Nigerian Journal of Polymer Science and Technology

Volume 20(1), 2025

ISSN: 1119-4111

A PUBLICATION OF THE POLYMER INSTITUTE OF NIGERIA

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Magaji Ladan, PhD.

Nigerian Journal of Polymer Science and Technology
ISSN: 1119-4111 Volume 20(1), 2025

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TABLE OF CONTENT

Nigerian Journal of Polymer Science and Technology, 2025, Vol. 20, pp1-10

Received on: 11/08/2024 Revised on: 11/09/2024 Accepted: 18/01/2025

THE MORPHOLOGICAL, THERMAL AND MECHANICAL PROPERTIES OF GROUND RUBBER TIRE (GRT) FILLED WASTE HIGH-DENSITY POLYETHYLENE (rHDPE)

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ABSTRACT

This research investigates the morphological, thermal and mechanical properties of ground rubber tire (GRT) filled waste high-density polyethylene (rHDPE), showing the effect of variable particle sizes. In the adopted methodology, the samples were prepared through melt mixing (using two-roll mill machine), tailed by compression molding, different blends of variable particle sizes were prepared (150 µm, 212 µm, 300 µm and 425 µm) and a control sample of 150g rHDPE was also prepared. The morphology, thermal properties and mechanical properties of the developed composites are analyzed using Scanning electron microscopy (SEM), Dynamic Mechanical Analysis (DMA), tensile and flexural tests respectively. The SEM result shows some inhomogeneity and poor dispersion of the GTR filler which attributed to improper stress transfer along the interface and formation of cracks in the developed polymer composited, causing reduction in mechanical strength. A more homogenous morphology with reduced defects was observed upon increasing the filler content from 150µm to 212µm, leading to an improved interfacial adhesion with the HDPE matrix. Further increase (from 212µm to 300µm) gave more homogenous micrograph but addition of GTR particles up 425µm led to rough surface. For thermal behavior, as the different sizes of the GRT filler were introduced into the HDPE matrix, the storage modulus decreases, attributed to the material softening caused by the soft rubber particles which result in lower rigidity except for sample made with 150 µm. Incorporation of 300 µm particles of GTR results in higher rigidity, which similarly gave more homogenous micrograph with uniform dispersion. The result also shows that, increasing the GTR particles causes decline in the flexural stress and modulus, having similar trend with the tensile modulus. The elongation at break also shows a decline with addition of the different particle sizes of the filler, with the exception of sample 300µm.

Keywords: Morphological, Ground Rubber Tire (GRT), Waste High-Density Polyethylene (rHDPE), Scanning Electron Microscopy (SEM), Dynamic Mechanical Analysis (DMA)

INTRODUCTION

Composite material are widely used in various industries such as construction, automotive, aerospace, and packaging due to their desirable properties such as high strength, light-weight, and cost-effectiveness. Polymer composite in particular have gained significant attention as they offer potential of using recycled materials, which are cost effective and eco-friendly. Ground rubber is one of the recycled material which can be used to replace virgin fillers in polymer composites. High-density polyethylene (HDPE) is a popular polymer matrix for composite materials due to its excellent mechanical and thermal properties (Egodage,Harper and Walpalage, 2009).

The thermal and morphological properties of a composite material play a pivotal role in determining its suitability for various application.Thermal properties such as thermal conductivity, thermal diffusivity, and specific heat capacity are important parameter to consider as they affect the heat transfer characteristic of the material also the morphological properties such as surface morphology, microstructure, and particle size distribution are also important as they determine the mechanical and physical properties of the composite material
(Rajalingam, Sharpe and Baker,2013).
The aim of this research is to analyse the morphological and thermal properties of ground rubber filled with HDPE as ground rubber is one of the recycled materials which can be used to replace virgin fillers in polymer composites if the result come out to be positive.
The objective was to convert both the ground rubber and HDPE into powder of various particulate size (150µ, 212µ, 300µ, 425µ) and evaluate the morphological properties (Scanning electron microscopy 'SEM') and the thermal properties (Dynamic mechanical analysis 'DMA') alongside the Tensile strength and the Flexural strength.
The research shows that Polymer matrix thermoplastic composites are generally non-biodegradable and are therefore a major contribution to environmental pollution. The difficulty in rubber recycling lies in the fact that rubber is a thermoset material and attempts to recycle it in a manner similar to plastics often lead to non-desired results. The volumes of discarded tires. Ground tire rubbers in low particle sizes would be a good option for this type of application. Although the lack of adhesion of ground tire rubber with the rest of the polymers makes this practice hard also with some problems associated with the storage and elimination of end-of-life tires lead to growing world-wide environmental concerns and problems. This is why there is a need to seeking friendly and eco-friendly solutions for the recovery and recycling of grounded tires and discarded High Density Polyethylene (HDPE) composites.

MATERIALS AND METHODS

Materials

The polymer used in this project was sourced locally around Ahmadu Bello University Samaru Campus, Zaria, Kaduna. The polymer used were mainly HDPE waste bottles, which were washed, rinsed and dried to remove contaminants. The cleaned HDPE bottles were then crushed to reduce the size and allow melting to proceed easily.

The rubber powder obtained was separated from other particles and sieved using 150µ, 212µ, 300µ and 425µ sieve sizes at Department of Civil Engineering Ahmadu Bello University, Zaria. The sample was stored in a container prior to compounding.

Equipments

Some of the equipment's used are: Rubber powder, HDPE (waste), two roll mill machine (CPS183 North Bergen U.S.A), gigital weighing machine, Compression moulding machine (DT8679-7585 Wenzhou zingiaug chine), Changda shredding machine, Universal Material testing machine (Cat Nr. Model:261- 100KN- Enerpac), Digital Tensile testing machine (TM2101-T7), Ruler, Sieves (150µ,212µ,300µ,425µ), Distilled water, DMA Machine, Scissors, Hydraulic press machine, Mold (120mm/240mm/4mm), SEM machine (JOEL JSM-7600F).

METHODS

Compounding and Compression

The composite was compounded using two-roll mill machine, which consist of two cylindrical oppositely rotating roll with an adjustable knobs, which help to increase or decrease the nip of the rollers at a rotational speed and control temperature.
The composite was prepared using the following ratios:

Table 1.1: Matrix and reinforcements composition

Samples	Amount of HDPE(g)	Size of rubber powder/ amount of rubber powder(g)
Control	150g	_

150µ	135g	150µ/15g
212µ	135g	212µ/15g
300µ	135g	300µ/15g
425µ	135g	425µ/15g

The matrix (HDPE) was melted in the two rolls machine at a temperature of 180℃, then the filler was added with the aid of the rotating heated rolls and mixed together for about 20 minutes. As the materials melt the nip was reduced to make the melt form a band. Then, a knife-like object is used to remove the band from the rolls. This is done on a hydraulic press machine, which makes use of hydraulic pressure.

After blending, the band formed was fitted into a mold plate of (240mm/120mm/4mm) and wrapped with aluminium foil paper to which silicon oil was applied for easy removal of the sample after cooling. The mold was then mounted on the bottom plate with an oversized pressure valve tightened and pressure built-up using the handle, the top and bottom plates of hydraulic press was pressed against each other with the sample in-between the plates under pressure of 10MPa. The sample was pressed for about 15mins at a temperature of 220℃, then the presser was removed and placed for cooling. After cooling, the samples were removed from the aluminium foil paper and cut into different required dimensions for mechanical, thermal and morphological analysis.

CHARACTERIZATION

The following tests were carried out on the composites

Morphological Analysis

The morphology of the composite, was observed using Scanning Electron Microscopy (SEM). The ground rubber filled HDPE composite materials with varying rubber particles content were studied using a scanning electron microscope (FESEM, Joel MT, model JSM-7600F) in order to ascertain the interfacial adhesion and smooth cross section of all the specimens fabricated.

Thermal Analysis

The thermal behavior of the composite material was analysis with various specimens subjected to Dynamic Mechanical Analysis (DMA), which applies a sinusoidal force and measures the samples response at a given temperature. The samples were studied at: Frequency/ frequencies: 2Hz, 5Hz and 10Hz, Amplitude: 60um, Heating rate: 6k/min and the End temperature: 120°C.

Mechanical Test

Tensile Strength

The tensile strength of the composite samples depends on the strength of the materials, length of the material and the material matrix interaction. This test was used to determine the tensile modulus, percentage elongation and tensile strength of the materials. The samples were cut into dumbbell shape according to the ASTM D638-98 standard. The required dimension of each sample used was 100m×30mm×3mm. The test was carried out using Universal Materials Testing Machine (Model, TM2101-T7 10KN) at the department of Polymer and Textile Engineering, Ahmadu Bello University, Zaria. The machine provides a mechanism for applying different measurable loads to the sample with a device to measure the change in the length of the sample. The sample was attached to the machine through a clamp grip. The actual procedure is to apply the stretching load to the sample starting from a zero value to an ultimate value when the sample fractures.

$$\text{Tensile strength} = \frac{P}{A} \quad (1)$$

Where;

P = Breaking load in (N), A= Cross-sectional area of sample in (mm^2)

Tensile strain is the ratio is the ratio of extension of original length. It has no unit.

$$\text{Tensile strain } (\epsilon) = \frac{\text{Extended length}}{\text{Original length}} = \frac{\Delta l}{l} \quad (2)$$

Percentage elongation (elongation at break) is the ratio of extension of original length multiplied by 100.

$$\text{Elongation at break (\%)} = \frac{\Delta l}{l} X\ 100 \quad (3)$$

Tensile (Young) modulus is the measure of the ability of a material to withstand changes in length

when under lengthwise tension or compression. It is also equal to the longitudinal stress divided by strain.

Young modulus $(\gamma) = \frac{Stress}{Strain}$ (4)

Flexural Analysis

The test was carried out using the Enerpac Universal Testing Machine (100KV) and measured under a three-point bending approach according to ASTM D790. The samples were cut into rectangular bar with the dimension of 60mm× 30mm× 4mm.The was applied along a sharp line perpendicular to the length of the bar and at a point midway the gauge length of the support. The load at the point of fracture was recorded from which the cross-breaking strength was determined by using standard formulae. The flexural strength and modulus were calculated using the following equation;

Flexural strength = $\frac{3FL}{2bd^2}$ (5)

Flexural modulus = $\frac{FL^3}{4bd^3D}$ (6)

Where;

F = force (N), L = span length (mm), b =width (mm), d = thickness(mm), D= deflection (mm)

RESULTS AND DISCUSSION

Morphological Chracterization

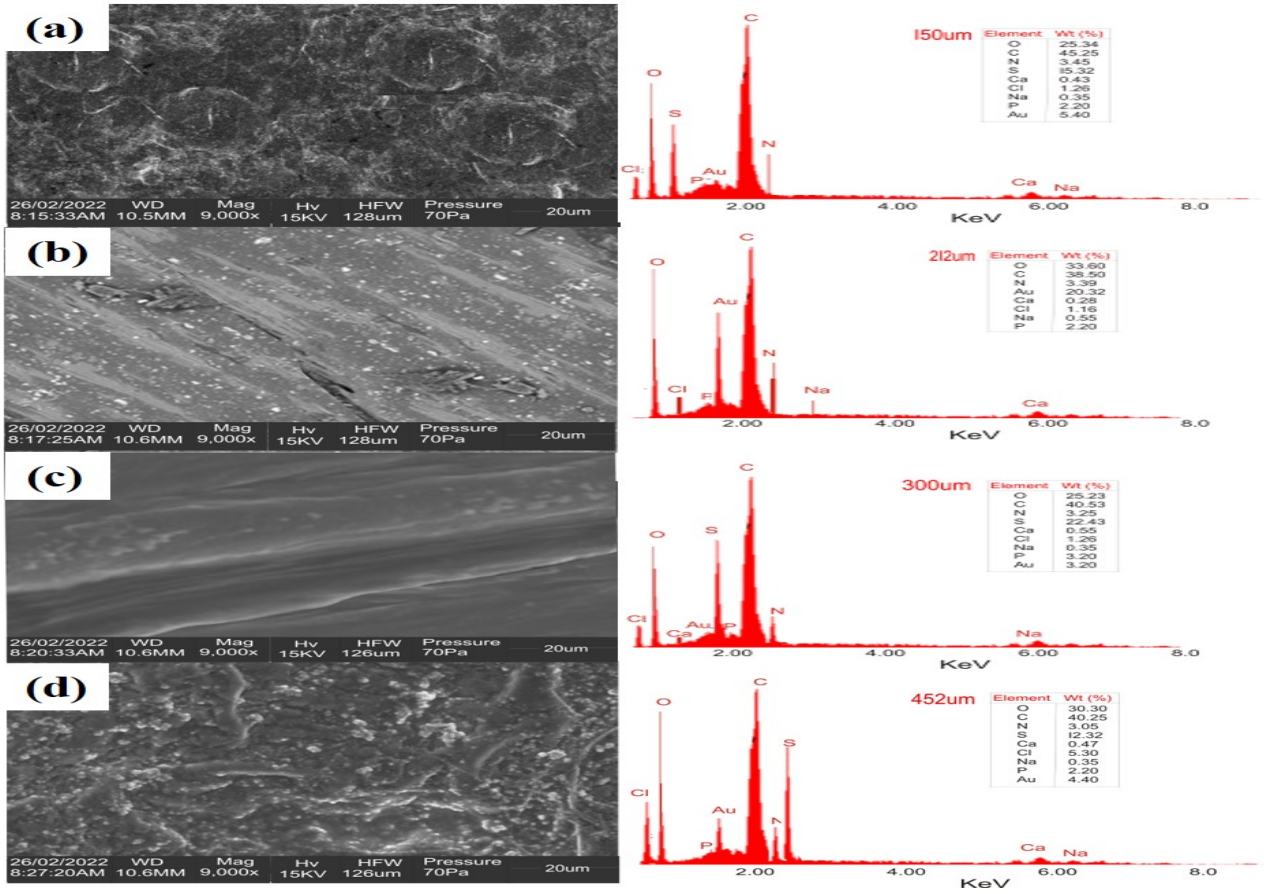

Plate 4.1: SEM image of developed HDPE filled Ground Rubber (GTR) at (a) 150µm (b) 212µm (c) 300µm (d) 425µm

SEM micrograph was used to determine the effect of different particle size of Ground Rubber on the developed HDPE composite, as illustrated in plate 4.1 above. (a) the Ground Rubber was poorly dispersed within the matrix (HDPE) which might result in improper stress transfer along the interface and formation of cracks. Hence, this might limit the interfacial adhesion within the developed composite causing reduction in mechanical strength.

Increasing the GTR concentration as shown in Plate 4.1(b) led to the agglomeration of weakly dispersed clusters and heterogenous morphology promoting voids formation at the interface attributed to incompatibility and high interfacial tension between the matrix and the filler. This led to interfacial voids, GTR pull-out from the HDPE matrix (Fazeli, Keley and Biazar, 2018). Incompatibility in the sample due the poor interfacial adhesion might cause catastrophic failure.

However, increasing the filler content from 150µm to 212µm improves the interfacial adhesion with the HDPE matrix leading to more homogenous morphology and reduction in defects like cracks, voids, agglomeration, cavity etc. Further increase in the filler concentration (from 212µm to 300µm) gave more homogenous micrograph and rough fractured surface which suggest possible effect of proper blend and uniform distribution of the filler. Proper blend suggests better interaction and proper dispersion of the GTR fillers in the matrix. Generally, an improved interfacial stress transfer is expected due to the difference in morphology. However, further addition of GTR particles up 425µm led to rough surface which causes interfacial gaps between the matrix and the filler. Comparing the surfaces, no particle agglomeration was seen in Plate 4.1(c) with fewer voids. Therefore, it is expected that the developed composite with fewer void might give better mechanical properties due to more effective stress transfer and better interfacial quality (Fazli *et al.,* 2022).

Thermal Characterization

The stiffness of the polymer blends with respect to interfacial bonding and phase morphology can be understood from the storage modulus curves (Ali and Rodrigue, 2021). The maximum energy stored by the material shows how rigid the materials could be and this could be seen from the curve as illustrated in Figure 4.2. which shows the effect of different particle sizes of GRT on the HDPE/GRT blends. The control which is 150 g of pure HDPE had a higher storage modulus which is as a result of the semi-crystalline nature of HDPE structure, which also yields high stiffness. As shown in Figure 4.2 below, as the different particle sizes of the GRT filler were introduced into the rigid HDPE matrix, the storage modulus decreases except for sample made with 150 µm, attributed to the material softening caused by the soft rubber particles which result in lower rigidity. Hence, incorporation of 300 µm particles of GTR results in higher rigidity, ascribed to better stress transfer between the phases as a result of better interaction between matrix and the GTR. As seen in Plate 4.1, the sample with 300 µm gave proper blend which reduce the interfacial tension between the matrix and the GTR causing higher storage modulus and better interfacial interaction

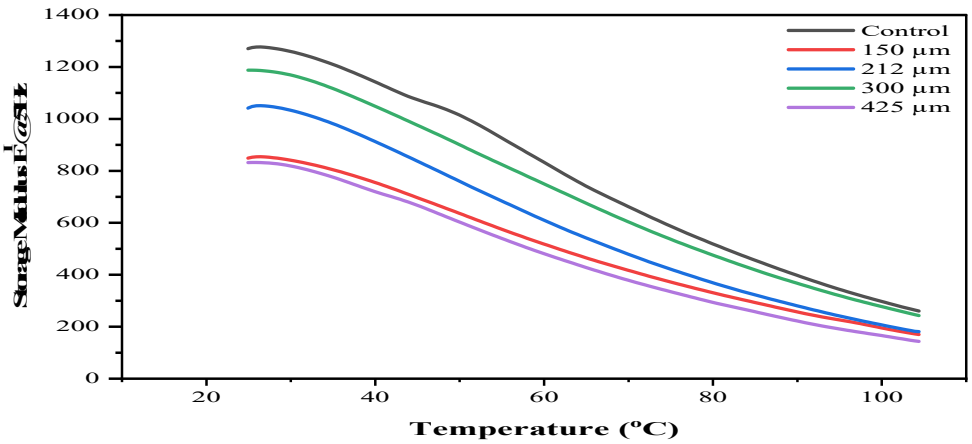

Figure 4.2: The storage modulus of the unreinforced and reinforced GTR/HDPE polymer composite as a function of temperature.

The loss tangent (tan δ) of the developed samples with variation in the GTR concentration is illustrated in Figure 4.3. Generally, it is expected that damping is affected by friction resulting from the sliding effect between the filler and matrix and also the quality of the blend interface (Zhao et al; 2019). As expected, the increase in the concentration of GTR particles led to increase in the loss modulus since the GTR particles enhances the viscoelastic property of the composite. Also, the rise in the loss modulus is attributed the complex crosslink density and the presence of carbon black which reduce or prevent mobility within the polymer chain. Low peak intensity is observed for reinforced samples and this indicate improved compound elasticity. Hence, lower energy is required for molecular chain motion as the samples move close to rubber state from glassy state (Ali and Rodrigue, 2021).

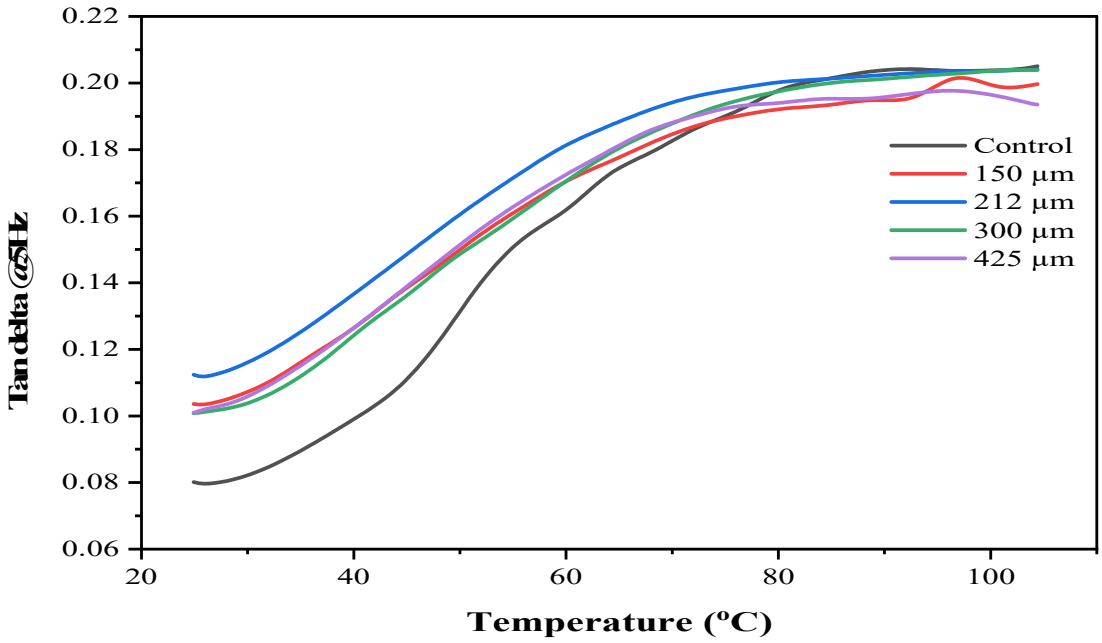

Figure 4.3: Tan delta of the unreinforced and reinforced GTR/HDPE polymer composite as a function of temperature.

Mechanical Analysis

Tensile Test

With the inclusion of GTR particles in the matrix it causes reduction in the tensile properties attributed to the constraint in the stress transfer and the weak interfacial adhesion between the filler and the matrix. Figure 4.4 shows the tensile strength and tensile modulus of the unreinforced and reinforced GTR/HDPE polymer composite. In Figure 4.4, the addition of GTR particles reduced the tensile strength of the pure HDPE matrix. For instance, incorporating 150 µm and 212 µm of GTR particles in the matrix caused the decline in the tensile strength by 28 % and 31 % respectively. The inclusion of 212 µm particles of GTR) causes higher reduction in the tensile strength with a decline by 31 %. This could be attributed to more agglomeration as seen in Plate 4.1 and weak interfacial adhesion between the matrix and the filler causing easy initiation of crack in the sample and possible premature failure. The samples made with 300 µm and 425 µm gave the best tensile strength with 21.4 MPa and 21.5 MPa respectively. Similarly, the tensile modulus declines with the addition of the 150 µm GTR particles from 0.79 MPa to 0.71 MPa and further reduction was observed with increase in the particle size (see Figure 4.4).

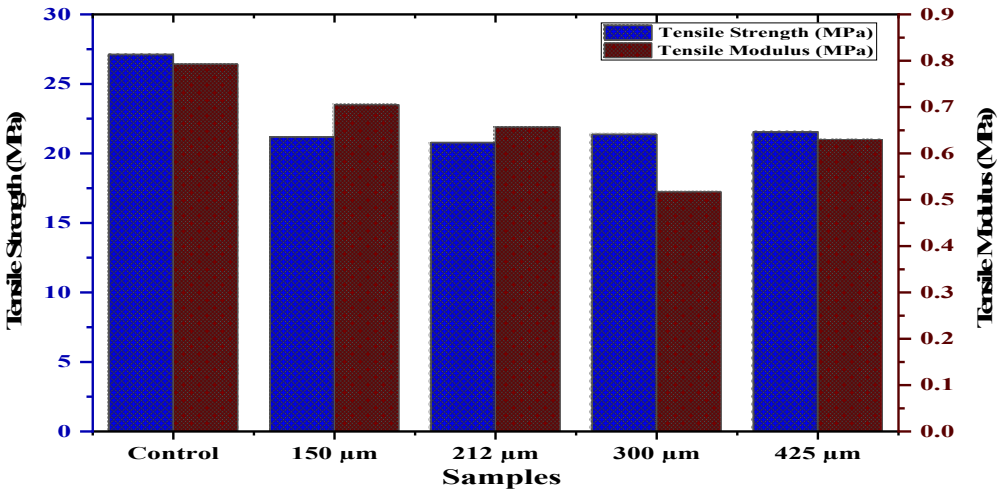

Figure 4.4 Tensile strength and Tensile modulus of the unreinforced and reinforced GTR/HDPE polymer composite

The effect of GTR particles on the elongation at break is an important parameter used to show the homogeneity and compatibility of the GTR particle/HDPE blend. Figure 4.5 illustrate the elongation at break of the produced GTR/HDPE polymer. The addition of the filler at different particle size causes decline in the elongation at break. also, the incorporation of 150 µm of the particles reduced the elongation at break from 34.1% to 30.1% the result shows that using higher particle size of GTR particles gave much higher elongation at break but increasing the particles from 300 µm to 425 µm resulted in the decline in the elongation at break from 41.4% to 34.2%. The high elongation at break seen in samples produced with higher particle size could be attributed to high affinity, better bond and good compatibility between the blend while this reduces the stress concentration point. It is expected that the presence of the GTR particles in the matrix might serve as point of crack initiation which could have hinder the flow or mobility of the thermoplastic

molecules. Hence, the elongation at break reported in this study gave similar trend with the values reported by Wang et al., (2018). The authors reported that the elongation at break was around 50 % and it was stated that high elongation at break causes good interfacial adhesion between the blend making initiation of cracks difficult.

