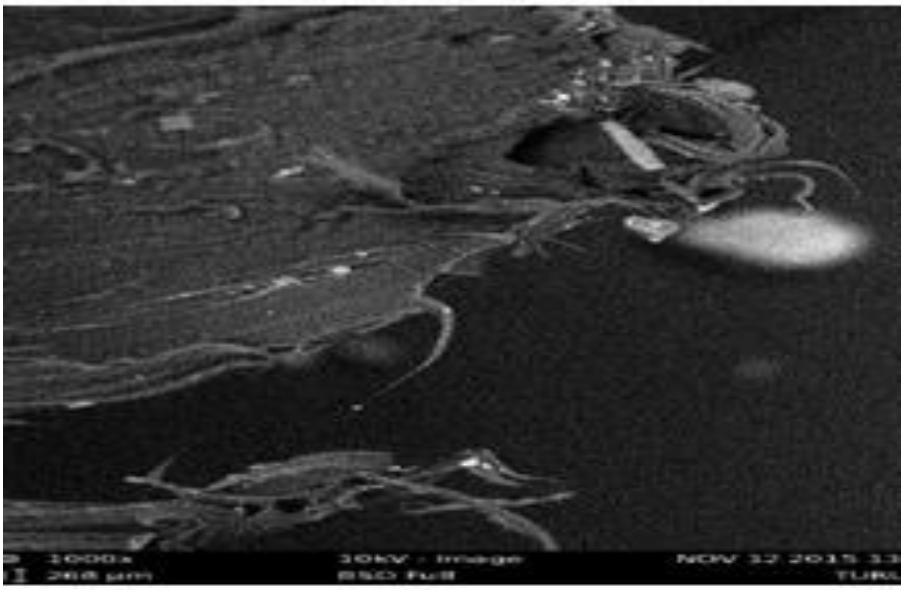

Plate 3: SEM micrograph of the tensile fracture surface of HDPE/Chrome tanned waste with additives

A ductile fracture surface was observed on Plate 1. This is evident by the links network seen, trying to resist deformation. Plate 2 and 3 shows links network, this a good interface between the additives, fiber and matrix used.

IV. Conclusion

Without additives, HDPE/Chrome tanned composites had higher modulus with lowers tensile strength and impact strength. The strong hydrogen bonding existing within the agglomerate hindered matrix-fiber interaction hence prevented stress transfer. The additives had influence the dispersion and enhanced mechanical properties and thermal stability of composites.

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