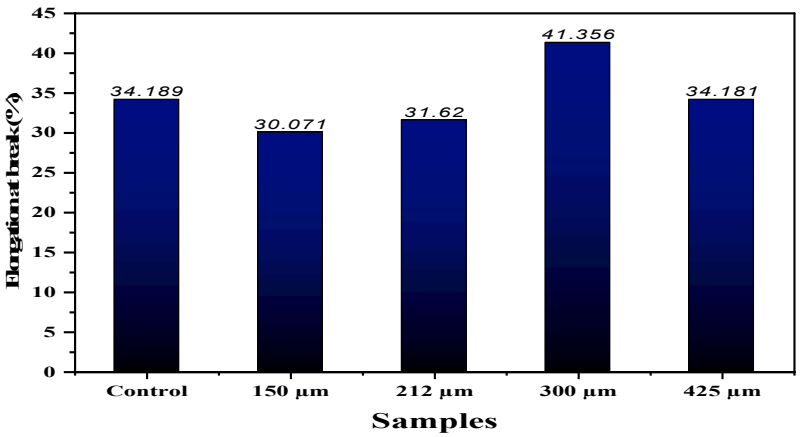

Figure4.4: Elongation at break of the unreinforced and reinforced GTR/HDPE polymer composite

Flexural Analysis

The flexural stress and modulus are shown in Figure 4.6, with continues increases of the GRT particles it causes decline in the flexural stress and modulus, having similar trend with the tensile modulus. The result obtained from this study is similar to that of Ali and Denis (2021), the addition of the GRT particles causes reduction in the flexural modulus by more than 30%. The flexural modulus dropped from 641MPa to 579MPa, when 150 µm GRT particles were first introduced resulting in 11% decline. Similar reduction can be seen for samples loaded with 212 µm, 300 µm and 425 µm of the GRT particles, which decline by 23%, 32% and 111% respectively. This decrease can be attributed to the presence of voids in the developed polymer blends. However, the developed sample with the largest particles gave the least flexural modulus attributed to the poor interfacial interaction between the filler and HDPE polymer molecules as seen in the SEM micrograph (Plate 2.1)

Hence, it could be concluded that the interfacial interaction and dispersion of the filler strongly influences the mechanical properties, and these are controlled by the particle size of the GRT filler.

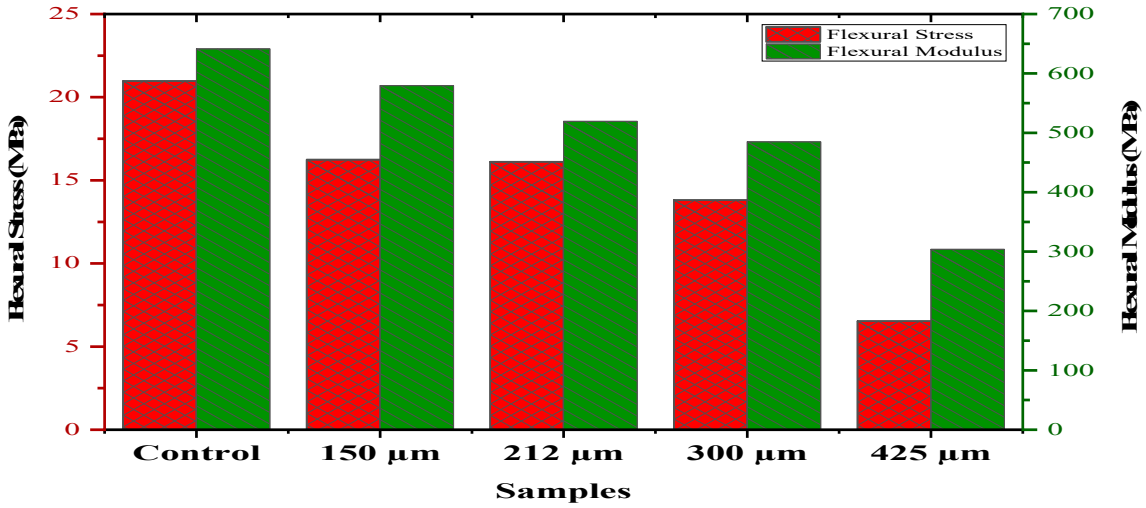

Figure 4.5: Flexural stress and Flexural modulus of the unreinforced and reinforced GRT/HDPE polymer composite

CONCLUSION

Waste GRT filler is blended with HDPE (matrix) to adhere and produce a hybrid composite with improved properties. Samples were produced by melt-mixing HDPE/GRT with varying particle sizes (150µm, 212µm, 300µm and 425µm) using a two-roll mill and a compression molding machine. Poor dispersion and defects were observed upon addition of bigger GRT particles which makes the entire material to possess poor mechanical properties as a result of their crosslinking. On the other hand, smaller particle sizes of the GRT (150 µm) with less voids gave good melting properties, higher crystallinity, as well as good tensile properties of the mixture, this is attributed to their higher specific surface area. This point can further be confirmed from the SEM Micrographs. The resulting composite with fewer voids gives better mechanical properties due to the homogeneity in particle dispersion. During the Dynamic Mechanical Analysis (DMA), it was observed that the incorporation of higher particle sized GRT (300µm) gave higher rigidity of the resulting composite. The loss tangent was deduced from the DMA result and it implied that when the size of the GRT particles increases, the loss modulus increases and vice-versa. Also, the tensile strength and tensile modulus of the developed polymer composite increased according to the amount GRT particle sizes in the HDPE, 300µm and 425µm had higher tensile strength of the among the resulting composites, this however is not applicable to the flexural modulus because, increase in the reinforcement particles led to decrease in the flexural modulus as well as the flexural stress.

Acknowledgment: The authors expressed their gratitude to the H.O.D and all the staffs of department of polymer and textile engineering and Department of Mechanical Engineering for their workshops, equipment used in the work.

Recommendations: The authors recommended more additional test to be carried out on the Dynamic Mechanical Analysis (DMA) to study the storage modulus curves which is a function of temperature and it can help to understand the stiffness of the polymer blends with respect to phase morphology and interfacial bonding.

Declaration of conflicting interests: The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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Nigerian Journal of Polymer Science and Technology, 2025, Vol. 20, pp11-27

Received on: 20/09/2024 Revised on: 03/11/2024 Accepted: 18/02/2025

STUDIES ON SOME PROPERTIES OF SNAIL SHELL AND CASSAVA PEEL POWDERED POLYPROPYLENE COMPOSITES.

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ABSTRACT

This study investigated some properties of snail and cassava peel-filled polypropylene composites. The snail shell and cassava peel powders of particle sizes (90µm) were incorporated into the polymer polypropylene matrix in a ratio of 14:3:3, 15:3:2 and 16:3:1 for polypropylene/snail shell/cassava peel; 17:3, 18:2 and 19:1 for polypropylene/cassava peel and 17:3, 18:2, 19:1 for polypropylene/snail shell powdered composites. The mixtures were prepared using injection molding machines at a hopper temperature of 200^0 C and at a rotor speed of 60rpm and at an average thickness of 3.00mm in accordance with American Society of Testing and Materials Standard, to determine the mechanical properties of the composite. The rates of bio-degradation and water absorption of the composites were also investigated for 120 days and 42 days respectively. Results showed that the tensile properties, the flexural properties as well as impact strength of the composite decreased with reference to the same properties of the neat polypropylene. However, the tensile properties, flexural properties and impact strength to these composites increased with increasing filler content loading. Again, from the results, the rate of bio-degradation and water absorption increased with increasing filler content loading. The results showed that the incorporation of cassava peel and snail shell powders into polypropylene matrix decreased the mechanical properties of the composite while the rate of bio-degradation and water absorption increased with time.

Key words: Polypropylene, Biodegradation, Snail, Cassava, Composite, Absorption

1.0 Biodegradation of organic materials by microorganisms like fungi and bacteria, is defined as the process by which this happens (Vart et al, 2012). Biodegradable plastics are plastics that can be broken down into low-weight chemicals and non-toxic byproducts once they have served their useful purpose (Vander., 2011). There are three stages to the biodegradation process; the first of which is bio-deterioration, which occurs when a material is exposed to the abiotic factors of the outdoor environment and undergoes a series of undesirable actions that weaken its mechanical, physical, and chemical properties. Temperature, light, oxygen, water, and hemicals are all examples of abiotic variables (Muller, 2005; Hueck, . 1996). The second phase of biodegradation, known as bio-fragmentation, is a lytic process in which a bond inside a polymer is severed, resulting in the generation of oligomers and monomers. Both aerobic and anaerobic digestion could be used to break down the material (Lucas, . *et al.,* 2008). Assimilation is the third phase of biodegradation (Lucas, . *et al.,* 2008), and it involves the incorporation of the bio-fragmentation by-product into the microbial cells.

Compositing stemmed from three main reasons, which include reduction in cost of production, strength improvement and enhancement of biodegradability (Carraher, 2014). In the reduction of cost in production, it is observed that the materials used as fillers are mostly organic waste and such are acquired at little or no cost compared to ceramic materials and other inorganic materials. Plastic materials are more costly than these supposedly worthless organic wastes. Thus, compositing reduces the amount of plastic materials used thereby reducing the cost of production of these materials (Carraher, 2014; Shama *et al*, 2018). For strength improvement, these composite materials contain non-plastic substances that constitute mostly of organic fibers, these non-plastic materials tend to act as an interfacial adhesive and have interfacial interaction with plastic constituents (kutnar, and Muthu, 2016). The interfacial adhesion holds plastic particles together. Comparison of the physical characteristics of the composite to those of the pure plastic is an efficient method of confirming this idea (Hueck,1996).

2.0. EXPERIMENTAL

2.1 Sample Collection and Preparation

Cassava Peel.

The cassava peels were obtained from a local farm near Ovogo in Emohua Local Government Area of Rivers State of Nigeria and it was identified by the curator in the Department of Plant Science and Biotechnology of University of Port Harcourt. The cassava peels were carefully selected to ensure that only the peels were used. The selected cassava peels were thoroughly washed and dried in the sun for 96 hours, and thereafter it was ovum dried at one hundred and thirty (130 ^{0}C) for 4 hours. The dried cassava peels were ground using a locally fabricated grinding machine and the powder obtained thereafter was sieved using 90 µm sieve to obtain a uniform particle size. The sieved cassava peel powder was oven dried for 4 hours at 130 ^{0}C and it was kept in an airtight container for further analysis (Carraher, 2014)

Snail Shell

The snails were sourced from a local market in Choba near the University of Port Harcourt. The shells were carefully removed and thoroughly washed using distilled water. The snail shells were sun dried for 120 hours and thereafter ovum dried at 130 ^{0}C for five hours. The dried snail shells were ground using locally fabricated grinding machine and the powder obtained thereafter was sieved using 90 µm standard laboratory test sieve to obtain a uniform particle size. The sieved snail shell powder was oven dried at 130 ^{0}C for four hours and thereafter, it was stored in an air tight container in order to prevent it from absorbing atmospheric moisture before further analysis.

Polypropylene

The polypropylene (PP) granules (Density 0.956 g/cm^3) were obtained from Indorama Petrochemicals, Eleme near Port Harcourt Rivers State, Nigeria.

2.2 Determination of Moisture Content.

The moisture content of the fillers Snail Shell Powder (SSP) and Cassava Peel Powder (CPP) was determined according to the method as reported by ASTM D570. Each filler (SSP and CPP) was weighed and the initial mass recorded as W_1. Thereafter, the fillers (SSP and CPP) were ovum dried at the temperature of 100 ^{0}C until a constant mass was obtained. The final weight of the filler was recorded as W_2 and the percentage of moisture content was calculated using the formula (equation 1):

$$\% \text{ Mc} = \frac{W - W2}{W1} \quad \text{Equation 1}$$

Where W_1 = initial weight

W_2 = final weight

Mc = moisture content.

2.3 pH Measurement

The pH of the powder was determined according to the standard procedure for determination of pH of solids. Snail shell powder and cassava peels powder measuring 3g each were dissolved in separate beakers containing 100ml of distilled water. The solution was agitated with a magnetic stirrer for 30 minutes for proper dissolution in water and a pH meter equipped with temperature sensor was used to monitor changes in reading.

2.4 Preparation of Polypropylene Composites

The composites were prepared using an injection molding machine at Ceeplast Industries Limited, Aba in Abia State. The mixing was done in a beaker and later transferred to a hopper of the injection moulding machine at the temperature between 180 ^{0}C- 210 ^{0}C through the nozzle at the temperature of 235 ^{0}C - 285 ^{0}C at the rotor speed of 60rpm. The average thickness of the formation was 3.00mm.

The pulverized cassava peel powder, snail shell powder and polypropylene granules were mixed in different proportion to produce polypropylene composite as shown in Table 2.1:

Table 2.1: Sample Composition

Samples	Percent weight composition		
PP (g)	SSP(g)	CPP(g)	
PURE PP	200	-	-
PP/SSP-10	190	10	-
PP/SSP-20	180	20	-
PP/SSP-30	170	30	-
PP/CPP-10	190	-	10
PP/CPP-20	180	-	20
PP/CPP	170	-	30
PP/SSP-30/CPP-10	160	30	10
PP/SSP-30/CPP-20	150	30	20
PP/SSP-30/CPP-30	140	30	30

PP; polypropylene, SSP; Snail Shell Powder, CPP; Cassava Peel Powder.

2.4 General Method for Preparation of Polypropylene and Composites.

Pure samples of polypropylene granules measuring 200g were introduced into the hopper of injection molding machine whose temperature was set at 230 ^{0} C, the granules were allowed to melt in order to form a uniform paste. However, under the influence of pressure in the hopper, the paste was moved to the nozzle of the injection molding machine and the temperature of the machine was set at 260 ^{0}C and the paste obtained was transferred to a mold where it solidified and took the shape of the internal dimension of the mold to cool, collected, labeled appropriately and was stored for further analysis.

The procedure was carried out on the samples of polypropylene granules, snail shell powder and cassava peel powder of different proportion as indicated in Table 3.1. However, in the formulation of composites, the hopper and nozzle temperature are set at 200^0 C and 230^0 C respectively.

2.5 Water Absorption

Following the standard procedure for water absorption test, samples of pure polypropylene (PP) materials (plastic) and samples of composite materials of different formulation were cut into six pieces each, at Science and Engineering Workshop, University of Port Harcourt. The dimension of specimens is 25mm x 25mm of 3.00mm thickness. The samples were oven dried at 50 ^{0}C for four hours in order to remove absorbed moisture. Each sample was weighed using electric weighing balance, the thickness was also measured using micrometer screw gauge, and the initial weight and the initial thickness were recorded as W_i and L_i respectively. Thereafter, the sample of pure polypropylene (plastic) and the sample of the composites materials of different filler formulation were immersed in a different 400ml of beaker containing 200ml each of distilled water for forty-two days. After an interval of seven days, one sample for each formulation was taken out of the water, dried with towel and then weighed immediately and the final weight was recorded as (W_f) and the final thickness was also determine and recorded as L_f. The weight gain of each sample was computed as percentage weight (%M_w). The percentage water absorption was calculated by using the equation:

$$M_w\ (\%) = \frac{Wf - Wi}{Wf} \times 100 \qquad \text{equation 2}$$

Where M_w (%) =Weight gain

W_f = Final weight

W_i = Initial weight

2.6 Biodegradability Test

Following the standard procedure for evaluating and determining the biodegradation properties of neat PP (plastic) sample and composite materials. Each sample formulation was cut into four pieces that has the dimension of 25mm x 25mm of 3.00mm thickness, these were oven dried at 50 ^{0}C for four hours in order to remove absorbed moisture. Each of the sample was weighed and the weight was recorded as W_i. The samples were buried in the ground at the depth of 25cm beneath the ground on 25th June, 2022 for a period of 120 days. Thereafter, one sample of each formulation was exhumed after interval of 30 days. It was thoroughly washed in order to remove soil particles, sun dried for 12 hours and then weighed with electric weighing balance and its final weight was recorded as W_f and the final thickness as L_f. The percentage of reduction in weight of the sample was calculated using the equation:

$$B_r\ (\%) = \frac{Wi - Wf}{Wi} \times 100 \qquad \text{equation 3}$$

Where Wi = initial weight

W_f = final weight

Br = % of biodegradation

2.7 Mechanical Properties Testing

The sample of neat polypropylene (plastic) and the composite materials of different filler formulation were characterized for some mechanical properties at Engineering Materials Development Institute, Akure in Ondo State.

2.7.1 Tensile Strength

The test for tensile strength was conducted on clean polypropylene and composite components with varying filler formulations. The Universal Instron Checking Machine (model 3369) was used for this purpose, with a constant cross head acceleration rate of 1mm/min. The samples were machined into a dumbbell form with a length of 100mm, a width of 18mm for the two edges, and a width of 13mm for the central part. The samples, each with a thickness of 3.00mm, were then subjected to testing following the standard process outlined in ASTM D 638. The load, duration at the yield point, and the load-extension curve were measured and the provided findings represent the average values for each sample.

2.7.2 Flexural Strength

The flexural strength test of neat polypropylene samples and the composite materials of different filler formulation was determined by using three-point test on the samples. The test was done using Universal testing machine (model 3369) operated at a crosshead speed of 2mm/min. The samples were cut into horizontal bars of length (100mm) and width (18mm) of 3.00mm thickness. The samples were tested one after the order according to the ASTM D790 standard procedure. The load-deflection data was obtained, recorded and graph plotted. The results presented are the average result of each sample.

2.7.3 Impact Strength

The notched impact strength of the neat polypropylene (plastic) samples and the composite materials of different formulation were tested on an impact tester (CG TOYOSEIKI, NO 556 Impact test). Each of the sample was cut into a rectangular bar shape of length (100mm) and the width (18mm) of 3.00mm thickness in accordance with ASTM D6110 standard. Different values were determined and the results presented are the average of each sample.

3.0 RESULTS AND DISCUSSION

The results obtained from the characterization of mechanical properties, rate of water absorption and biodegradation studies on the formulated polypropylene composites are presented in Tables, Figures and graph in chapter three.

3.1 Moisture Content

Moisture content of Cassava Peels Powder (CPP)

Initial weight = 4.01g

Final weight = 3.95g

% weight loss = 1.50 %

Moisture content of snail shells powder (SSP)

Initial weight = 4.00; Final weight = 3.89

% weight loss = 2.75 %

The moisture content of the Cassava Peel Powder (CPP) was found to be 1.5% and that of Snail Shell Powder (SPP) was also found to be 2.75%. It showed that the fillers used for the compositing contains very minimal amount of moisture and so the effects of the moisture content of the fillers were very negligible on the properties of the composites.

3.2 pH Measurement of Cassava Peel (CPP) and Snail Shell Powders (SSP)

CPP = 6.32

SSP = 8.01

The pH of cassava peel and snail shell powders were 6.32 and 8.01 respectively. The pH result showed that SPP is basic which could be attributed to higher content of calcium carbonate while that that of CPP showed that it is acidic.

3.3 Biodegradation

The results obtained from the biodegradability studies are presented in tables and graph. Relating to Figures 3.1 to 3.6, the results showed that the rate of biodegradability increased in proportion with its duration in the soil with increase in the amount of filler content loading.

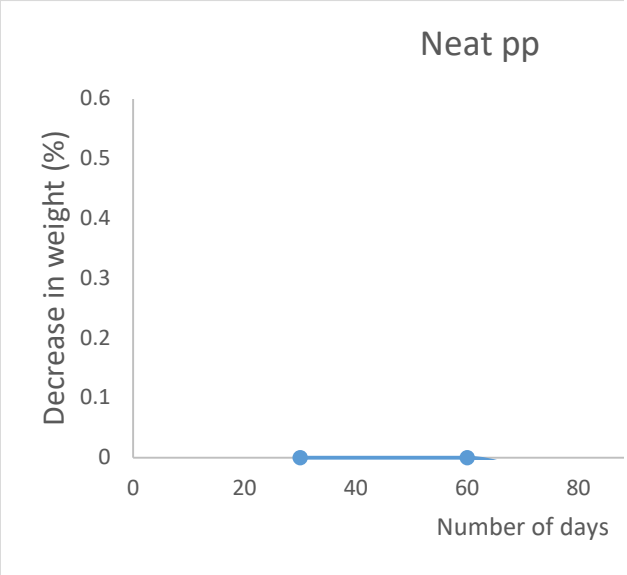

Figure 3.1: Graph of percentage weight loss in biodegradation of neat PP

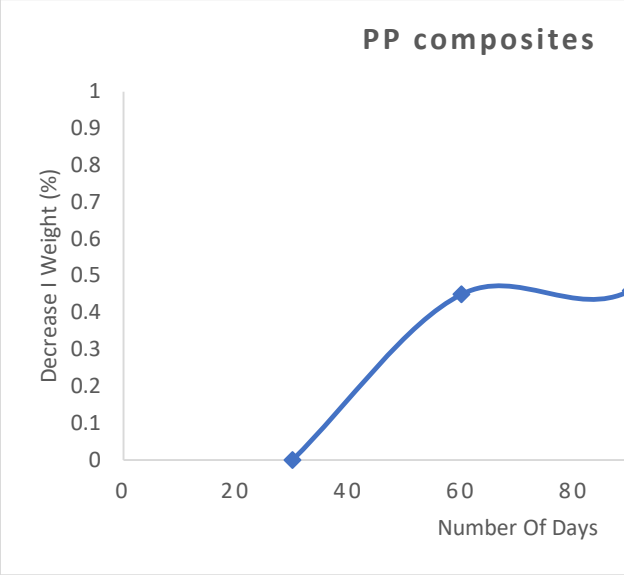

Figure 3.2: Graph showing percentage weight loss in biodegradation of 190g PP/10g SSP

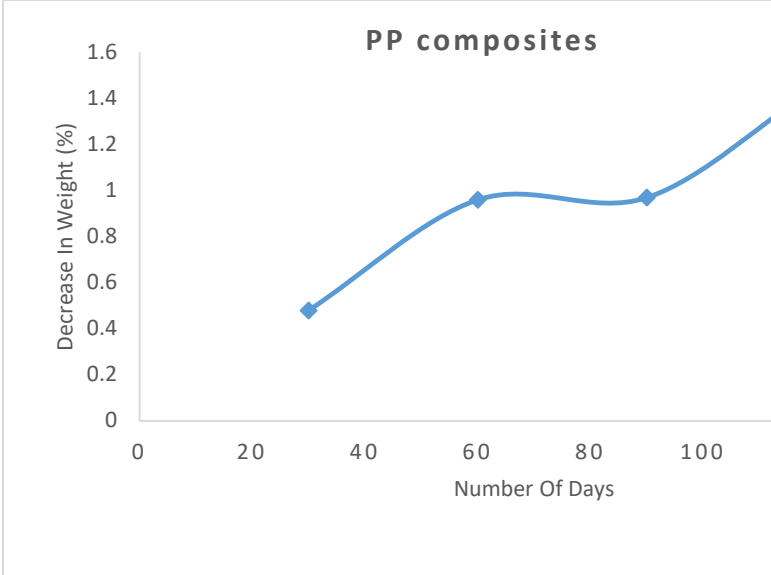

Figure 3.3: Graph showing percentage weight loss in biodegradation of 170g PP/30g SSP

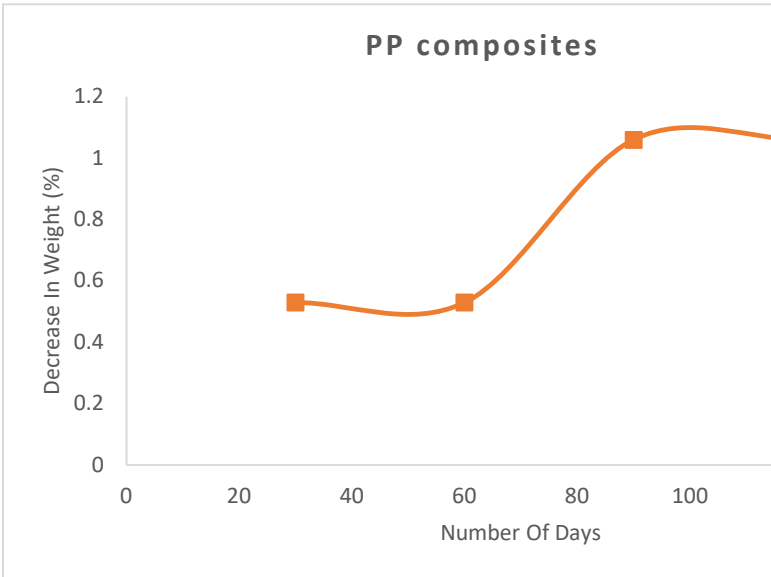

Figure 3.4: Graph showing percentage weight loss in biodegradation of 190g PP/10g CPP

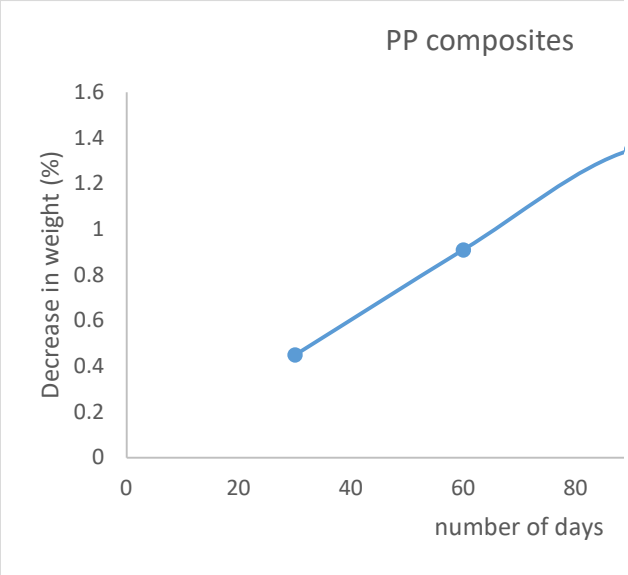

Figure 3.5: Graph showing percentage weight loss in biodegradation of 170g PP/30g CPP

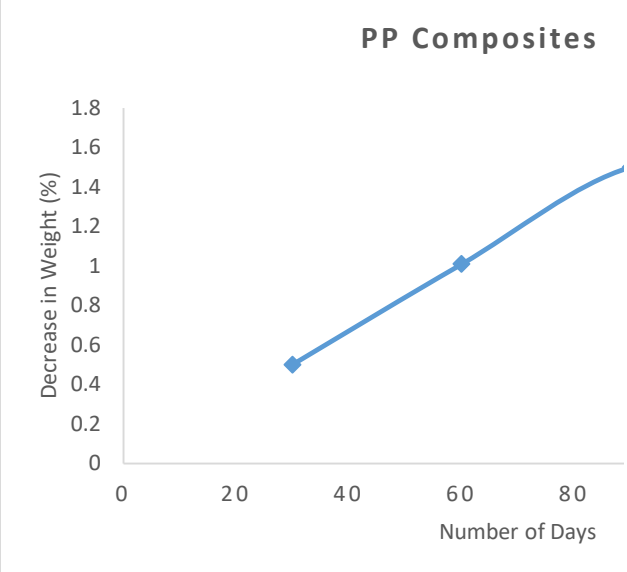

Figure 3.6: Graph showing percentage weight loss in biodegradation of 150g PP/30g SSP/20 CPP

The results showed that the composites responded to the microbial attack after thirty days in the soil. It was also observed that there was continuous microbial attack as long as the composites were buried in the soil. These led to a steady decrease in weight of the composites except the neat PP which maintained a constant weight until after 120 days before a slight decrease in weight was noticed. The results also showed that the rate of biodegradation increased as the amount of filler content of the composites is increased for all the formulation (PP/SSP, PP/CPP, PP/SSP/CPP). This trend was similar to the study **by Farahana** *et al,* 2015. The rate of biodegradation for composites increased as the filler content loading is increased as a function of time in all formulation.

3.4 Water absorption test

The results from the water absorption studies are presented in table and graph. Referring to figure 3.7 to 3.13 below, the results showed that the rate of water absorption increased with increase in the amount of filler proportional with its duration in water.

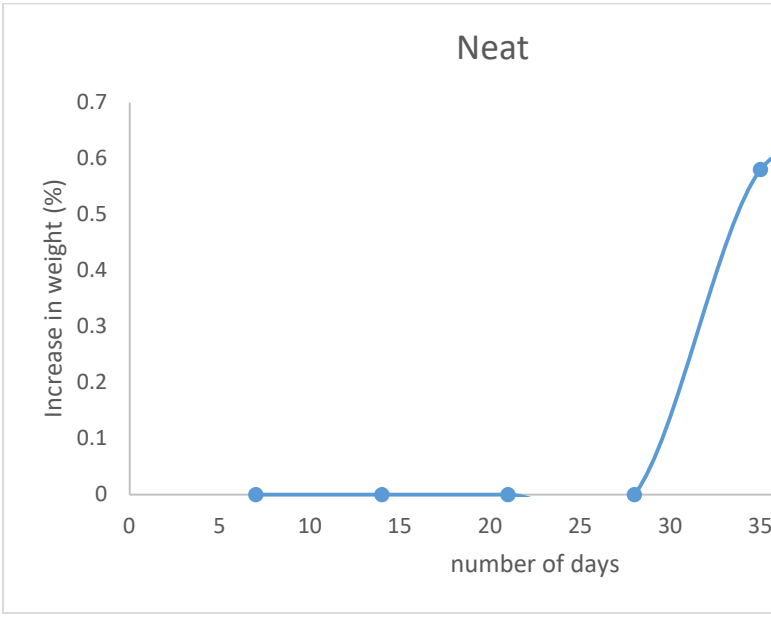

Figure 3.7: Graph showing the percentage weight gain in water absorption neat PP

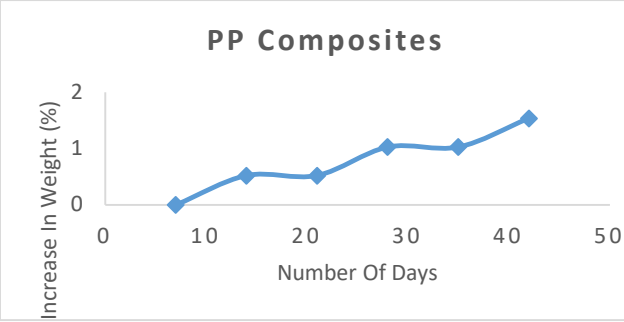

Figure 3.8: Graph showing the percentage weight gain in water absorption of 190g PP/10g SSP

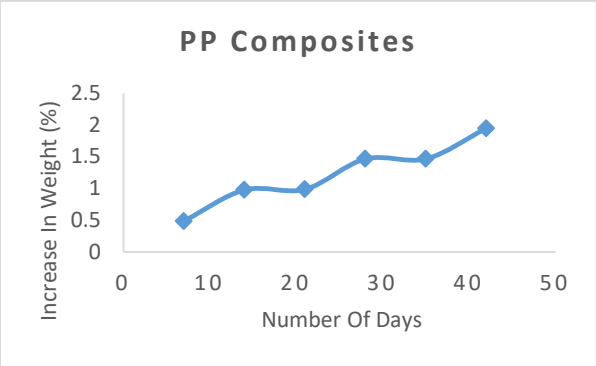

Figure 3.9: Graph showing the percentage weight gain in water absorption of 170g PP/30g SSP.

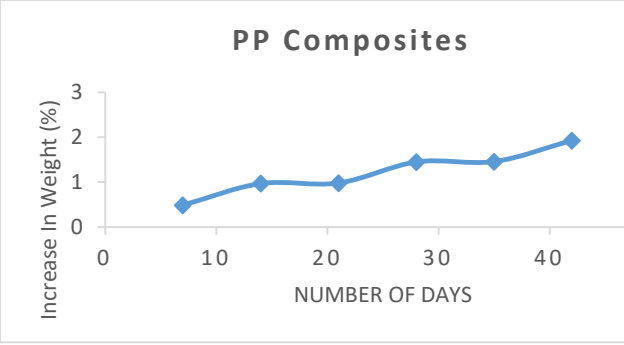

Figure 3.10: Graph showing the percentage weight gain in water absorption of 190g PP/10g CPP

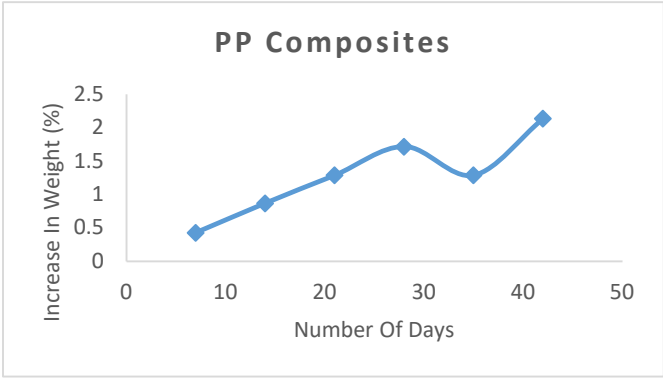

Figure 3.11: Graph showing the percentage weight gain in water absorption of 170g PP/30g CPP

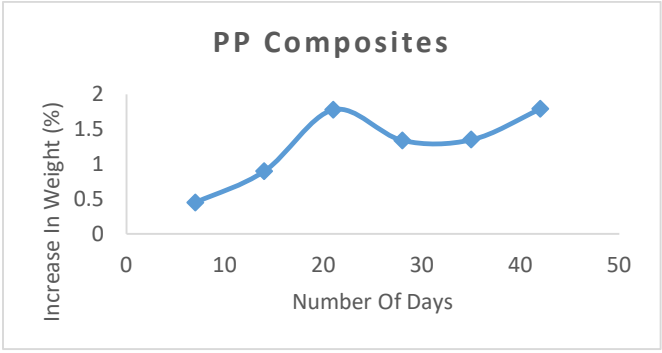

Figure 3.12: Graph showing the percentage weight gain in water absorption of 160g PP/30g SSP/10g CPP

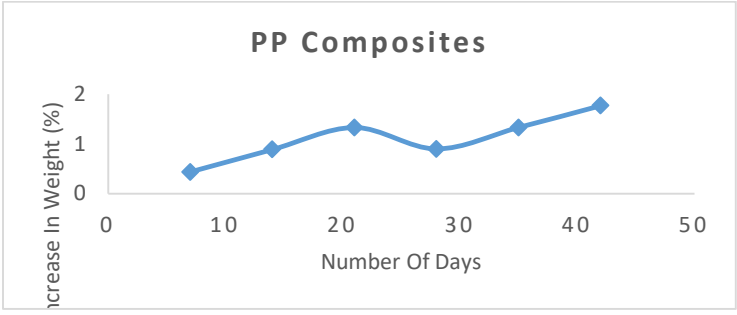

Figure 3.13: Graph showing the percentage weight gain in water absorption of 140g PP/30g SSP/30g CPP.

The water absorption of polypropylene (PP) composites as illustrated in the above figures showed increase in water absorption with increase in filler content in proportion to their duration in water for all the investigated composites. All the prepared polypropylene composites absorbed more water than the neat PP. The filler loadings were incorporated into the polypropylene matrix. It was observed that the rate of water absorption in CPP filled composites was found to be higher than that of SSP and CPP/SSP filled composites. The rate increase of water absorption of CPP filled composite decreases in the form as 170gPP/30g CPP >180g PP/20g CPP >190g PP/10g CP

3.5 Mechanical Properties.

The results from the mechanical properties studies such as tensile strength, tensile modulus, flexural strength, flexural modulus, elongation at break and impact strength are presented in graph, charts and Tables as shown in Figures 3.14 to 3.17. The results showed that they increased with increase in the amount of fille

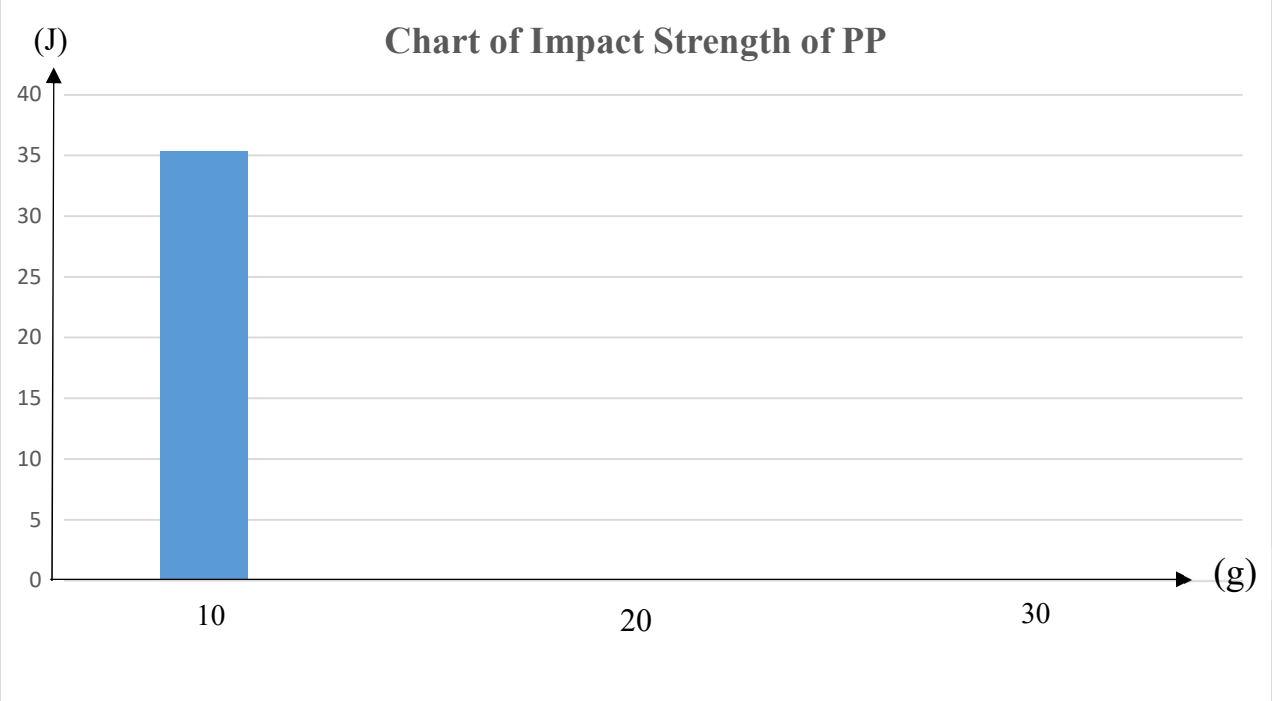

Figure 3.14: Chart Showing Impact Strength of Neat PP

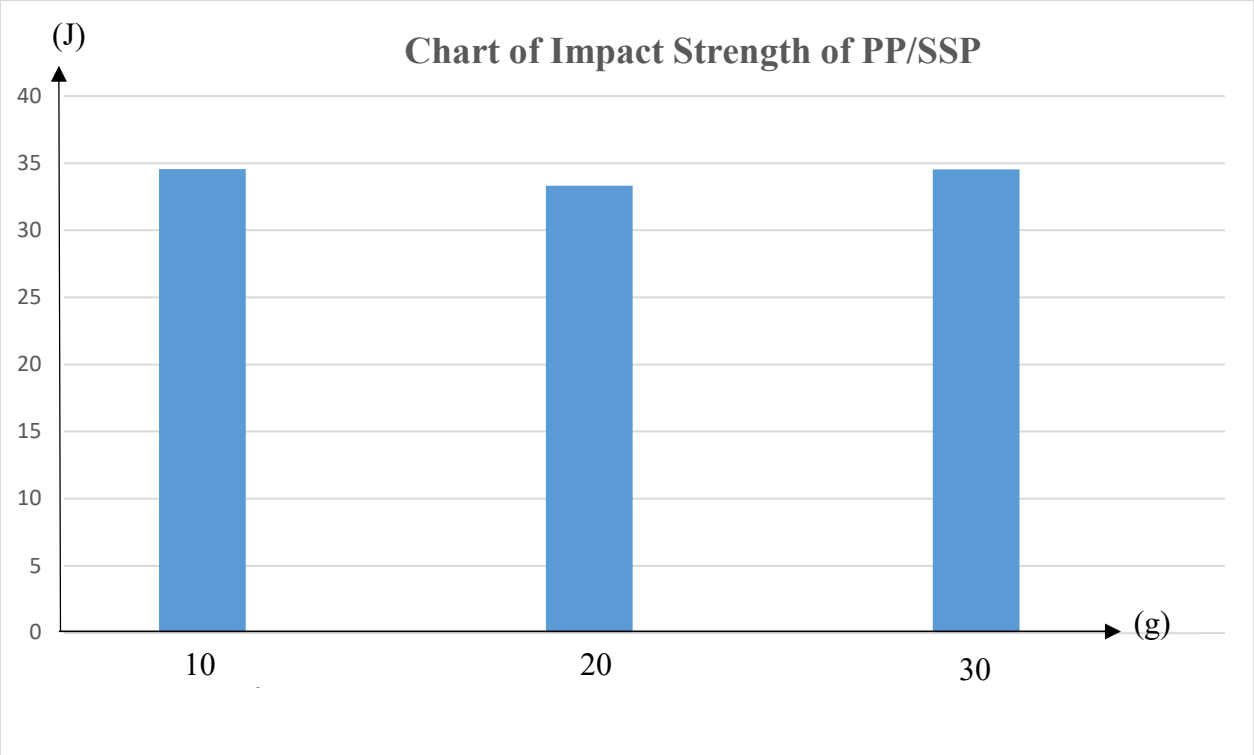

Figure 3.15: Chart Showing Impact Strength of PP/SSP Filled Composites

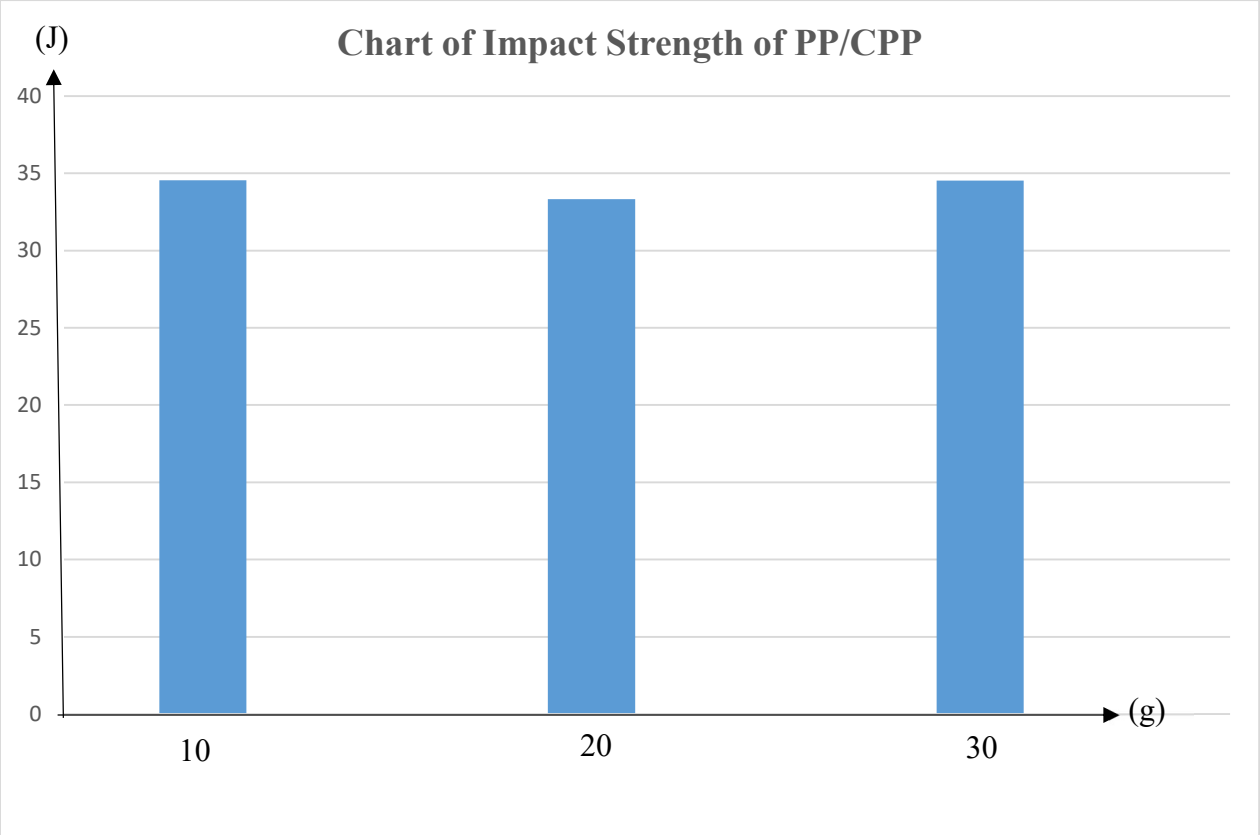

Figure 3.16: Chart Showing Impact Strength of PP/CPP Filled Composite.

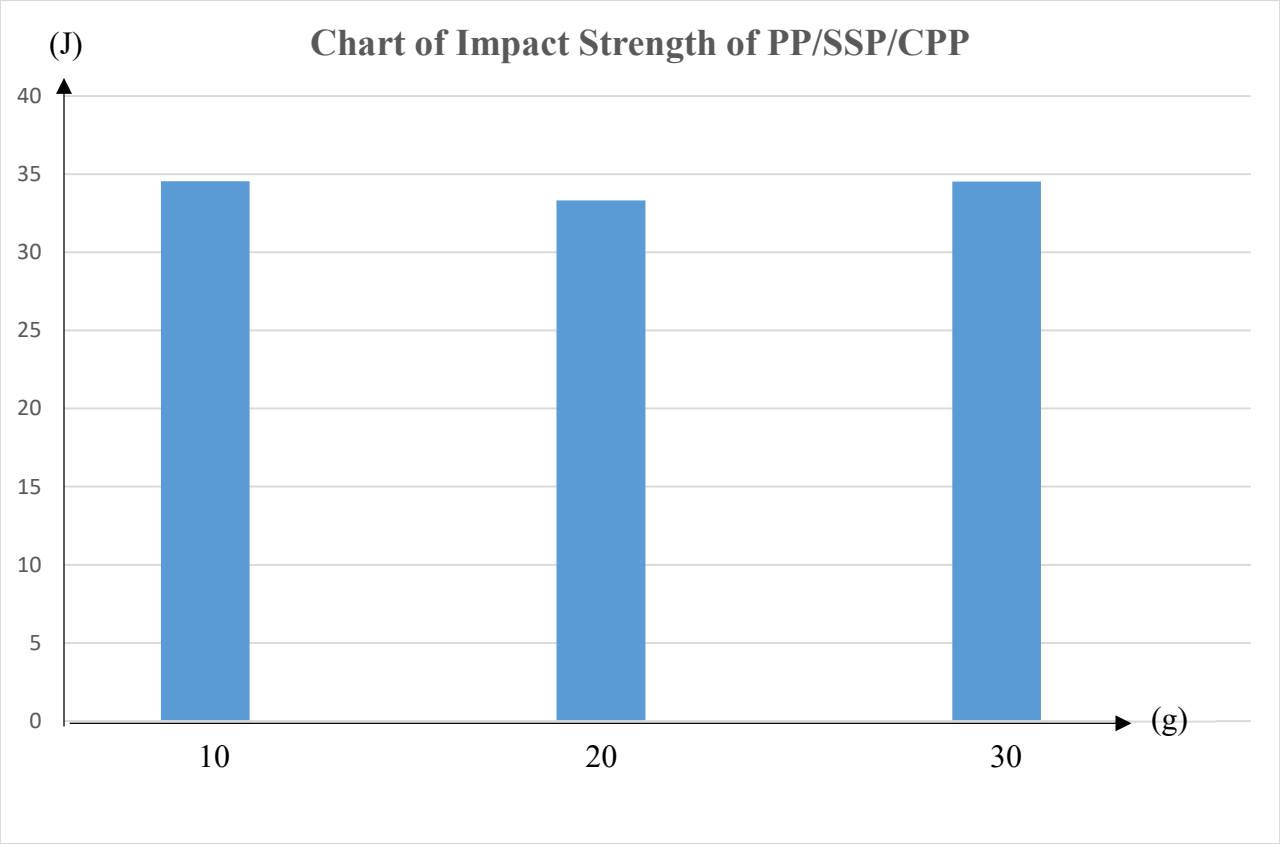

Figure 3.17: Chart Showing Impact Strength of PP/SSP/CPP Filled Composite.

3.5.1 Impact Strength

Impact strength is the amount of energy a material can withstand when a certain load is applied on it before its failure. The effect of filler loading on the impact strength of cassava peel powder (CPP), snail shell powder (SSP) and CPP/SSP filled polypropylene composites is shown in figures 3.15 to 3.17. The results showed that there was decrease in impact strength of all the composites with reference to the impact strength of pure polypropylene which is at 35.36J. Figure 3.15 Showed that the impact strength for polypropylene composite (PPC) of snail shell powder (SSP) increased with increase in filler loading at 30wt % of filler compared with 10wt %. This could be attributed to the fact that SSP has better interfacial adhesion to PP and the presence of calcium carbonate in the snail shell particles which is hard and rigid enhances the impact strength of the composites. This is similar to the study by **Lumlong** *et al* ,2018 However, figure 3.16 showed the impact strength for PPC of CPP and it was observed that the impact strength decreased with increase in filler content loading; 34.00J for 10wt % of filler content to 33.86J for 30wt % of filler content. This could be attributed to the incompatibility of the filler and matrix, thus reducing the ability of the composites to withstand stress with increasing filler content loading. This is similar to the study by **lumlong** *et al,*(2018) and **Nwiyoronu** *et. al.* (2022). Also, the same observation was made on impact strength for PPC of CPP/SSP as illustrated in figure 3.17; the result showed that 160g PP/30g SSP/10g CPP was recorded to be 34.56J while 140g PP/30g SSP/30g CPP were recorded to be 34.54J. This could be attributed to poor interfacial adhesion between filler and the matrix. This is in accordance with the study by **Nwiyoronu** *et al,* (2022) and **Mubarak,** (2018).

Table 3.1: Result of Tensile Properties of Polypropylene and Composites

S/No	Samples/Filler content loading (wt %)	Tensile strength
1	Neat PP	35.86861
2	190g PP/10g SSP	26.56087
3	180g PP/20g SSP	21.39059
4	170g PP/30g SSP	23.80425
5	190g PP/10g CPP	19.59904
6	180g PP/20g CPP	15.35894
7	170g PP/30g CPP	15.01377
8	160g PP/30g SSP/10g CPP	21.74107
9	150g PP/30g SSP/20g CPP	22.02067
10	140g PP/30g SSP/30g CPP	23.59140

Table 3.2: Result of Flexural Properties of Polypropylene Composites

S/No	Filler content loading (wt %)	Flexural strength	Flexural modulus
1	Neat PP	161.10087	7106.62842
2	190g PP/10g SSP	33.35299	1419.35730
3	180g PP/20g SSP	29.72039	1319.90719
4	170g PP/30g SSP	18.06021	617.39955
5	190g PP/ 10g CPP	34.49079	1453.61824
6	180g PP/20g CPP	22.18974	1684.67045
7	170g PP/30g CPP	32.62745	1319.47044
8	160g PP/30g SSP/10g CPP	57.21847	2548.68374
9	150g PP/30g SSP/20g CPP	33.57255	909.02042
10	140g PP/30g SSP/30g CPP	49.93065	1915. 25307

Note; Polypropylene (PP), Cassava Peels Powder (CPP), Snail Shells Powder (SS), D (neat PP), A1 (190g PP/10g SSP), A2 (180g PP/20gSSP), A3 (170g PP/30g SSP), B1 (190g PP/10g CPP0, B2 (180g PP/20g CPP), B3 (170g PP/30g CPP), C1 (160g PP/30g /10g CPP), C2 (150g PP/30g SSP/20g CPP), C3 (140g PP/30g SSP/30g CPP)

3.5.2 Tensile Strength

Tensile strength is the ability of a material to withstand maximum amount of stress while being pulled without failure. Figures 27 to 36 with reference to Table 3.1 showed the result obtained from filler content loading of cassava peel powder (CPP), snail shell powder (SSP) and CPP/SSP polypropylene composites, it was

observed that there was a general trend of decrease in tensile strength for all the polypropylene composites when compared with the tensile strength of neat polypropylene. The tensile strength of polypropylene composites of SSP was observed to have decreased with increase in filler content loading. From the illustration in figures 28 to 30, it is clear that the higher the filler content, the lower the tensile strength. This may be attributed to the rate of dispersion and filler matrix interaction. Also, the same observation was made on the tensile strength of polypropylene composites of CPP as shown in figures 31 to 33. However, in the results obtained from tensile strength for polypropylene composites of CPP/SSP as shown in figures 34 to 36 and table 1, the tensile strength of these composites were observed to increase with increased filler content loading. 140g PP/30g SSP/30g CPP were observed to acquire higher tensile strength than others. The trend of tensile strength increased with filler content loading were related as 160g PP/30g SSP/10g CPP < 150g PP/30g SSP/20g CPP < 140g PP/30g SSP/30g CPP have. This may be attributed to better dispersion and filler matrix interaction. The results obtained similar to the study reported by Ofem, *et. al.* (2020) and Chris- Okafor, (2016).

3.5.3 Tensile Modulus

The effect of type of filler and filler content loading on the tensile modulus are shown in Table 3.1. Tensile modulus is a mechanical property that measures the resistance of material to elastic deformation. Table 3.1 showed that the tensile modulus of SPP filled composites and CPP filled composites increased as filler content is increased. The filler content is measured in 10wt %, 20wt % and 30wt % respectively. There was a slight decrease in tensile modulus strength of CPP filled of filler content at 30wt %. However, the tensile modulus strength of CPP/SSP combined filler decreased with increase in filler content loading. The results also indicated that all the filler content loading in all the polypropylene composites formulated are lower than that of the neat polypropylene except that of 160g PP/30g SSP/10g CPP that is slightly higher. This observation may be due to the presence of crack in the matrix due to dispersion and interaction of filler particles. This is similar to the study reported by Daramola *et. al.* (2015).

3.5.4 Flexural Strength

The effect of filler loading on the flexural strength of snail shell powder (SSP), cassava peel powder (CPP) and SSP/CPP filled polypropylene composites (PPC) is shown in Table 3.2. Flexural strength is one among the useful parameters of materials in structural application which denotes the ability of material to resist deformation under load before yield point. Generally, with reference to flexural strength of neat polypropylene as presented in and Table 3.2, there was a decrease of value in the flexural strength of all the PPC. Results have shown that the flexural strength for PPC of SSP were observed to decrease with increased filler content loading. The filler content loading of all the composites is in the increasing trend of the form as 10wt % < 20wt % < 30wt %. Also, showed that the flexural strength for PPC of CCP decreased with increased filler content loading. Moreover, figure 40 showed that the flexural strength for PPC of SSP/CPP decreased as the filler content loading is increased. All these could be attributed to an uneven dispersion of the filler in the matrix of PP and non-homogeneity that led to weak bonding. This observation is similar to the study by Chai (2016) and deviated from the observation made from the study reported by Onuegbu, *et. al.* (2011) and Chris-Okafor, (2016).

3.5.5 Flexural Modulus

The flexural modulus of all the polypropylene composite decreased with reference to the flexural modulus of pure polypropylene as illustrated in Table 3.2. The flexural modulus for PPC of CPP reduced with increase in amount of filler content loading. Moreover, it was observed that the flexural modulus for PPC of SSP/CPP reduced with increase in amount of filler content loading. This is similar to the study reported by Daramola, *et. al.* (2017).

3.5.6 Elongation at Break

Deformation at break for SSP polyethylene composites is shown to rise with increased filler content in Table 3. 1, which displays the effect of filler percentage loading on the elongation at breakage properties of polypropylene composites. At the filler concentrations utilized (10g, 20g, and 30g), filler can be viewed as a structural element embedded inside the polymer matrix. However, as filler content increases, elongation at break values for CPP and CPP/SSP thermoplastic composites fall. Table 3.1 provides an example of this. There might not be enough in there to keep the polypropylene molecule around for long. Further, it is possible that a larger concentration of stain at the level of concentration under study might cause wetting between the polypropylene and the filler, resulting in essentially a non-brittle matrix. Similar findings were observed in a study by Chitra, (2016).

3.6 Conclusion.

The results obtained from the incorporation of cassava peel and snail shell powders into polypropylene matrix showed a decrease in mechanical properties of the composites. The trend was noticed in the mechanical properties such as tensile strength, tensile modulus, and elongation at break, flexural strength, flexural modulus and impact strength of all the composites. However, there was an increase in the percentage of water absorption to the duration of its immersion in water for all the composites whereas the rate of biodegradation of the composites were found to be increasing with increase in the amount of filler and the number of days it remained in the soil. This study has confirmed the effect of filler loading on the polypropylene matrix with snail shell and cassava peel powders with the characterization and monitoring test. The results summarized in Tables 3.1 and 3.2 showed the trend of reduction. The rate of biodegradation was greatly enhanced with the incorporation of filler into the matrix of polypropylene. With the exception of neat polypropylene all the prepared composites investigated showed significant water absorption with duration in water absorption test.

DECLARATION OF CONFLICTING INTERESTS.

The authors have declared no conflict of interests.

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Nigerian Journal of Polymer Science and Technology, 2025, Vol. 20(1), pp28-43

Received on: 20/09/2024 Revised on: 29/10/2024 Accepted: 12/01/2025

COMPARATIVE STUDY OF ALKALI AND SILANE TREATED SUGARCANE BAGASSE FOR MECHANICAL REINFORCEMENT IN EPOXY RESIN NANO COMPOSITES

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ABSTRACT

The nano composite of sugarcane bagasse and epoxy resin were prepared through the hand layup technique by using a glass mold. The fiber was initially treated with caustic soda and silane solution prior to the composite fabrication. Three different polymer composites (untreated, alkali, silane) at six different weight percentage of SCBP reinforcement (0wt%, 5wt%, 10wt%, 15wt%. 20wt% ,25wt%) were fabricated. Tensile, Flexural, Impact and Hardness tests were carried out. Both alkali and silane treated SCBP nano composite have better tensile strength than the untreated composite. The tensile strength and flexural modulus of all the composites decreases slightly as the fiber loading increases. The tensile modulus, flexural strength, impact, hardness of the fabricated composites was found to be increasing with increase in SCBP loading. With the exception of hardness test, the silane treated SCBP nano composites shows better properties than the alkali treated and the untreated SCBP nano composites for all the parameters.

Keywords: Sugarcane Bagasse Powder, Alkali Treatment, Silane Treatment, Epoxy Resin.

1.0 INTRODUCTION

Agriculture is at the heart of sub-Saharan Africa's economic growth. This contributes significantly up to roughly 50% to the GDP in sub-Saharan Africa. Through agro-industries, the refining of crops into a refined product increases value according to Lesego et al. 2016. A significant agricultural crop that is produced all over the world is sugarcane. Sugarcane produces a significant amount of waste. Global socioeconomic development and growth have found this to be relevant. Asia was the original home of sugarcane. Typical weather that is humid and subhumid is ideal for sugarcane growth. (Makul et al., 2016).

By 2050, due to population growth, protecting and enhancing the means of subsistence for small-scale families and tenant farmers has become problematic (United Nations, 2015). This is because unsustainable practices and soil degradation have put agricultural natural resources under duress. The low yield has been documented in the last ten years despite advancements in technology. The high cost of processed and raw food is a result of this worldwide. Consequently, protecting and improving tenant farmers' and small-scale families' means of subsistence has become problematic. (Carvalho et al., 2017). To meet the world's growing and changing need for sustenance, significant advances in resource efficiency and the reduction of waste generated from sugarcane are therefore necessary, and they may even be able to stop environmental damage. More money needs to be spent on research and agriculture, especially in emerging nations. In order to

encourage the adoption of sustainable production, this is necessary. This will support the realignment of implicit and explicit agriculture to fulfill the needs of the growing population, as well as farmers, ecosystems, and communities in adapting to reduce and create resilience against the unsustainable agriculture productivity. (Carvalho et al., 2017).

Bagasse comprises roughly 45–50% water, 2–5% sugar that has been dissolved, and 40–45% fibers. After the juice is extracted, it is a byproduct of the sugarcane business. The components of sugarcane bagasse are cellulose (36.0%), pentosans (26.0%), lignin (20.0%), and ash (2.2%). Molasses and mill mud are further by products (Kemausuor et al., 2018). The main chemical constituents of bagasse are cellulose, hemi cellulose and lignin. (Debnath, 2009). Composite materials formed by natural fiber and polymeric matrices constitute a current area of interest in composite research. (Mileo *et al.,* 2011).

There exists an excellent application in fabricating bagasse-based composite toward a wide array of application in building construction such as Roads, Boards and block as reconstituted wood, pump and flowing tiles to mention a few. (Yadav *et al.,* 2015). Sugarcane bagasse is the residue obtained from extracting the sugarcane juice in industries for sugar or wine. (Danso, 2017).

Alkali treatment can lower polymerization, lignin concentration, and hemicellulose in the fiber. Alkaline treatment can affect the number of reaction sites on fiber surfaces and increase surface roughness, leading to improved mechanical characteristics. (Bam *et al.,* 2019). The use of sugarcane bagasse increased the tensile and flexural characteristics of materials. The highest tensile and flexural strength were observed at 15wt% fiber loading. Composites with 15wt% fiber loading demonstrated improved thermal stability compared to other samples. (Jumaidin *et al*., 2021).

Mahesh et al. 2018 reported that the tensile modulus of fiber-reinforced polyester composites treated with silane improved by 150%, whereas the tensile strength of fiber-reinforced polyester composites treated with acetylated and alkali significantly increased. Furthermore, acetylated, permanganate, and silane-treated fiber-reinforced composites showed higher flexural modulus and flexural strength compared to untreated panels.

The investigation of the effect of chemical treatment on the mechanical properties of SCB fibers was achieved by Mansour *et al.* (2021). It explains that when compared to untreated SCB fibers, the alkali treatment of SCB greatly increases the tensile strength and modulus of all fiber-reinforced composites. When compared to untreated SCB fibers, the impact and hardness parameters of the SCB/LDPE composite are also markedly improved by the alkalization treatment of SCB. When fiber content increased from 10% to 30% of the total weight, chemical resistance decreased. In a NaOH solution, composites have demonstrated maximal absorption.

MATERIALS AND METHOD

Table 1: Materials and their sources

SN	MATERIALS	SOURCES

1	Fresh sugarcane bagasse waste	Sugarcane center in samaru, Zaria
2	Epoxy resin (grade 3554A)	Juneng Nigeria Limited, Enugu state
3	Hardner (grade 3554 B)	Juneng Nigeria Limited, Enugu state
4	Distilled Water	Chemistry department, ABU Zaria
5	Glass mold	Polymer and Textile Engineering, ABU Zaria
6	Weighing balance	Polymer and Textile Engineering, ABU Zaria
7	Stirring rod	Polymer and Textile Engineering, ABU Zaria

SAMPLING AND TREATMENT

The sugarcane bagasse was collected from Samaru cane center, Zaria, Kaduna State. It was then washed thoroughly with distilled water to remove both access sugar and dirt particles and then dried in an open air for 48 hours. The dried sample was then grinded to a more smaller particle size and then ball milled for 80 hours using a laboratory mill machine from the department of chemical engineering, Ahmadu Bello University.

The bagasse fiber was then divided into three portions. The first portion remain untreated while the other two portions were subjected to Alkali and silane treatment respectively.

ALKALI TREATMENT

The sugarcane bagasse fiber was treated with 5%wt solution of NaOH for 2 hours at room temperature. The fiber was then rinsed thoroughly with distilled water and dried at room temperature for 3 days. (Vijay *et al.,* 2019).

SILANE TREATMENT

The pretreated bagasse fiber was soaked in a concentration of 5%wt of 3 amino propyl trimethoxy silane solution diluted in water and Acetone. (concentration by 50/50 volume). For 2 hours. The fiber was then dried indirect sunlight for three days after removing it from the solution. (Mylsamy *et al.,* 2020).

COMPOSITE PREPARATION

The composite was prepared in the department of Polymer and Textile engineering laboratory, ABU Zaria. A hand layup technique was adopted by using a glass mold having a size of 200cm by 150 cm by 5cm via manual mixing using a stirring rod. The resin used was epoxy resin which was prepared in the ration of 2:1 amount by weight of epoxy resin and the Hardner. The overall weight of the composite is 100 grams. There was a variation in the composition of the epoxy resin and the sugarcane bagasse fiber. The weight of the sugarcane bagasse which was the reinforcement to that of the matrix was given in table 3.3. The measured matrix was thoroughly mixed in a container and stirred at low speed for 15 minutes to achieve uniformity. The mixture was then poured onto a 5gram SCBP. It was then cured for 24 hours at room temperature and then removed from the mold. To achieve faster and easier removal of the composite from the mold, Vaseline was used as a releasing agent which was applied onto the surface of the mold prior to applying the mixture of the matrix onto it. The fabricated composite was then cut into a suitable dimension to facilitate for further analysis based on the ASTM standards

Table 2: Nomenclature of the SCBP\Epoxy resin composites material

COMPOSITE	RATIO	MATRIX (g) 2:1		SCBP(g)
		Epoxy resin	Hardner	
0wt%SCBP\Epoxy resin	100:0	66.60	33.30	0
5wt%SCBP\Epoxy resin	95:5	63.33	31.66	5
10wt%SCBP\Epoxy resin	90:10	60.00	30.00	10
15wt%SCBP\Epoxy resin	85:15	56.66	28.33	15
20wt%SCBP\Epoxy resin	80:20	53.33	26.66	20
25wt%SCBP\Epoxy resin	75:25	50.00	25.00	25

TEM STUDIES

TEM studies was carried out in accordance with ASTM F1877. For study under an electron microscope, the sample should be transparent to allow the passage of electron beams through it. To achieve this semitransparent nature, the sample is sectioned into fine sections using glass or diamond knife attach to a device known as ultramicrotome. The device has a trough that is filled with distilled water. The section cut is collected in this trough and are then moved to a copper grid to be viewed under the microscope. The size of each section should be between 30nm and 60nm to get the best solution. During preparation of the sample for this study, the sample undergoes fixation, dehydration, infiltration, polishing, cutting and staining

FTIR analysis

FTIR analysis was carried out in accordance with ASTM E1252. FTIR allows the measurements of variation in the fiber composition after chemical treatments. The chemical structure of both pretreated and treated sugarcane bagasse will be evaluated by FTIR spectrophotometer. The sample will be prepared by mixing the material with KBr in a proportion of 1:200 for all spectra. 16 scans will be accumulated within a 4cm resolution. (Cerqueira *et al.,* 2011).

Tensile test

The tensile test was carried out in accordance with ASTM D638 using testicle properties tester. A maximum force of 10KN was applied. The samples to be tested has a dimension of 100mm by 15mm by 5mm of length width and thickness respectively. A crosshead speed of 2mm per minute was used. The specimen was held in the grip of the testing machine and tightened firmly to prevent slippage. The resistance and elongation of the specimen were detected ND recorded by load cell until rupture occurs. Breaking point, elongation at break and tensile modulus were determined and recorded from the test.

Flexural Test

The flexural test was carried out using enerpac universal material testing machine in accordance with ASTM D790. With a maximum load of 100KN and cross bead speed of 5mm/minutes. The samples have a dimension of 100mm by 30mm by 5mm of length width and thickness respectively. The samples were positioned horizontally on the samples compartment of the machine and the test was carried out. Flexural strength and modulus were determined and recorded.

Impact test

The impact test was carried out in accordance with ASTM E23 using the chary impact tester. Samples were tested at room temperature by a single swing of the pendulum hammer using Norwood. The samples dimensions were 100mm by 11mm by 5mm of length width and thickness respectively. Each sample was placed on a vice and clamped firmly. The pendulum hammer was raised to the required height and the released to strike the sample at once. The impact energy absorbed by the sample was recorded. The impact strength of the sample in joules by square meter was recorded.

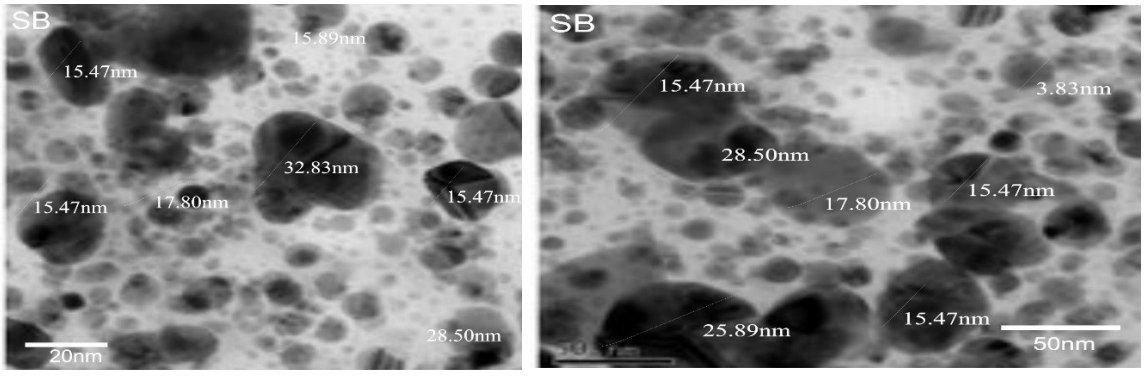
Hardness test

This test was carried out using Vickers hardness tester with maximum capacity of 0.1kgf (150hz) in accordance with ASTM D2220. The test was carried out at temperature 23+2 degrees Celsius. The sample was mounted on the specimen compartment and then the indentation point was focused thereafter. Five different points were indented on each sample and the hardness value were recorded each. The average other the five reading was calculated and recorded. The specimen dimensions were 30mm by 10mm by 5mm of length width and thickness respectively.

RESULTS AND DISCUSSION

TRANSMISSION ELECTRONIC MICROSCOPY (TEM)

The transmission electronic microscope studies as shown in figure 1 shows a representative sample of nano particles with a relatively spherical shape. The particles are mostly dispersed with some aggregation observed. The size distribution is narrow with an average particle size of 19.3nm at a range of 20nm, 50nm and 100nm. This TEM result shows that the nano particles have a uniform size distribution with an average size of 19.3nm. The spherical shape and dispersed state of the particles shows a high degree of uniformity and stability. These results confirm the expected size range of the SCBP which is essential for their intended applications.



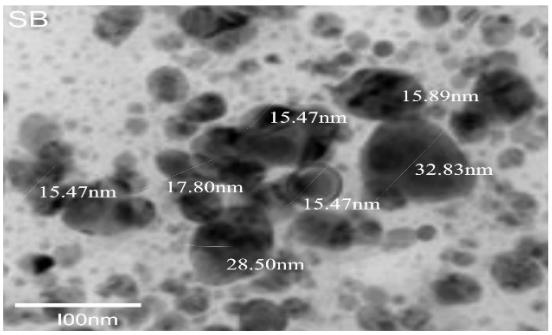


FIGURE 1: TEM image of SCBP at 20nm, 50nm and 100nm

FTIR

Figure 2 shows the FTIR spectra of SCBP of the untreated and the modified alkali and silane treated ones. For the alkali treated SCBP, the spectra show peaks that are attributed to SCBP. For the untreated SCBP, the hemicellulose and lignin show an obvious peak of 1733cm^{-1} and 1242cm^{-1}, the peak for both the hemicellulose and lignin is weaker for the alkali treated SCBP which suggest that they were removed by the Alkali treatment. As for the silane SCBP, its IR spectrum is relatively similar to that of the untreated SCBP bar the little reduction of the hemicellulose and lignin. However, there is an identifiable peak of Si-O-C at 1323.2 cm^{-1}. This bond is formed between the coupling agent and the bagasse. This result is in agreement with Orue *et al.* (2016). They studied, The effect of alkaline and silane treatments on mechanical properties and breakage of sisal fibers and poly lactic acid/sisal fiber composites. Their result show that alkali treatment helps in the removal of hemicellulose and lignin from the sisal fiber and silane treatment modifies the surface properties of the fiber hence improving the strength and stiffness of the fiber. It also improves the compatibility of the fiber with the polymer. Silane treatment did not result in the loss of any peak in the FTIR spectra, the removal of hemicellulose and lignin observed is attributed to the alkali treatment. Si-C peak was not observed in this study most likely due to the low silane concentration used. (Mu et al., 2023).

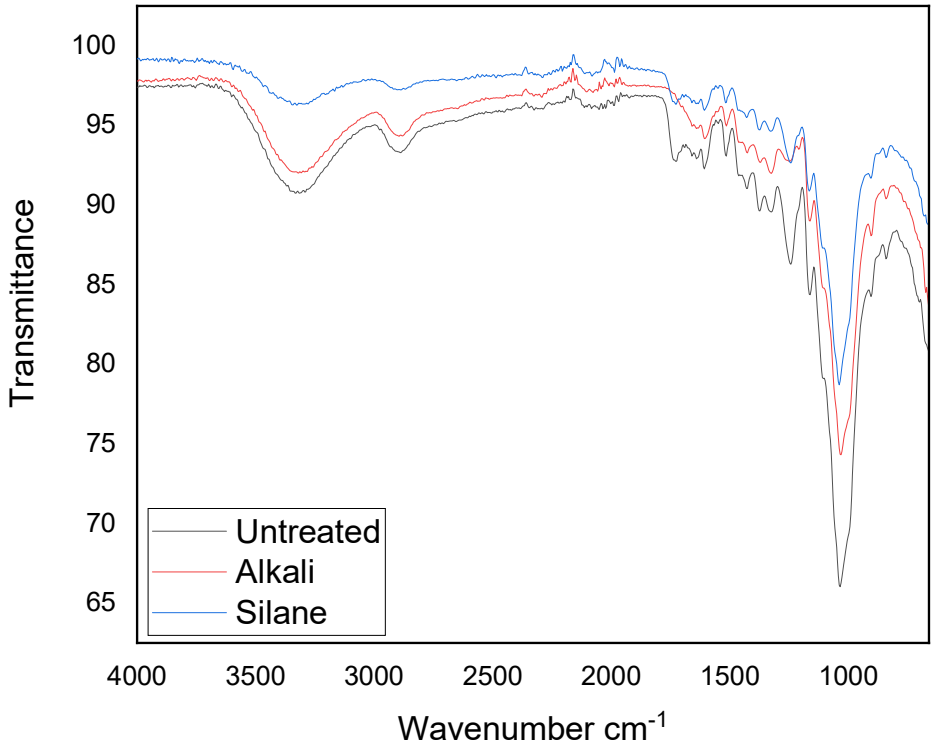


FIGURE 2: FTIR spectra of untreated, alkali and silane treated SCBP.

TENSILE STRENGTH

The tensile strength of Sugarcane bagasse reinforced epoxy nano composite was shown in figure 3 An increase in tensile strength from 5wt%, 10wt%, 15wt% of SCBP was observed for both the Untreated, Alkali and silane treated nano composite. A value of 24.83MPa, 24.99MPa and 30.08MPa were observed for the untreated SCBP, 27.84MPa, 28.06MPa and 31.12MPa for the Alkali treated and 21.92MPa, 25.25MPa and 40.29MPa for the silane treated SCBP nano composite. This is due to reinforcement effect which shows efficient stress transfer from the matrix to the fiber. Beyond the 15wt%, a decrease to 29.63MPa and 26.83MPa for the 20wt% and 25wt% was observed for the untreated, 29.69MPa and 27.1MPa for the Alkali treated and 30.27MPa and 28.26MPa for the silane treated SCBP nano composite. Increase in fiber loading up to 15wt% increases the tensile strength of the composite which shows that the interfacial adhesion between the fiber and the matrix increase simultaneously. It can be seen that there was a sudden decrease in the tensile strength of the SCBP nano composite as the fiber loading increases. This decrease in tensile strength is due to an increase in fiber loading from 15 to 25wt% leading to poor interfacial adhesion between the matrix and the reinforcement (Subramonium *et al.,* 2016). Both alkali and silane treated SCBP nano composite have better mechanical properties than the untreated SCBP nano composite with silane treated SCBP nano composite having the highest tensile strength. This result is in agreement with kanan *et al.* (2023). Who studied the effect of alkali and silane treatments on the polypropylene composite reinforced by marine Posidonia fiber waste. The silane treatment

significantly improves tensile characteristics compared to the NaOH treatment. An investigation of tensile strength was carried out, decrease in 5% loading was observed due to poor particles distribution. Later increase in 10% and 15% was observed. Before it decreases again at 20wt% and 25wt%. hence the tensile strength was achieved at 15wt%. (Alewo *et al.,* 2015).

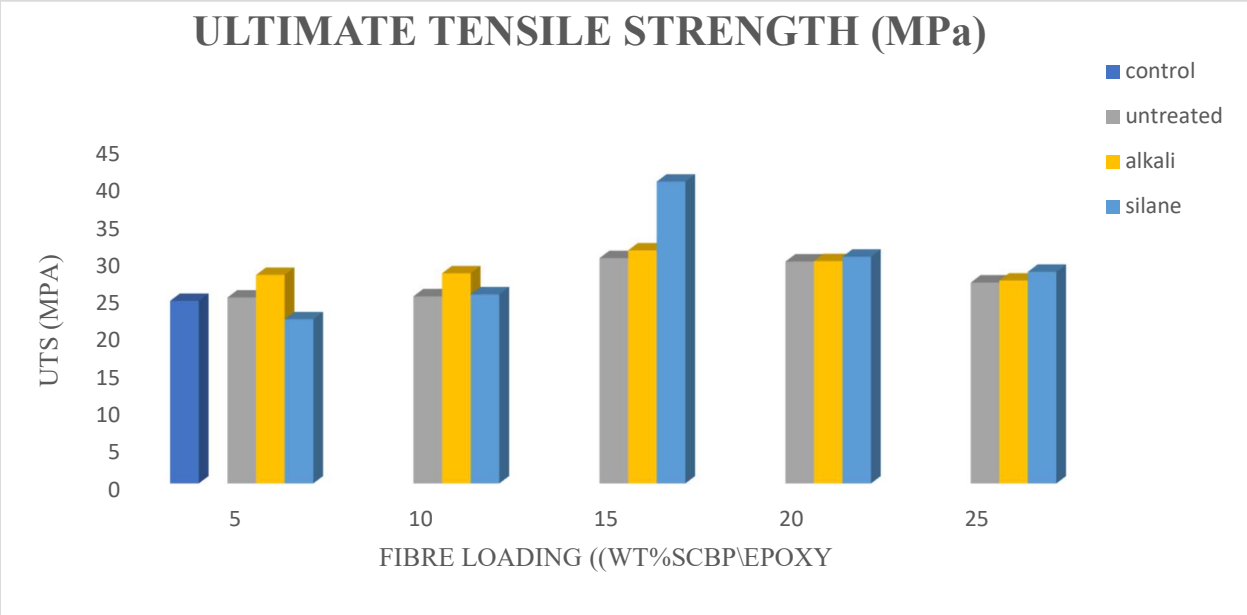


FIGURE 3: TENSILE PROFILE OF SCBP\EPOXY NANO COMPOSITES

TENSILE MODULUS

Figure 4 shows the result for modulus of elasticity. An increase in the modulus of elasticity with increase in fiber load was observed for both the untreated, Alkali treated and silane treated SCBP nano composite respectively. Untreated SCBP nano composite has 2.39MPa for 5wt%, 2.48MPa for 10wt% 2.83MPa for 15wt%, 2.87MPa for 20wt% and 2.93MPa for 25wt%. Alkali and silane treated SCBP nano composite has 2.67MPa and 2.71MPa for 5wt%, 2.79MPa and 2.77MPa for 10wt%, 2.87MPa and 2.92MPa for 15wt%, 3.09MPa and 3.5MPa for 20wt% and 3.19MPa and 3.85MPa for 25wt%. Addition of reinforcement into the matrix increases young modulus which continue to increase with increasing reinforcement. This increase in reinforcement causes the contact surface between the fiber and the matrix to increase, this helps the fiber and the matrix to achieve greater cohesive energy between them while increasing the mechanical properties. It was also found that increase in fiber content increases the tensile modulus of the fiber reinforced composite. (Kaewkuk *et al.,* 2013). Both Alkali and silane treated SCBP

nano composite shows improved modulus of elasticity than the untreated SCBP nano composite. Similar trend was observed by Sujaritjun *et al.* (2013). Based on their study on PLA polymer reinforced with Bamboo, grass and coconut fibers, the tensile modulus of the composite increased with increase in fiber loading because incorporation of the fiber improves the stiffness of the material. Increase in tensile modulus of the raffia palm fiber reinforced composite from 0% to 5% concentration was observed and a decrease was observed by increasing the concentration to 10% 15% and 20%. (Anike *et al.,* 2014).

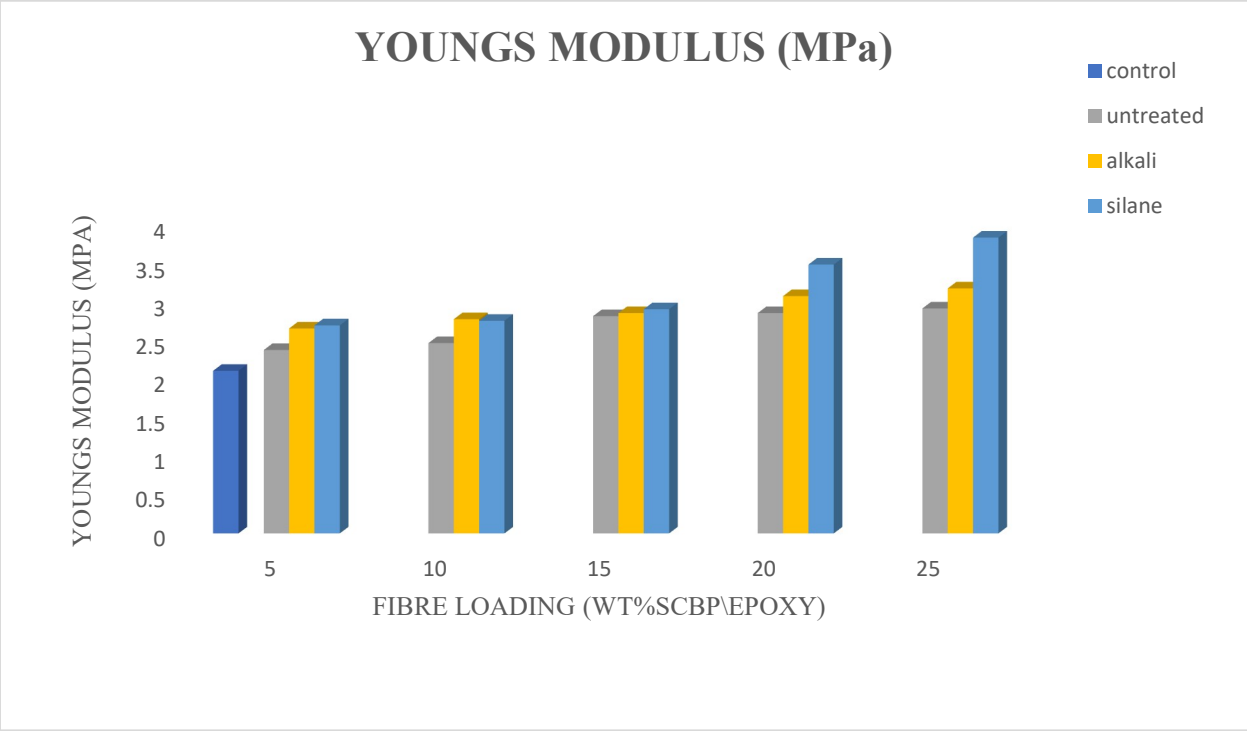


FIGURE 4: YOUNG MODULUS PROFILE OF SCBP\EPOXY NANO COMPOSITES

ELONGATION AT BREAK (%)

Figure 5 shows the elongation properties of SCBP\Epoxy nano composite. Neat SCBP nano composite sample have the highest percent elongation of 12.28%. both the Alkali, silane and the untreated SCBP nano composite have the highest percent elongation of 10.5%, 10.66% and 10.31% respectively at 5% fiber loading and the lowest percent elongation of 9.23%, 9.52% and 9.63% at 25% fiber loading. Hence it can be deduced the elongation properties of the SCBP nano composite decreases with increase in fiber load. Both the Alkali and silane treated SCBP nano composite have higher elongation than the untreated SCBP nano composite. The silane treated SCBP nano composite have the highest elongation than both the alkali treated and the untreated SCBP nano composite. This result follows the same trend with wang *et al.* (2006). on the study of Bamboo fiber composite, a decrease in the elongation of the fabricated composite

was observed as the fiber loading increases. This is due toincrease in discontinuity of the polymer matrix as the content of the fiber increases. Surface treatment with benzoyl chloride in PLA/SCBP composites was studied by Yelwa *et al. (*2023). It was observed that there is decrease in the elongation of the composite as the fiber loading increases. The result for elongation at break of bio composite shows that the elongation at break decreases with increase in fiber loading for both the alkali and silane treated composites. (Shehu *et al.,* 2016).

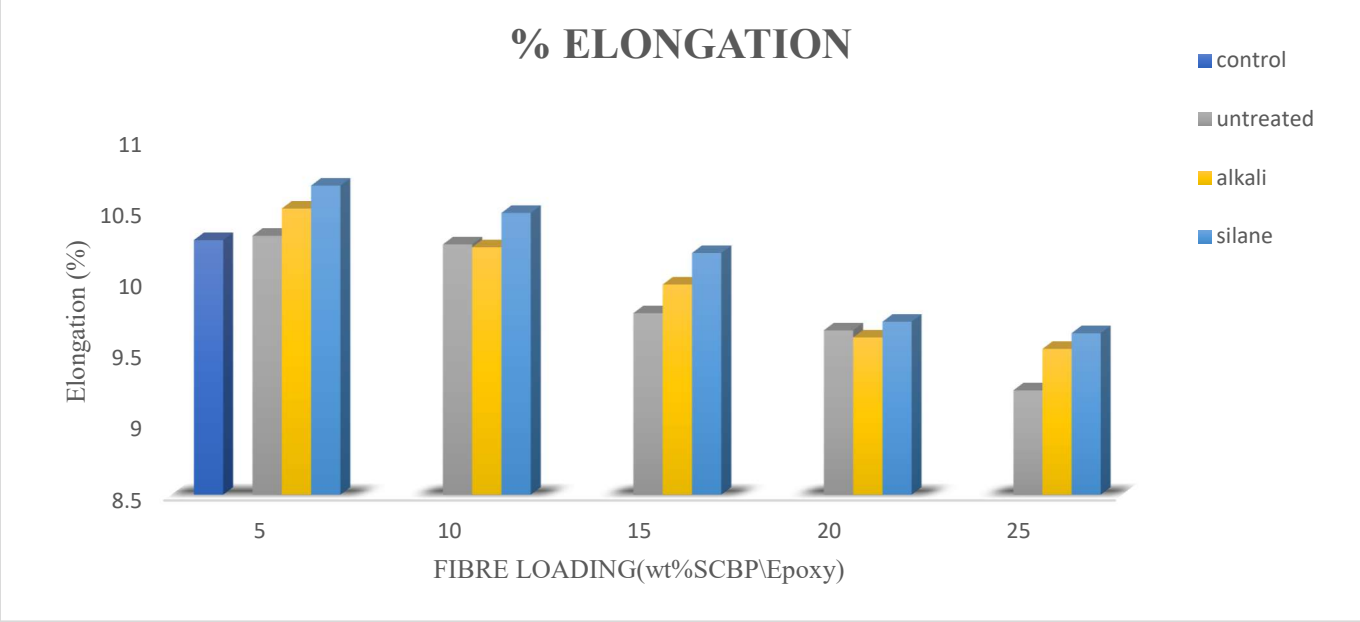


FIGURE 5: ELONGATION (%) PROFILE OF SCBP\EPOXY NANO COMPOSITES.

FLEXURAL STRENGTH

The flexural property of the composite depends on the ductility of the matrix and the strength of the fiber. (Parmiggiani *et al.,* 2021). The flexural strength of the SCBP\Epoxy nano composite was shown in figure 6 Flexural strength of 5wt%, 10wt% and 15wt% were 25.15MPa, 25.76MPa and 31.74MPa found to be increasing with increase in fiber load for the untreated SCBP nano composites. beyond which a decrease in the flexural strength was observed for 20wt% and 25wt% at 29.77MPa and 27.31MPa respectively. Alkali and silane treated SCBP\Epoxy nano composite both shows increase in flexural strength for 5wt%, 10wt% and 15wt% fiber loading at 27.61MPa, 27.87MPa, and 38.36MPa for the Alkali SCBP nano composite treated and 25.4MPa, 26.86MPa and 44.49MPa for the silane treated SCBP nano composite respectively. A drop in the flexural properties was observed for the 20wt% and 25wt% at 35.65MPa and 28.7MPa for the Alkali treated and 37.48MPa and 34.0MPa for the silane treated SCBP nano composite. Both silane and Alkali treated SCBP nano composite have higher flexural strength than the untreated SCBP nano composite which indicates that both the chemical treatments

improve the flexural property of the SCBP nano composite. The increase in flexural strength of alkali treated fiber reinforced composite can be due to the fact that the fiber become tougher and more fibrillated than the untreated fiber resulting in a better fiber matrix interface. Sahai et *al.* (2022). in their study of mechanical properties of sisal fiber reinforced polyester composite also found that flexural properties of the sisal composite are enhanced after alkali and silane treatments with silane having the highest flexural strength than the Alkali and the untreated composite.

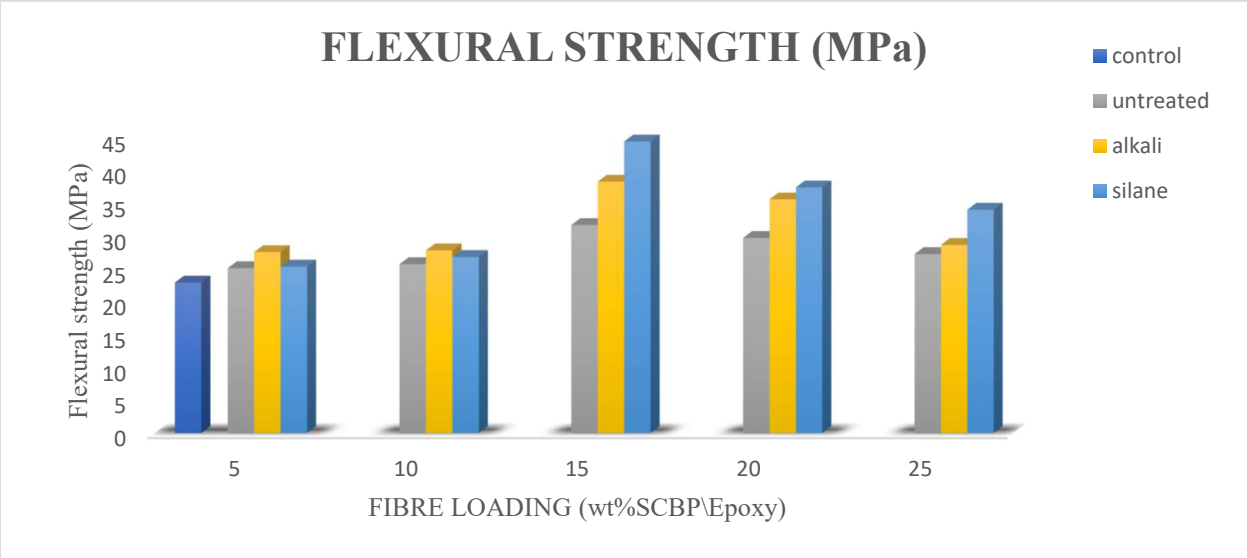


FIGURE 6: FLEXURAL PROFILE OF SCBP\EPOXY NANO COMPOSITES.

FLEXURAL MODULUS

Figure 7 depicts the flexural modulus of untreated, Alkali and silane treated SCBP\Epoxy nano composite. It was found to be 1095.25MPa, 1142.66MPa, 1741.86MPa, 1547.76MPa and 1291.34MPa for untreated SCBP nano composite at 5wt%, 10wt%, 15wt%, 20wt% and 25wt% respectively. It can be observed that the flexural modulus is increasing with increase in fiber loading up to 15wt% before it decreases at 20% and 25% fiber loading. The same trend was found in both the Alkali and silane treated SCBP nano composite with Alkali having 1331.77MPa, 1601.39MPa, 1726.78MPa, 1650.02MPa, 1331.64MPa and silane having 1331.72MPa, 1689.81MPa, 1953.68MPa, 1707.4MPa, 1657.35MPa both for the 5wt%, 10wt%, 15wt%, 20wt% and 25wt% respectively. Alkali and silane treated SCBP nano composite have higher flexural modulus than the untreated SCBP nano composite. Coir fibers in a poly (butylene succinate) matrix for reinforcement. The findings demonstrated that, in comparison to untreated coir fiber-reinforced composites, alkali-treated fiber composites offered greater flexural modulus at all fiber loading levels. The best flexural characteristics were shown by treated fiber composites at 25% fiber loading. (Sever *et al.,* 2011).

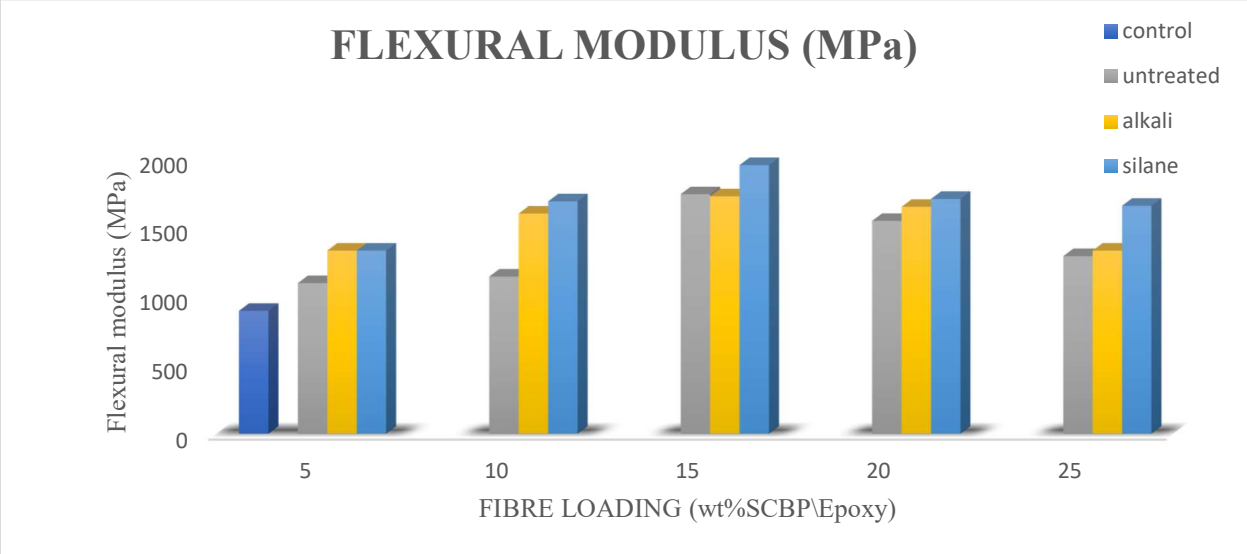


FIGURE 7: FLEXURAL MODULUS PROFILE OF SCBP\EPOXY NANO COMPOSITES.

IMPACT TEST

Impact test was carried out on the SCBP\Epoxy nano composite to study its ability to resist deformation in response to a sudden load.as shown in figure 8, for the alkali treated SCBP nano composite, 0.225 J/m^2 at 5wt% loading, 0.233 J/m^2 at 10wt%, 0.25 J/m^2 and 0.3 J/m^2 at 15wt% and 20wt% and 0.375 J/m^2 at 25wt%. The silane treated SCBP nano composite have 0.2 J/m^2, 0.216 J/m^2, 0.266 J/m^2, 0.3 J/m^2, and 0.333 J/m^2 or the 5wt%, 10wt%, 15wt%, 20wt% and 25wt%. the untreated composite has 0.2 J/m^2, 0.233 J/m^2, 0.25 J/m^2, 0.266 J/m^2, and 0.316 J/m^2 for the 5wt%, 10wt%, 15wt%, 20wt% and 25wt% respectively. It can be observed that all the Untreated, Alkali and silane treated SCBP nano composite increase with increase in fiber loading. Both the alkali and the silane treated SCBP nano composite significantly have higher impact strength than the untreated SCBP nano composite. This shows that both the alkali and silane treatments improve the impact property of the SCBP nano composite. This result is in agreement with the findings of Sahai *et al.* (2022). they found that Alkali and silane treatment both improves the impact strength of sisal fiber reinforced polyester composite. The impact parameter of alkali treated SCB\LDPE was studied, results show improvement in the strength of the fabricated composite as compared to the untreated composite. (Mansour *et al.,* 2021). Dennis *et al.,* (2017). reports that the alkali treated composite have higher impact strength than the corresponding untreated composites.

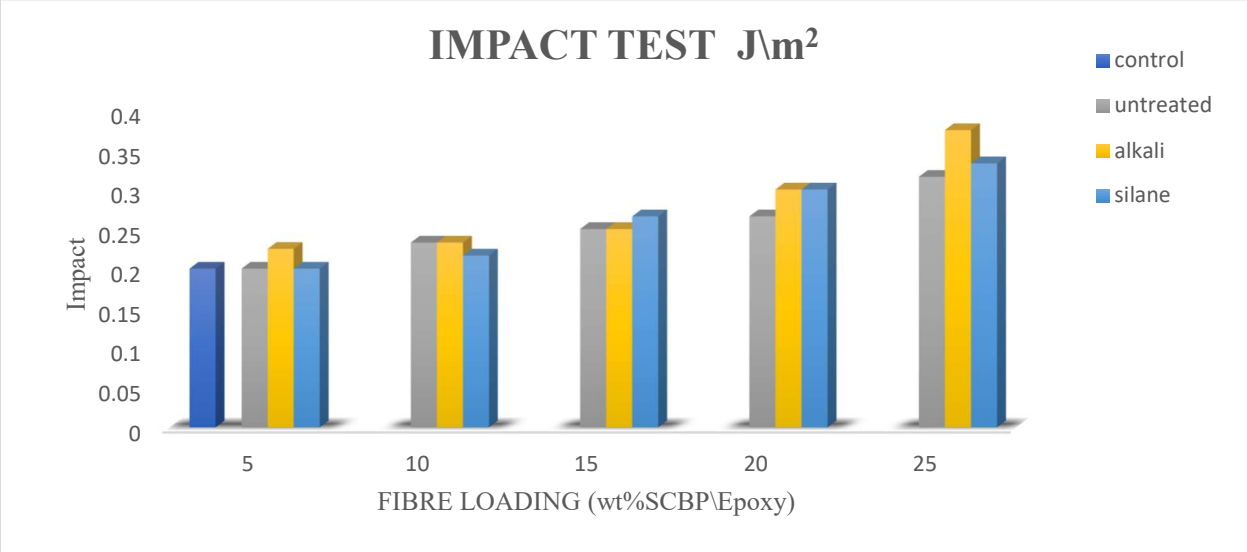


FIGURE 8: IMPACT PROFILE OF SCBP\EPOXY NANO COMPOSITES

HARDNESS TEST

Figure 9 shows the hardness values of SCBP\Epoxy nano composite for the untreated, Alkali and silane treated composites. The untreated SCBP nano composite have 19.5 HV, 24.13 HV, 37.03 HV, 48.73 HV and 57.8 HV for the 5wt%, 10wt%, 15wt%, 20wt% and 25wt%. on the other hand, the alkali treated CBP nano composite have 22.6 HV, 41.7 HV, 47.36 HV, 57.46 HV and 65.86 HV for the 5wt%, 10wt%, 15wt%, 20wt% and 25wt%. it can be observed that both the untreated and alkali treated SCBP nano composite increase with increase in fiber load. Alkali treated SCBP nano composite have better properties than the untreated nano composite. In the case of silane treated nano composite, a similar trend is shown as the hardness keep increasing with increase in fiber loading with the value of 21.4 HV for 5wt%, 28.46 HV for 10wt%, 37.86 HV for 15wt%, 53.16 HV and 54.43 HV for 20wt% and 25wt% respectively. Silane treated nano composite shows better properties than the untreated nano composite at 5%, 10% and 15% fiber loading. But at 25% fiber loading, the untreated appears to have higher fiber loading than the silane nano composite. Alkali treated have higher hardness strength than both the silane and the untreated SCBP nano composite. The mechanical characteristics of polypropylene Bagasse fiber composite was studied by subramonion *et al.* (2016). The result shows that hardness of the fabricated composite was found to be increasing with increase in fiber loading. Chemical treatment on natural fiber disrupt hydrogen bonding withing the cellulose structure which rendered the filler more hydrophobic. This chemical modification promotes mechanical interlocking between fiber and the matrix thus increasing hardness of the composite. From the result in can be deduced that increase in fiber loading for the chemically treated increases the hardness more than the untreated composite. (Anike *et al.,* 2014).

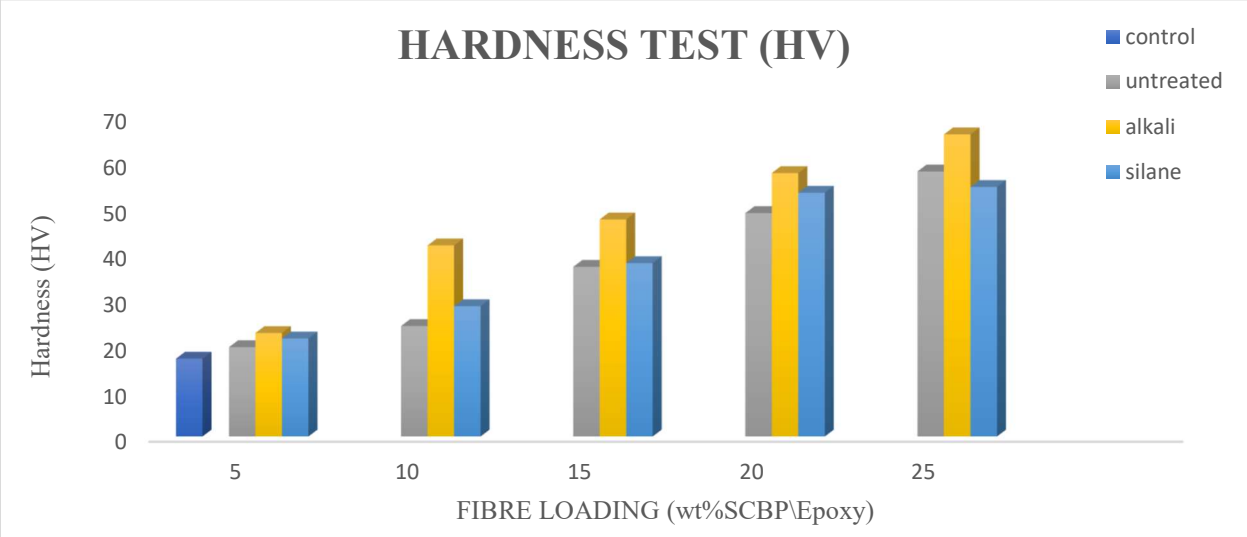


FIGURE 9: HARDNESS PROFILE OF SCBP\EPOXY NANO COMPOSITES

CONCLUSION

The mechanical properties of SCBP\Epoxy resin nano composites for the untreated, Alkali and Silane treatment at different formulations was carried out successfully and the following conclusions were made:

i. The tensile properties of SCBP\Epoxy resin nano composites increase with increase in fiber loading for both the untreated, alkali and silane treated composites up to 15wt%, beyond which it decreases because the matrix have become saturated. Silane treated composites have better tensile strength than the corresponding alkali and untreated composites.

ii. Flexural property of the composites for both the alkali and silane treated showed better bending strength than untreated SCBP\epoxy composite. Silane treated composites have highest impact strength than alkali and the untreated, all of which increases as the fiber loading increase. Hardness follows the same trend as the impact test but alkali treated composite have the highest value than the silane and the untreated.

iii. Despite its significant importance, silane treatment is very costly and that made it less useful as compared with the alkali treatment of the SCBP/Epoxy nano composite.

RECOMMENDATIONS

To further this research work and utilize Sugarcane bagasse powder better, the following recommendations are made:

i. The potential of sugarcane bagasse as reinforcement in another matrix should be investigated.

ii. Other chemical modifications of the sugarcane bagasse powder should be studied on the epoxy resin matrix and another polymer matrix. Examples of chemical treatments include Acetylation, benzoylation, maleated coupling agent to mention a few.

iii. Other characterization such as creep test to show its ability under constant stress, wear test to measure the changes caused by friction, Time temperature superposition, chemical resistance test to study its resistance to Strong acid and bases, thermogravimetric analysis should be carried out to study the longtime performance of the composites.

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NJPST Volume 20(1), 2025 ISSN: 1119 - 4111 Mohammed et al.
Nigerian Journal of Polymer Science and Technology, 2025, Vol. 20(1) pp44-55

Received on: 13/09/2024 Revised on: 09/10/2024 Accepted: 12/02/2025

PRODUCTION AND INVESTIGATION OF PHYSICAL AND TENSILE PROPERTIES OF WASTE POLYETHYLENE – BAOBAB FRUIT SHELL POWDER COMPOSITE

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ABSTRACT
In this study, the physical and tensile properties of the Waste polyethylene-baobab fruit shell composite were investigated. The highest and the lowest water absorption capacity of the samples were observed to be 12.24 % at 30 wt% and 0.02 % at 0 wt% respectively. the lowest density value (930 kgm^{-3}) at 0 wt% BFS and the highest value (1110 kgm^{-3}) at 30 wt% BFS. The tensile properties showed lowest value of Tensile strength of 10.722 MPa at 0 wt% BFS and increased to highest value (13.827) MPa at 15 wt% BFS, Tensile modulus from 0.871 GPa at 15 wt% BFS to highest value of 1.448 GPa at 30 wt% BFS. Elongation at break were 15.153% at 15wt% BFS and 8.404% 30wt% being the lowest and largest values respectively. The morphology and dispersion of the composites revealed poor filler dispersion.

Keywords: Tensile properties, waste polyethylene, baobab fruit shell powder and composite

1.0 INTRODUCTION

In the world today the need for the development of new products with more efficient material is very important. This makes composites play a major role considering their composition (Santhosh *et al.,* 2014). They consist of reinforcement embedded in a matrix, mixed and bonded together on a macroscopic scale (Shubhra and Alam 2013). This excellent combination gives improved properties which cannot be obtained with any single material (Mallik *et al.,* 2015). Composites made from polymeric materials are gaining dominance as important substitute for metals in various industrial applications such as automotive, marine, sporting goods, aerospace, electronics and construction industries due to their significant properties such as light weight and corrosion resistance (Almaadeed *et al.,* 2013). Particulate reinforced composites have high thermal conductivity and are isotopic in nature. Fillers in particulate composites can be glass, carbon, aramid etc (Vijay *et al.,* 2017).

The distribution of Baobab Trees (Adansonia digitata L.) across Southern Africa is estimated to be about 28 million trees. This gives an annual yield of 673,000 tons of whole baobab fruit and 108,000 tons of baobab fruit pulp powder. An average mature baobab fruit produces about 200 kg of fruit per season. The fruit shell of baobab tree hangs singly on long stalks with ovoid, woody and indehiscent shell 20 to 30cm long and up to 10cm in diameter. The shell contains numerous hard brownish seeds, round or ovoid up to 15mm long which are embedded in a yellowish-white floury acidic pulp. The ripe fruit pulp appeared as naturally dehydrated, powdery whitish colored with slightly acidulous taste mostly use as food and drinks. There is presently less economic importance attached to the shells, they are often discarded abundantly, thereby littering the environment (Kmatou, 2011).

Musa *et al,* (2018) studied the mechanical properties of a composite produced from Recycled Low Density Polyethylene (RLDPE) with sawdust powder filler. The study reported an increase in hardness with increase in filler loading, while the impact strength and compression strength decrease with filler loading. Ashish *et al,* (2022) investigated the properties of composite developed from silica sand and recycled thermoplastics The maximum compressive and flexural strength were found to be 46.20 N/mm^2 and

6.24N/mm^2 with minimum water absorption and sliding wear rate of 0.039% and 0.413 × 10^{-8}kg/m respectively. The hardness of a composite developed from High density Polyethylene and low Density polyethylene and sand particles at %0wt% LPE, 20wt%HDPE and 30wt% sand particles is 37.0 HV. Negasi *et al,* (2020) investigated the properties of developed recycled Low Density Polyethylene reinforced with Pineapple Leaf Fiber (PALF) composite. The result showed an increase in tensile, impact and flexural strength to the optimal level of 30% fiber weight. The water absorption increased with increase PALF weight. Alexander *et al,* (2022) investigated the mechanical properties of Recycled Low Density Polyethylene (RLDPE) filled with sawdust powder. The study reported an increase in hardness with increase in filler loading, while the impact strength and compression strength decrease with filler loading. Pankaj (2022) conducted a study on development of sand-plastic composites using silica sand and recycled thermoplastics mixture from post-consumer products. The developed composite was characterized for water absorption compressive strength, flexural strength and sliding wear. The maximum compressive and flexural strength obtained were 46.20 N/mm^2 and 6.24 N/mm^2 respectively while the minimum water absorption (%) and wear rate were found to be 0.039 and 0.143×10^{-8} kg/m respectively. Athanas (2011) investigate the use of plastic waste as binding material in the development of composite using sand particles as reinforcement. It was found composite produced using plastic waste has porosity value less than 5% while that of micro-concrete is more than 10% and with more abrasion resistance when compared to other composite. Omosebi and Abbas, (2021) conducted a study on a composite produced from recycled pet bottles wastes with improved strength and reduced flammability. The highest compressive strength was at 30wt% and 70wt% respectively is 6.88MPa.

Polyethylene is commonly used in food packaging. It is a popular synthetic polymer with huge hydrophobicity and molecular weight. Since polyethylene is not biodegradable, using it for the production of disposal or packing materials causes many problems, the main problem being environmental pollution and land shortage problems for landfills (Temitope *et al.,* 2022).

Findings from this work indicate that valorisation of LDPE waste sachet baobab fruit shells can be a value-addition, affordable waste management method for producing biocomposites towards building applications. The baobab tree, also known as the tree of life is a common tree found in northern Nigeria, and widely used as food, medicine and shelter. Its fruit shells are waste products of many local industries. In some part of northern Nigeria such as Borno State baobab fruit shells are discarded or used as fodder for domestic farm animals. In Nigeria, baobab fruit shells are abundant in the Northern region and serve as a source of income for farmers. Despite the abundance of fruit shell, their use as fillers in composites has not been widely published. Therefore, fruit shells as bio-filler can add value to it.

2.0 MATERIALS AND METHODS

2.1 Materials

Baobab fruit shell and waste polyethylene weighted about 5.0 and 7.0 kg respectively, were sourced from Mayo-Belwa local government area, Adamawa state, Nigeria.

2.2 Methods

The Baobab fruit shell and waste polyethylene were manually washed using tap water to remove dust, dirt and sand particles, air dried. The baobab fruit shell was ground into powder using grinding machine and sieved to 250µm using standard test sieve to obtain finer and uniform particle size while the polyethylene waste broken into smaller pieces using knife.

Fabrication of the composites was carried out by compounding and compression moulding techniques at 20 % filler loading using two rolls mill and compression moulding machines. A steel mould of 150 × 120 × 5 mm was used. The control sample was the unfilled waste polypropylene. The matrix and filler were mixed for 5 min in two rolls mill to achieve a homogenous mixture. The mixture was placed in the mould treated with releasing agent. The maximum pressing temperature, pressure, time and cold pressing or pressure holding time were 160 ^{0}C, 5 N/mm2, 15 min and 5 min respectively (Lawal *et al*., 2023). After cooling, the composite was removed and conditioned in an oven at 70 ^{0}C for 48 hr before testing.

Table 1. Formulation of wPE / BFS Composites

Sample ID	A	B	C	D	E	F	G
wPE wt%	100	95	90	85	80	75	70
BFS wt%	0	5	10	15	20	25	30

2.3 Physical Properties

2.3.1 Water Absorption Test

The test was conducted in accordance with ASTM D570-98, in which the specimens were immersed in water for 24 h at a temperature 23 ± 1°C, then for another 24 h until no further weight gain is noticed. The weight gain was then measured using Sartorius MC201P high sensitivity balance 20 min after being removed from the water, for each immersion. The mass of water absorbed was calculated from the following equation:

$$M_{wabs} = M_{avf} - M_{avi} \ldots\ldots\ldots\ldots\ldots\ldots 2.1$$

Where: M_{wabs} *is the mass of water absorbed*

M_{avf} *is the average final mass after immersion*

M_{avi} *is the average initial mass before immersion*

The percentage water absorbed is given by the equation:

$$\%M_{wabs} = \frac{(M_{avf} - M_{avi})}{M_{avi}} \ldots\ldots\ldots\ldots\ldots 2.2$$

2.3.2 Density Determination

The density of the composite was determined in accordance with ASTM standard D 792-13 (Method A) by using a Sartorius MC201P high sensitivity balance. Before the Measurements, all samples were dried at 50 °C for 18 hours. The specimens were weighed in air using the balance with a precision of 0.1 mg after which were weighed when immersed in distilled water at 21°C using a sinker and wire to hold the specimen completely submerged as required. Precautions were taken to ensure that no air bubbles were trapped prior to taking the reading. The averages of samples taken were calculated as composite density. The following equations were used to identify the specific gravity and density of the BFS/ rPE composites.

$$\boldsymbol{Sg^{21^{\circ}C}} = a/(a + W - b) \ldots\ldots\ldots\ldots\ldots 2.3$$

Where: $Sg^{21^{\circ}C}$ is specific gravity of the composites at 21^0C; a is the mass of specimen, without sinker, in air; b is the mass of specimen and sinker completely immersed and of the wire partially immersed in gas-free distilled water at 21^0C; W is the mass of totally immersed sinker and partially immersed wire.

$$\boldsymbol{D^{21^{\circ}C}} = \boldsymbol{Sg^{21^{\circ}C}} \times \mathbf{0.99799} \ldots\ldots\ldots \mathbf{2.4}$$

Where: $D^{21^{\circ}C}$ is the density of the composites at 21^0C; 0.99799 g/cm^3 is density of the water at 21^0C.

2.4 Tensile Properties

2.4.1 Tensile Test

Tensile strength is a measurement of the ability of a material to withstand forces that tend to pull or stretch it apart before breaking. The aim of the experiment was to determine the values of tensile modulus, percentage elongation and maximum tensile strength of the composite material. The test was conducted as per ASTM D3039 (ASTM 2014) using specimen of dumbbell shape with a width of 10mm, length of 100mm and thickness of 3mm. Two fine marks were made on the samples with distance of 40mm apart as the gauge length. The sample was mounted on the tensometer. It was ensured that the ends of the test piece were fitted into the grip of the tensometer. The grip was held between the tension head and operating screw. The load was applied gradually by turning the operating handle. The force applied to the specimen was transmitted to the chart roller which is attached

to a graph paper. Turning of the operating handle leads to gradual increase of the load at the middle span until fracture occur. The test was carried out at turning speed of 50 mm/min. The force and extension was obtained from the load and extension curve from the graph paper. Two specimens from each composition of were used.

2.4.2 Morphological Properties

To study the morphological properties of baobab fruit shell powder / waste polyethylene composites**,** tensile fractured specimens were viewed using scanning electron microscope (SEM), PHENOM PRO X (Phenomworld, Eindhoven, Netherlands) (ASTM E986-04 2017). The sample with appropriate size was fitted in the specimen compartment, mounted and clipped on a holder. Before observation, the sample was made to be electrically conductive by coating it with platinum. This was achieved with a gold–palladium alloy in an argon-inert environment.

3.0 RESULTS AND DISCUSSION

3.1 Water Absorption

The effects of filler loading on water absorption property for recycled Polyethylene-Baobab shell composites for 504hrs immersion are showed in Figure 4.1. The absorption of water is an important parameter while working with cellulose-based fillers, because high humidity worsens the mechanical properties of the material and change the dimensions. The effect of water absorption is an important consideration where the material has been designed for applications in contact with water. From the results the ability of the composites to absorb water after exposure at ambient temperature was studied during (504Hours) twenty-one days. The results revealed that percentage (%) water absorption of recycled Polyethylene-Baobab shell composites increased with increase in BFS filler content. This increase is attributed to the water ability to saturate the surface of the material and diffused into the core of the material with the help of non-fully embedded hydrophilic filler. The highest water absorbed by the composite is 12.24%. The maximum water absorption of floor tile composite developed from recycled PET reinforced with natural fiber at 30wt% and 70wt% respectively is 0.98% (Omosebi and Abbas, 2021). Figure 4.1 shows the amount of water absorbed by the composites increased with increase in the Baobab shell powder content in the composites. This is in agreement with results of similar works by Danladi and Tunde (2013). This property is due an increase in the amount of hydrophilic filler in the composites. This is attributed to hydrophilic nature of the Baobab shell particles (BSP) capable of absorbing water, this is to say that the higher the filler loading the higher the water absorption. Similar trend was observed by Shehu *et al.,* (2019.

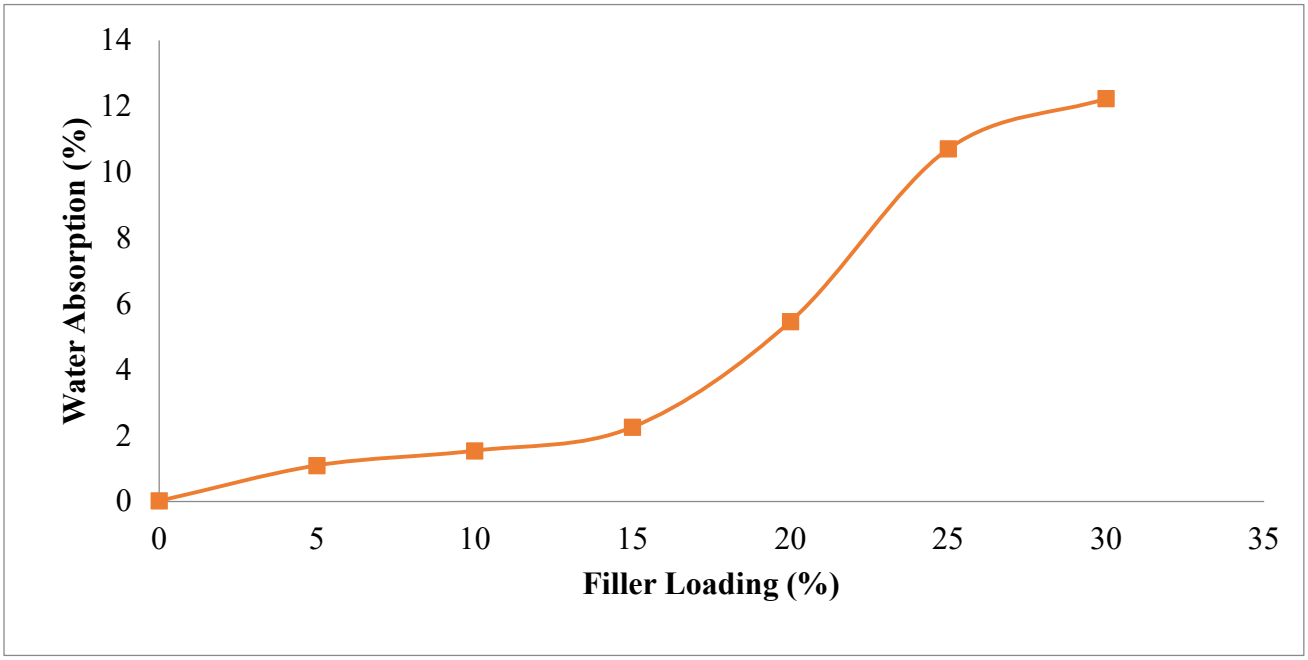

Figure 3.1: Water Absorption versus filler loading (%) for Polyethylene waste / Baobab shell Powder Composites

3.2 Density

The results obtained during this research work on the density of recycled Polyethylene-Baobab shell composites are shown in Figure 4.2. From the graph obtained, it is shown that the density of the composites increased with increase in Baobab shell particles. This behavior was due to the introduction of Baobab shell fillers into the Polyethylene matrix. Incorporation of Baobab shell particles with mass per unit volume of 0.45 gcm^3 into Polyethylene matrix with density of 0.940 gcm^3 which explained why as the filler content increases the density of the composites increased. These findings are in line with the results obtained by Chandrasekar *et al.,* (2023). The highest density values were seen at 30% with 1.11 g/cm^3 while the lowest were observed at 5% with 0.93 g/cm^3. Neat polymer (0%) showed higher density values at 0.94 g/cm^3 than 5wt% with 0.93 g/cm^3 due to the introduction of fillers into the matrix which may cause air to be trapped in the material causing micro voids in the composites which has adverse effect on the properties of composites hence, reduce the density of the material. The highest density of floor tile composite developed from recycled PET reinforced with natural fiber at 30wt% and 70wt% is 1.688 gcm^{-3} (Omosebi and Abbas, 2021).

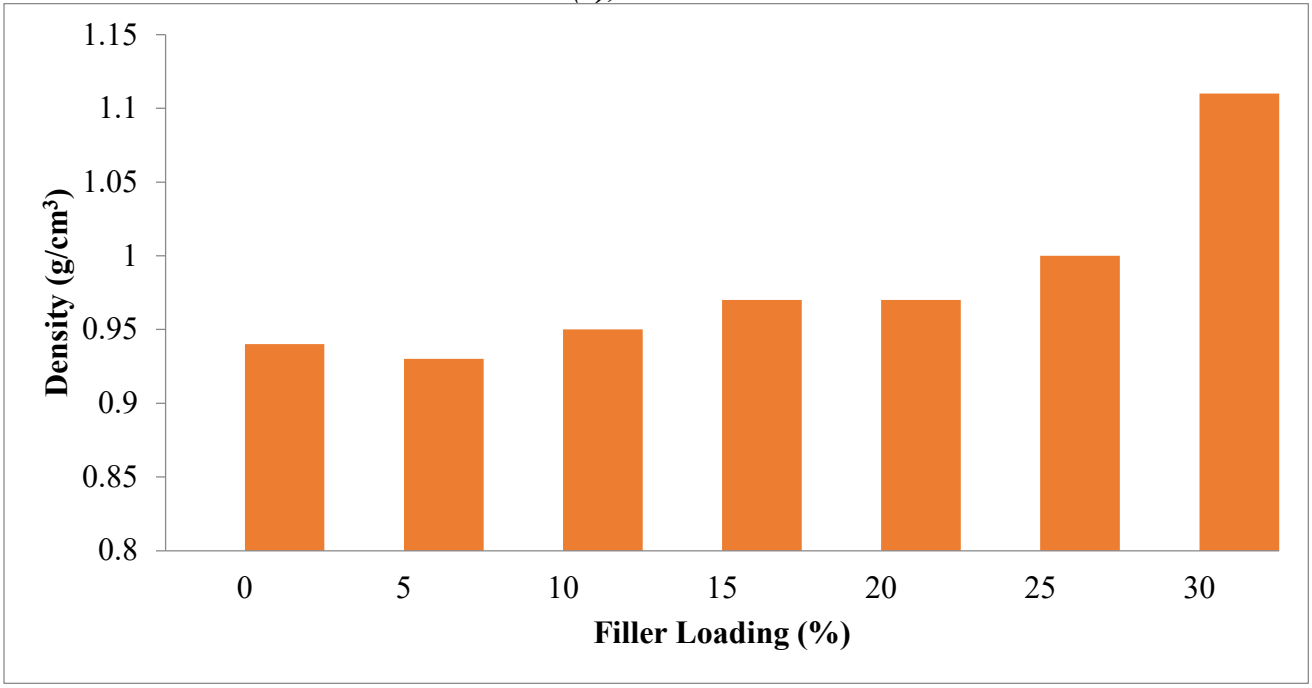

Figure 3.2: Density versus filler loading (%) for waste Polyethylene / Baobab shell Powder Composites

3.3 Tensile Strength

The effects of filler loading on tensile strength of Polyethylene Waste-Baobab shell composites were studied and depicted in Figure 4.1. It was observed that the tensile strength increased from 10.798 MPa to 13.822 MPa for 5% and 15% filler loading respectively. The increase in tensile strength is attributed to better interfacial adhesion between the filler and the matrix as a result of good wettability of the filler particles by the polymer matrix. Maryann *et al.,* (2020) reported that there was an increased tensile strength of the unfilled epoxy (sample A; 0 wt%) from 33 to 48 MPa with the inclusion of 10 wt% fibre into the epoxy matrix. This could be attributed to the ability of the matrix to wet the filler at low concentration. However, at higher filler loading above 15 wt% the tensile strength decreased significantly and remained steady up to 40%. Unfilled polymer (0%) showed lower tensile strength at 10.722 MPa compared to 5% and 15% filler loading due to ability of the Baobab shell particles to support stress transfer from the matrix. Sudden decreased can be seen with increase in filler loading from 15% to 30% filler loading. This decrease is attributed to weak interfacial adhesion between the Polyethylene Waste and Baobab shell particles as a result of poor wettability. As the filler loading increased the wettability decreased and the matrix begin to lose its binding ability which in turn reduced filler / matrix interfacial interaction therefore caused the tensile strength to decrease. An increase in filler loading leads to the reduction in tensile strength because of uneven distribution of Baobab shell particles in the matrix. This adversely affects the stress transfer from the matrix to the filler. This was also reported by researchers such as Musa *et al.,* (2019), Danladi *et al.,* (2017).

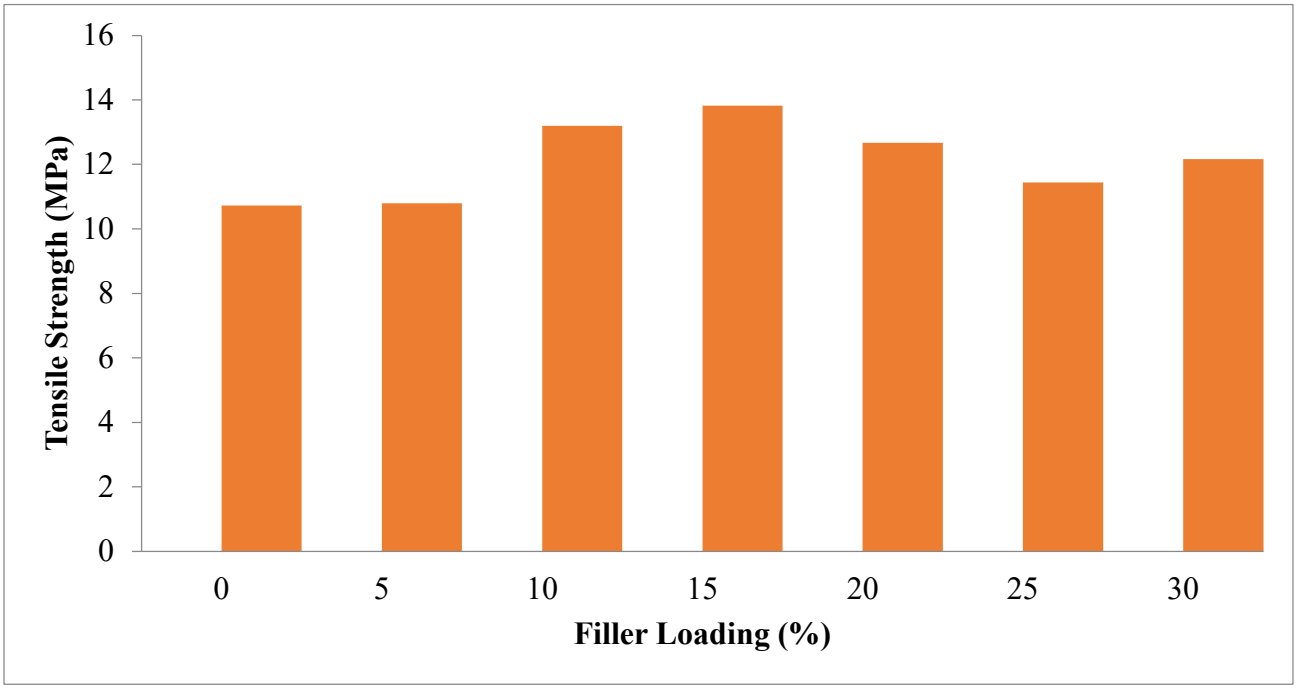

Figure 3.3: Tensile Strength versus filler loading (%) for waste Polyethylene / Baobab shell Powder Composites

3.4 Elongation at Break

The effect of filler loading on elongation at break of Polyethylene Waste-Baobab shell composites are given in Figure 4.2. The elongation at break of the composites increased with increase in filler loading from 9.387% at 0 wt% BFS to 15.153% at 15wt% BFS, thereafter a significant decrease was observed from 10.425% and 8.404% at 25wt% and 30wt% BFS respectively. This observation highlights the fact that the incorporation of much filler into polymer matrix improves the stiffness of the composites thus reducing toughness, that is to say the addition of the rigid filler decreased the ductility of the polymer matrix. This is because of the reduction in the bond strength at the filler / matrix interface. Similar trend has been reported by other researchers such as Muktari *et al*., (2019). He found out that incorporation of rigid filler into the polymer matrix decreased the flexibility of low-density polyethylene. From Figure 4.2 it can be seen that 20% filler loading had lower tensile strength of 9.566 MPa than 25% filler loading with 10.425 MPa. This could be due to voids formation during processing. Furthermore, incorporation of more filler into the polymer matrix reduced its molecular chain mobility leading to a decrease in elongation at break.

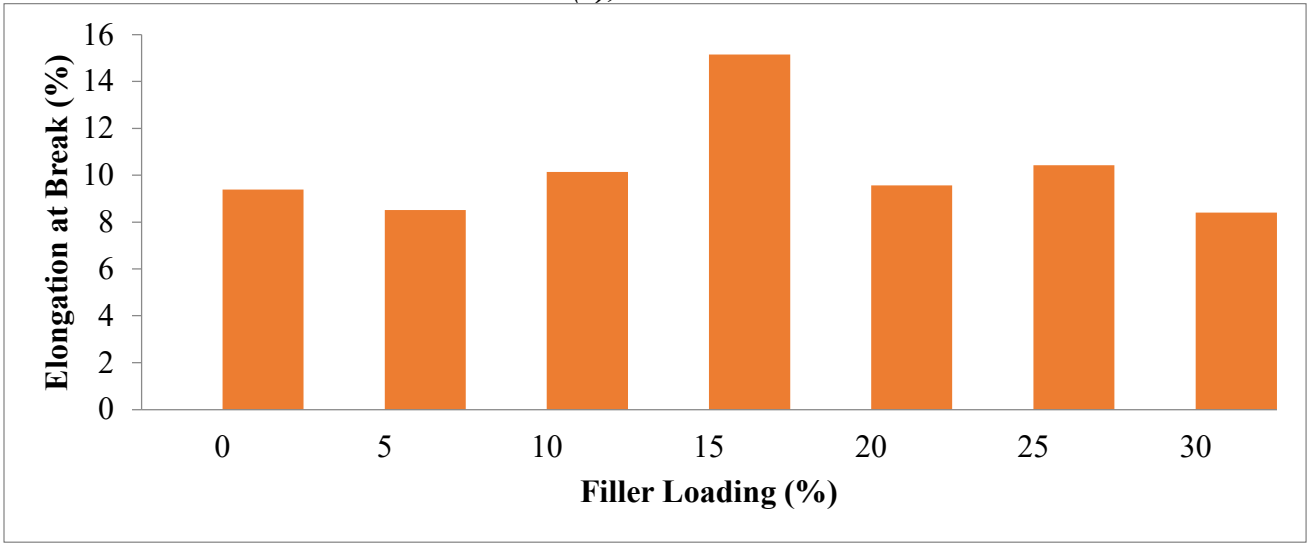

Figure 3.4: Elongation at Break versus filler loading (%) for waste Polyethylene / Baobab shell Powder Composites

3.5 Tensile Modulus

The results of tensile modulus of Polyethylene Waste-Baobab shell composites are presented in Figure 4.3. From the results a progressive increase was observed from 0% to 30% filler loading. This behaviour is due to an increase in stiffness of the material as a result of restriction or reduction in polymer molecular chain mobility which improved the material's rigidity. The incorporation of the Baobab shell particles into the matrix attributed to the stiffening effect and rigidity to the composites. The lowest tensile modulus was seen at 15% and 25% filler loading with 0.871 GPa and 1.097 GPa respectively. The deviation from this linearity as noticed from decline in 15%, and 25% is believed to have occasioned by initial matrix cracking and the end of the curve represents the ultimate stress which may have been as a result of agglomeration of Baobab shell particles within the Polyethylene matrix. Similar event was observed by Adekomaya and Adama, (2017).

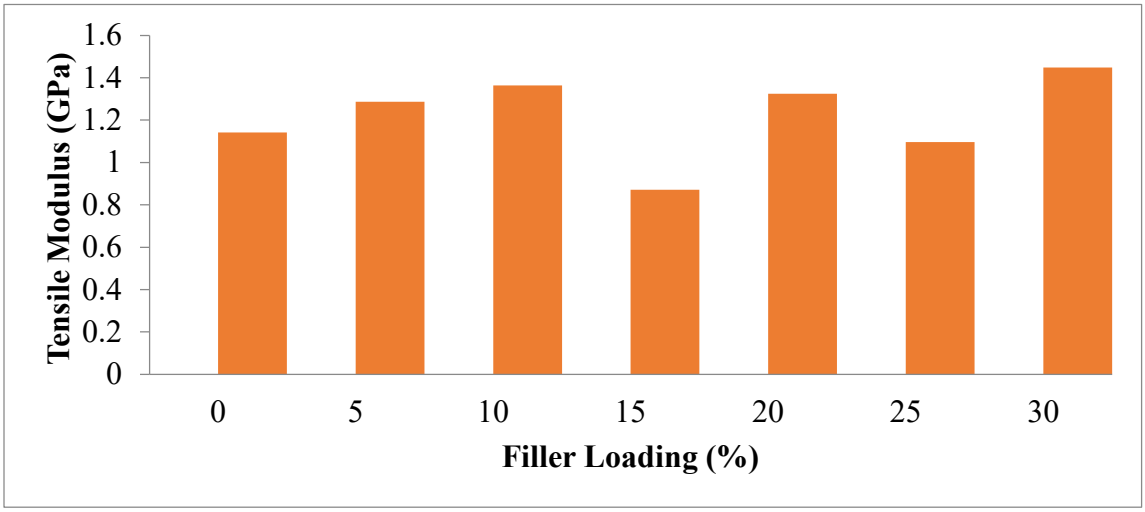

Figure 3.5: Tensile Modulus versus filler loading (%) for waste Polyethylene / Baobab shell Powder Composites

3.6 Morphological Properties

The effect of Polyethylene Waste-Baobab shell particles interaction was investigated using scanning electron microscopy (SEM) PHENOM PRO X (Phenomworld, Eindhoven, Netherlands) as shown in Plates I and II. 15% and 30% BFS samples were considered for microstructural analysis was due the best properties they shown. SEM micrograph of 15% Polyethylene Waste-Baobab shell composites depicted in Plate I showed better dispersion of filler particles within the polymer matrix structure. This is the reason for higher strength of mechanical properties such as hardness and compressive strength. From Plate I few agglomerations and crack was seen due to increase in the filler particles concentration within the polymer matrix, attributed to the low impact strength. Plate II shows more agglomerated filler particles and voids at 30% BFS loading compared to Plate I at 15% BFS loading. This is due to higher BFS particles concentration incorporated into the matrix leading to poor filler / matrix interaction as a result of difficulties associated with the dispersion of high filler content within the matrix. Wettability is always difficult at higher filler loading leading to poor / weak interfacial bonding between the filler and the matrix which caused the formation of voids during processing. Some authors (Ranganna *et al.* 2012) have reported that the development of voids in any composite is an indication of poor interfacial bond between the fiber and the matrix.

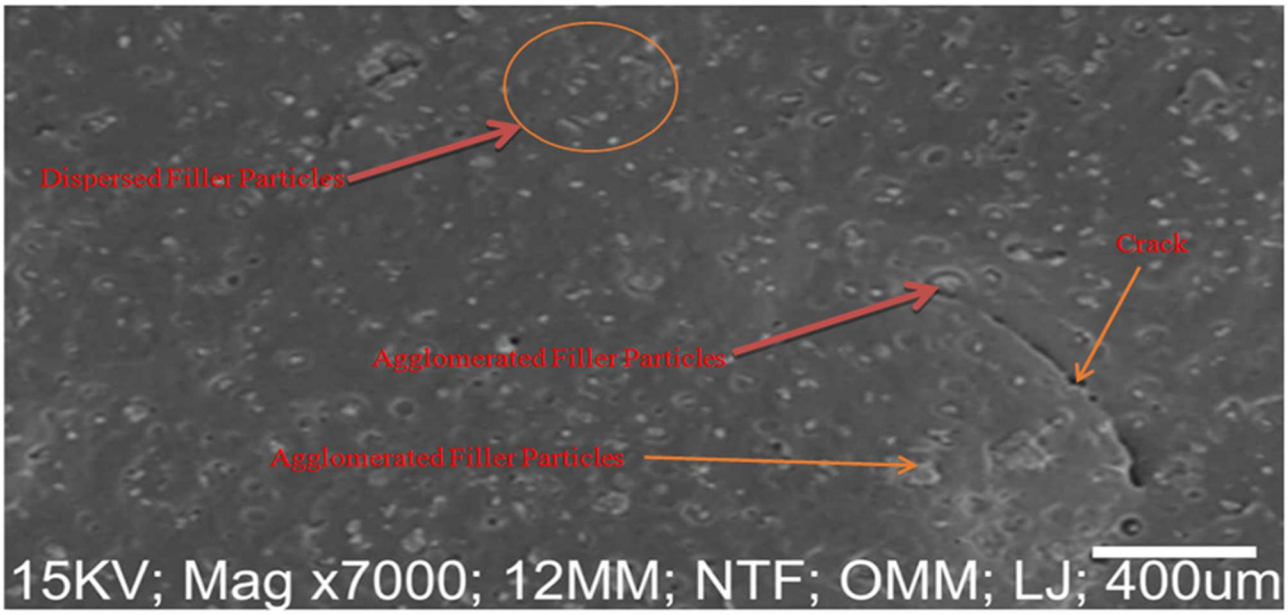

Plate I: SEM Micrograph of 15% Polyethylene Waste - Baobab Shell powder Composite

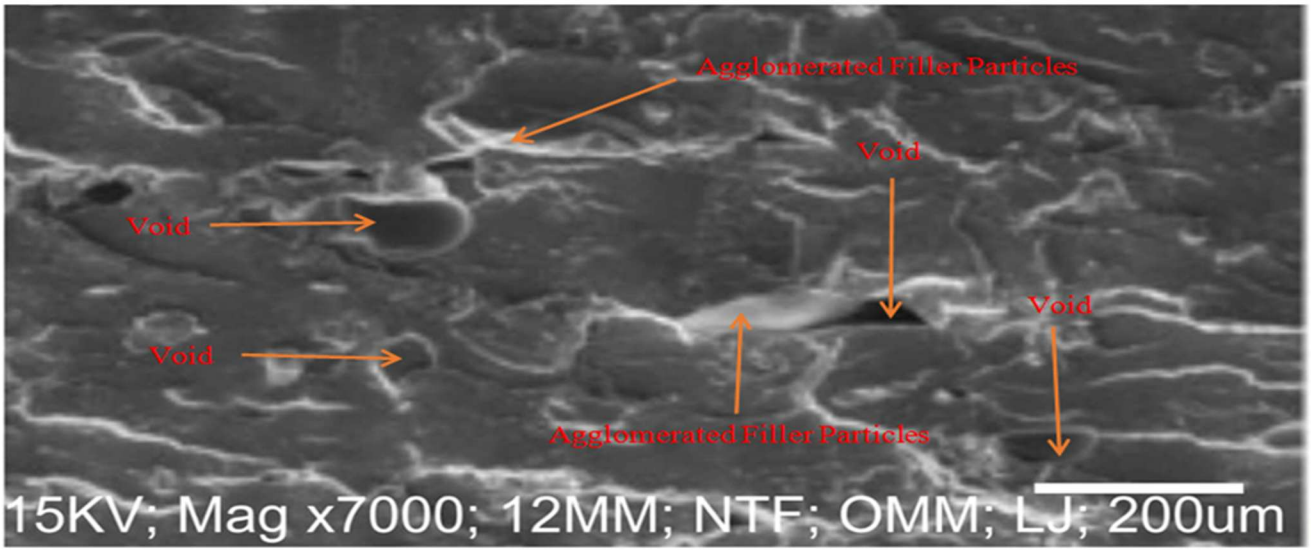

Plate I: SEM Micrograph of 30% Polyethylene Waste - Baobab Shell powder Composite

Conclusion

In this research, baobab powder was mixed with polyethylene waste at seven different ratios for the development of baobab polyethylene waste composites. Physical and tensile properties were investigated using ATSM standards. It was established that the addition of baobab filler in to polyethylene waste increased properties of the composite such as water absorption, density, tensile strength, tensile modulus and a decrease in elongation at break. Water absorption was increased to 12.24 % from 0.02 %. and the density value from 930 kgm^{-3} to 1110 kgm^{-3}. The tensile properties showed an increase of Tensile strength from 10.722 MPa to 13.827 MPa, Tensile modulus from 0.871 GPa to 1.448 GPa. Elongation at break was reduced from 15.153% to 8.404%.

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Nigerian Journal of Polymer Science and Technology, 2025, Vol. 20(1), pp56-63

Received on: 20/11/2024 Revised on: 03/01/2025 Accepted: 10/02/2025

THE STUDY OF POLYLACTIC ACID AND NANOCLAY ON THE DEGRADATION PROPERTIES OF LOW-DENSITY POLYETHYLENE COMPOSITES.

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ABSTRACT

A study was carried out to check the effect of using polylactic acid, Nano clay and glycerine as compatibilizer on the degradation property of virgin and waste low density Polyethylene which is the major component used in producing polyethylene bag. Virgin and waste samples of polyethylene, polylactic acid and Nano clay were obtained locally and compounded using the two-roll mix and the compression moulding machine to produce the composites. Moulded samples produced were cut accordingly using ASTM specification for the tests. Tests carried out included tensile, flexural, hardness, impact, water absorption, soil burial test. Results showed improved tensile, flexural, hardness strength as compared to the control sample (100% Virgin Polyethylene). The addition of polylactic acid, Nano clay and glycerine showed good interfacial bonding between the matrix and the fillers which improved the mechanical properties, water absorption and aided degradation during soil burial test. As the amount of filler content increased it affected the impact test due to the brittle nature of both Nano clay and polylactic acid.

Keywords: *Low density polyethylene, Nano clay, polylactic acid, glycerine, degradation. physio-mechanical properties*.

INTRODUCTION

Poly(lactide) (PLA) has unique properties like good appearance, high mechanical strength, and low toxicity; and good barrier properties have broadened its applications. Numerous researchers have studied the different properties of PLA alone and in combination with other polymers as blend or copolymer. The studied carried out by Auras and others (2004) on the mechanical, physical, and barrier properties of PLA films. These two films were compared with polystyrene and polyethylene terephthalate (PET). Low glass transition temperature of PLA limits its usages in thermally processed packages. Because of its deformation and it slow melting temperature, it is better to use it for heat-sealing and thermoforming applications.

PLA films have good tensile strength with higher values than polystyrene but lower than PET had lower Tm (melting point) and T_g (glass transition temperature) than PET which makes PLA better for heat-sealing and thermal processing. In terms of barrier properties of PLA, the permeability coefficients of CO_2 and O_2 were lower than those of PS and comparable to those of PET. For tensile modulus and flexural modulus, PLA has the highest value in comparison to PS, PP, and HDPE (Mbuge, 2017). The disposal problem due to non-

degradable petroleum based plastics has raised the demand for biodegradable polymers as means of reducing the environmental impact. PLA is useful for producing loose-fill packaging, compost bags, food packaging, and disposable tableware. Due to its bio-compatibility and biodegradability, PLA has also found ample interest as a polymeric scaffold for drug delivery purposes (Nicolas, 2019).

Polyethylene, with the chemical formula $[-CH_2-CH_2-]_n$ (where n denotes that the chemical formula inside the brackets repeats itself to form the plastic molecule) is made in low- and high-density forms. Low-density polyethylene (LDPE) has a density ranging from 0.91 to 0.93 g/cm^3. Polyethylene products are very common in our daily life. For examples, food and pharmaceutical packaging film, wire and cable insulation and pipe. Therefore, the production of polyethylene is humongous as is one of the most popular used polymer materials in day-to-day life. Polyethylene and polypropylene represent about 92% of the synthetic plastics produced, and they are used for production of plastic bags, disposable containers, bottles, packaging materials, etc. (Ploypetchara, 2014). An estimated more than 500 billion to 1 trillion plastic bags used globally disturb the eco-system and ultimately result into serious environmental issues of recycling these materials from the environment. The waste plastics that form particulate matter by UV irradiation and weathering increase surface area and mobility and thereby incorporate easily into the food chain, causing fatal injuries to all living organisms. The long-range structure and morphology of polyethylene have shown important roles, with amorphous regions being more prone to microbial attack than crystalline ones. This review focuses on the recent hypotheses and experimental findings regarding the biodegradation of polyethylene. (Li, 2018). The poly(lactic acid) or PLA is promoted as the environmental friendly material. Because of its property as a biodegradable plastics, PLA is designed to be used in applications such as medical devices, agricultural tools as well as packaging materials (Gupta and Kumar, 2007; Sin et al., 2013). The good degradation rates of PLA was found at/or above glass transition temperature (Tg ~55-60°C).

The use of nanoclays in food packaging has become of interest due to their importance in improving mechanical properties and barrier properties (Chaudhary, 2020). Further, nanoclay is abundant, cost-effective, and biocompatible with a diverse morphology and multiple chemical compositions, making it more important over other nanomaterials used in the advancement of materials science and technology.

Nanoclays are layered silicates with single layer of 0.7 nm thickness, while double layer is 1 nm thick. The interlayer can be modified using surfactants to improve the plasticity and swelling capacity. Surface properties of nanoclays depend on nanosheet charge, nature of surface atoms, and interlayer exchangeable cations. The surface of nanoclay is negatively charged owing to the substitution of Al^{+3} or

Mg^{+2} ions with silicon (Abulyazied, 2021).

MATERIALS AND METHODS

Virgin Low Density Polyethylene (Albarka Plastic, Kaduna), waste low density polyethylene (water satchet bags) from Kaduna Polytechnic, Kaduna, Polylactic Acid (JHD, China), nano clay (NILEST, Zaria), Glycerine (J. Chemicals limited Kaduna.)

Two roll mill (model: 5183 North Bergen U.S.A), Wenzhouzhiguang Compression Moulding Machine (model: 0557), Hounds Field Tensometer (model: W6466), Izod Impact tester model : 6757 pianezz-terino Italy), Vickers hardness testing machine (Model : MV1-PC), Analytical Digital Weighing Balance.

Samples Preparation

Using the formulation table below, six composites were produced using the two rolls mill machine in counter clockwise motion for a period of 5 minutes at a temperature of 170°C, upon achieving a band and bank formation of the LDPE on the front roll, polylactic acid was introduced and allowed to mix for 3 minutes with effective cross mixing. Nanoclay was added gradually to the band, cross mixed and allowed to mix for 3 minutes, then glycerine (plasticizer) was added onto the band. The composites sheet were labelled accordingly. The composites samples obtained from the mixing were placed in metal molds and then onto the compression molding machine for shaping at temperature of 150°C and pressure of 25 bar for 5mins with a dimension of 120mm x100mm x 3.2mm followed by cutting and preparation for further testing according to the ASTM standards for testing.

Table 1: Formulation and composition of LDPE/PLA/Clay composites

Sample	Low Density (LDPE) (g)	Polylactic Acid (g)	Nano	Glycerin (ml)
A	100	-	-	-
B	90	5	5	5
C	80	5	10	5
D	70	5	15	5
E	60	5	20	5
F	50	5	25	5

Methods

Determination of mechanical properties.

Tensile test

The tensile strength test was carried out using the Monsanto Tensometer (model no: W6466) according to ASTM D-638. A dumbbell shaped samples with gauge dimensions 50 mm x 10 mm x 3.2 mm were subjected to a tensile force and tensile properties such as tensile strength, Strain, modulus for each sample.

Flexural test

The flexural strength test on the blends was carried out in accordance with ASTM D-790. The specimen measuring 100 mm x 25 mm x 3.2mm was placed on a support span horizontally at 80 mm gauge length and a steady load was applied to the centre by the loading nose producing three-point bending until the sample specimen failed. The maximum load (N) and the corresponding deflection (mm) were recorded accordingly as the sample specimen failed. The flexural strength and flexural modulus were calculated

Impact test

The impact test was carried out according to the standard specified ASTM D-156; the specimen was cut to specimen dimension 64 mm x12.7 mm x 3.2mm and 45° notched was inserted at the middle of the test specimens from all the produced blend samples. The impact energy test was carried out using Izod Impact Tester (Resil impactor testing machine). The specimen was clamped vertically (IZOD) on the jaw of the machine and hammer of weight 1500 N was released from an inclined angle 240°. The impact energy for corresponding tested

specimen was taken and recorded. Impact strength was calculated and recorded accordingly.

Hardness test

The hardness tests were carried out in accordance with ASTM D2240 using Vicker Microhardness Tester. The sample was placed on the mounting stage and the indenter was lower until it come in contact with the sample at uniform pressure the reading indicating resistance to indentation displayed on the machine screen and recoded accordingly. This was repeated three (3) times at different positions on the sample and average hardness was taken using equation.

Average Hardness = (1st+2nd+3rd)/3

Water Absorption Test

The water absorption test was carried out on the composites. The samples were immersed in a container filled with water and then allowed to stay for 24 hours after which it was removed from the water, a dry towel was use to dry the water and reweighed to note the final mass. This was carried out for 75 days at an interval of one week. The result obtained was been used to calculate the percentage water absorption. Using the equation

% Water absorption = (Wf-Wi)/Wi x 100/1)

Where;

Wf = Final weight of sample

Wi = Initial weight of sample before immersion in water

RESULTS

Tensile results

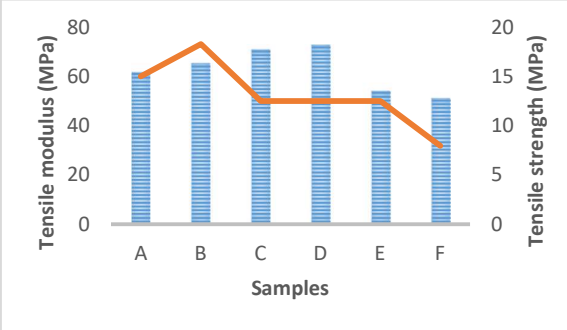

Figure 1: Result of effect of natural fillers on the tensile strength and modulus of polyethylene composite

Figure 1 showed that the control sample A had a tensile strength of 15.38MPa. Sample B had a tensile strength of 16.31 MPa. Sample C has the tensile strength of 17.66 MPa. Sample D has the highest tensile strength of 18.20 MPa. As the amount of filler content increased in sample E and F, a decrease in tensile strength was seen in sample E (13.50 MPa) and sample F has the lowest tensile strength of 12.75 MPa). Sample A tensile modulus was 60.07 MPa. From sample B to F the sample tensile modulus decreased as the amount of filler content increased. Sample F become more brittle as compared to sample B this is because more clay is in the sample hence making it more hard and brittle, the nanosheet surface is hydrophobic owing to Si–O covalent linkages. The hydrophilicity of nanoclays can be achieved using exchangeable hydrophillic cations. Nanoclay particles can absorb water and stacked silicates layers may swell. Incorporation of clay nanoparticles in polymers reveal improved mechanical, thermal, electrical, flame resistant, and gas barrier properties (Calambas, 2021). The introduction of nano clay into bio-based food packaging materials decreases the elongation at break value of the films, and thus overall elasticity of the nano composite is reduced by the inclusion of the nanomaterial. This is because nanoclay's stiffening and reinforcing properties create a network of polymeric phases and reduce the mobility of polymer chains as observed by the studies of

(Radfar, 2021).

Flexural test results

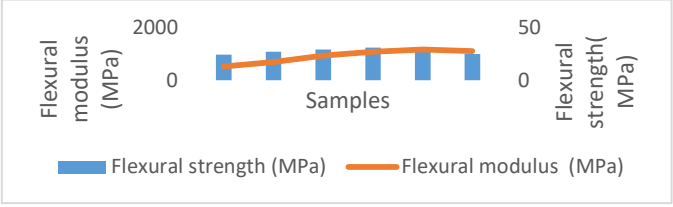

Figure 2: Result of effect of natural fillers on the flexural strength and modulus of polyethylene composite

Figure 2 showed that sample A had a flexural strength of 23.92MPa and a general increase was seen in the flexural behaviour (strength) up to sample D (30.94MPa). Sample E showed a decrease in flexural strength 27.36 MPa

followed by Sample F which had a value of 24.67 MPa. The flexural modulus for sample A was 523.776 MPa and the modulus kept increasing for sample B (692.76), C (929.67), D (1071.99) and E (1156.06). Hence the addition of nanaclay and polylactic acid increased the flexural modulus.

Impact test

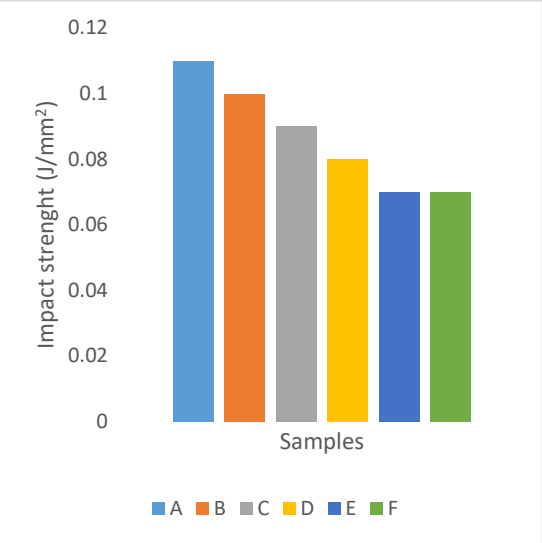

Figure 3 Result of effect of natural fillers on the impact strength of polyethylene composite

Results showed a decrease in impact strength as seen from sample A to sample F. The results revealed that as the amount of nanoclay and polylactic acid content increased, it decreased the impact strength, this could be attributed to the brittle nature of nanoclay and polylactic acid. The presences of LDPE particles between PLA chains also increased the mobility of PLA chains allowing it to deform easily (Radfar, (2020). Although the enhanced mobility of PLA chains might pass a positive effect to PLA/LDPE blends in terms of impact strength properties, but it had led to reduction of rigidity of the blends (Lu, 2005).

Hardness test

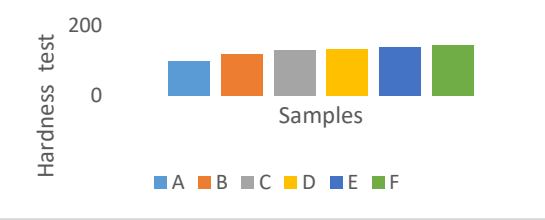

Figure 4: Result of effect of natural fillers on the hardness of polyethylene composite

Results showed an increase in the hardness of the composite. Sample A has the average hardness of 106.3 while sample F has the average hardness of 145.9. This can be attributed to the good interfacial bonding between the PE / nanoclay / Polylactic acid using glycerine as a compatabilizer. The primary purpose of incorporating a nanoparticle (reinforcement agent) into a biopolymer matrix is to improve the mechanical properties of the packaging material (Emadian, 2017).

Water absorption

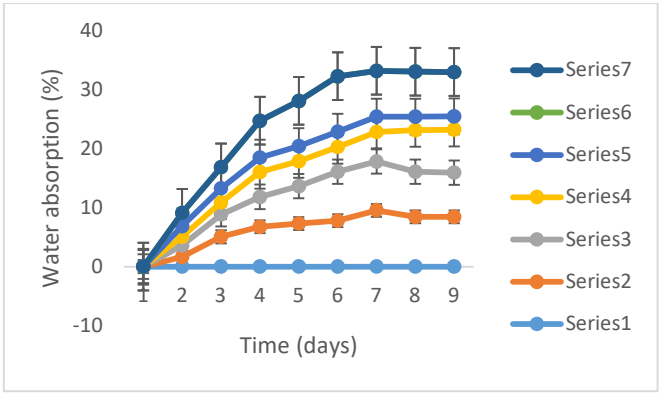

Figure 5: Result of effect of natural fillers on the water absorption properties of polyethylene composite

Results showed that all samples absorbed water every week due to the hydrophilic Polylactic acid and clay. Samples B, C, D showed maximum water absorption up to forty two days (7 week) and a decline in the water absorption rate. Sample E that contains 25% nano clay kept absorbing water even after 75 days as studied by other scholars. The water absorption capacity of nanoclays depends on the number of exchangeable cations in interlayer. PLA a biodegradable and compostable polymer was used to evaluate the biodegradable nature of nanoclay. The results of the biodegradation experiments demonstrate that the

biodegradation phase of nanoclay containing films began earlier than that of pure PLA films (Chadha, 2022). The influence of incorporation of clay nanoparticles in polymers reveal improved mechanical, thermal, electrical, flame resistant, and gas barrier properties (Abulyazied, 2021). The high surface area and nanometric size of the clays enable them to form an efficient interaction for transmitting tensile stress, nanoclays reduce the rate of biodegradation of the packaging materials. Nevertheless, most importantly, when considering the limited studies performed the migration levels of nanoclay are very low while it is non-toxic. A higher concentration of nanoclay film (1.5%) results in the production of aggregates, which degrades the mechanical characteristics.

Conclusion

1. A bio-composite was made using low density polyethylene, polylactic acid, clay as the filler and glycerine as the compatibilizer to aid the improvement of the physio-chemical properties of the composite as well as improve the degradation properties of the composite as observed in the water absorption test. The utilization of bio-nanocomposites based food novel packaging material has become of great interest in the food packaging industry, mainly due to its importance in the increment of biopolymer properties such as mechanical properties and the barrier properties of the packaging materials.
2. The results revealed that there was an increase in the tensile strength from the control sample A to sample D. Sample D had the best results with 70% LDPE, 5% polylactic acid, 15% nanoclay, 5% glycerine in terms of the tensile and flexural strength pointing to the fact that there was good interfacial cohesion between matrix and filler using glycerine as a compatibilizer and this improved mechanical property as seen. Polylactic acid has very good mechanical and thermal properties as compared to polyethylene and thus it improved the mechanical properties.
3. Results of hardness and water absorption showed an increase as natural filler content increased due to the hydrophilic nature of nanoclay and brittle nature of polylactic acid. The impact strength decreased as natural filler content increased. The nanoclay and polylactic acid aided the biodegradation of LDPE and this was seen in the water absorption test that the biodegradation phase of nanoclay began earlier than that of PLA and this lead to a loss of mass.
4. The bio-composite produced can be used in the production of plastic items with good mechanical and hardness properties such as children toys, waste bins and table tops or any plastic material which water absorbency is not of paramount significance. With the great importance of nanoclay in

enhancing the properties of polymers its industrial applications are very limited, still open to further research with the potency to develop a non-toxic, low-cost, environmental friendly food packaging materials with enhanced properties.

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Nigerian Journal of Polymer Science and Technology, 2025, Vol. 20(1), pp64-71

Received on: 12/11/2024 Revised on: 29/01/2025 Accepted: 18/03/2025

ASSESSMENT OF MODIFIED LEATHER WASTE ON CURE CHARACTERISTICS OF NATURAL RUBBER COMPOUND

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Abstract
Leather waste (buffing) were sourced, cleaned and modified. The modification revealed improved filler characteristics for both treated leather waste (TLW) and carbonized leather waste (CLW) in terms of, bulk density, moisture content, lignin content, cellulose content, hemicelluloses content, thermal stability and FTIR respectively. The results obtained were compared with carbon black (CB) filled vulcanizates. The cure characteristics of the compounded rubber showed improved scorch time (TLW; 2.59 - 2.02 min, CLW; 2.05 - 1.61 min, CB; 1.78 - 1.19 min) and cure time (TLW; 6.04 - 5.56 min, CLW; 5.93 - 4.51 min, CB; 4.77 - 4.45 min) decreased with filler loading while the cure rate index (TLW; 1.27 - 1.53 min^{-1}, CLW; 1.31 - 1.65 min^{-1}, CB; 1.40 - 1.74 min^{-1}), minimum torque (TLW; 4.10 - 5.08 kg-cm, CLW; 4.76 - 5.53 kg-cm, CB; 5.00 - 5.97 kg-cm) and maximum torque (TLW; 16.70 - 25.08 kg-cm, CLW; 19.44 - 26.19 kg-cm, CB; 20.04 - 27.95 kg-cm) increased with filler loadings from 10 phr – 50 phr. The research results showed that CLW and TLW can serve as alternative to CB for the production of polymer based articles such as shoe soles, floor-mats, oil seals, shock mounts etc. for some engineering applications.

Key Words: Buffing, Crosslink, FTIR, Leather, Vulcanizate

1. Introduction

The economic development of a country depends on the utilization of indigenous raw materials and their by-products (Li et al., 2017). As the pollution reduction can be possible by formulating cost intensive non-edible gelatin production thereby making leather industries eco-friendlier and environmentally compliant to buyers. Therefore, export earnings will be increased and the socio-economic status of people will be improved (El-Hout et al., 2022). Due to enhanced economic activities and rapid industrialization, tannery solid waste generation has increased dramatically in the last few decades. Tannery solid waste generation is a continually growing problem at regional and local levels due to rapid industrialization. Leather waste (buffing) is a fine powder of collagenous waste containing chromium, synthetic fat and other chemicals (Banon et al., 2021). Leather waste is generated when the leather is subjected to abrasion processes to achieve a uniform appearance. For every tone of skin or hide processed, about 2–6 kg of buffing dust is generated as solid waste. Circular economic strategies put pressure on the processing of wastes into secondary raw materials with the aim of their effective reuse instead of incineration or landfilling (Kumiawan et al., 2022). Recycling waste materials as filler for reinforcement of composites is of rising interest. Buffing dust is a tanning waste produced abundantly by local leather industry and its modification via chemical treatment and carbonization approach offers reduction of moisture absorption, increase in the surface roughness, decreasing the hydroxyl groups (Liu et al., 2019). Therefore, an attempt to use natural filler from leather waste as alternative filler for natural rubber was proposed (Popita et al., 2016). The choice of leather waste as the reinforcement in natural rubber composites is because it is renewable, biodegradable, non-toxic and abundantly available in Nigeria. It will also add value to local content thereby promoting industrial growth, economic development and sustainability.

1.1 Objective of Research Study

i. To obtain and characterize modified fillers
ii. To study the cure characteristics of the modified leather waste filled vulcanizates
iii. To assess the cure characteristics of the filled vulcanizates.

2.0 Materials and Method

2.1. Materials

The various materials used in this research include; Natural Rubber (NSR-10) obtained from Rubber Research Institute, Iyanomo, Benin City, Leather waste (Buffing) obtained from NILEST Metropolis and Environs, Zaria, Distilled water from Hadis Chemicals, Zaria, Kaduna State. Other materials obtained from British Drug House (BDH), England

include; Sodium hydroxide (NaOH), Tetramethyl thiuram disulphide, Mercarpto benzothiazole sulphenamide, Stearic acid, Sulphur, Trimethylquinoline (TMQ), Zinc Oxide, Processing Oil (Paraffin wax), Carbon Black (N330), Methanol, Sodium Thiosulphate, Iodine Solution, Standard Starch Solution, Sulphonic Acid.

2.2. Method

2.2.1 Preparation and Modification of Leather Waste

Leather waste was collected from NILEST metropolis, Zaria, Kaduna State. One portion of the buffing was carbonized at 650°C while the other portion was washed thoroughly using water and dried in open air for a period of 120 hours prior to pulverizing. The pulverized buffing was further ball-milled and soaked in 20% solution of sodium hydroxide solution for 1h at room temperature. Then solution was decanted and the filler washed to attain neutrality after which the powder was dried at room temperature and oven-dried at 75^{0}C for 1 hour (Tenebe et al., 2021). The reaction equation is shown in equation 1

$$Filler - OH + NaOH \rightarrow Filler - ONa + H2O \quad 1$$

a b

Plate I: Treated (a) and Carbonized Leather Waste (buffing) (b)

2.3 Characterization of Leather Waste (Buffing) Powder

The modified leather waste and carbon black-based fillers were characterized in terms of particle size, iodine value, moisture content, bulk density, pH, thermal stability, cellulose, hemicelluloses and lignin contents respectively and were used in compounding natural rubber.

2.3.1 Scanning Electron Microscope (SEM)

The micro-structural analysis was conducted in accordance with ASTM E2809-13. A specimen sample, usually non-conductive, was made conductive by coating with gold metal onto it and was cut into specified dimension using a sputter cutting machine (Li et al., 2020). The sample was placed on the column of the scanning electron microscope (SEM) where the image was focused using navigation camera and was transferred to electron mode in accordance to the desired magnification, which reveals the cracked areas, pores, bundles and voids present in the sample.

2.4 Characterization of the Natural Rubber

2.4.1 Determination of Dirt Content

The dirt content was determined in accordance with ASTM D1278-91a. The process involves homogenizing natural rubber in a two-roll mill and a test piece weighed out and cut into pieces. The piece of rubber is placed in a conical flask containing mineral turpentine. The flask with its content was placed in the oil bath and was heated to 135°C for 4 hours. On complete dissolution, the hot solution was filtered through a previously weighed, clean and dried sieve by decantation (Sharma et al., 2022). The dirt in the flask was washed into the sieve with a jet of warm mineral turpentine. The sieves with the dirt were dried in an oven and were recorded. The dirt content was calculated thus;

$$D(\%) = \frac{W_1}{W_2} \times 100 \quad 2$$

Where:

D = Dirt Content W_1= Weight of Dirt (g) W_2= Weight of test portion (g)

2.4.2 Determination of Volatile Matter

The volatile matter was determined in accordance with ASTM D5668-19. A test portion of 10g were weighed and passed twice through the Two-roll mill. The milled test piece was folded loosely and was placed on a properly labeled watch glass which was fed into an oven maintain at 100°C for 3h after which the test piece was removed and cooled for 30min. The volatile matter were expressed as percentage of the test portion (Tenebe et al., 2013).

$$Volatile\ Matter\ (\%) = \left(\frac{X - Z}{X}\right) \times 100 \quad 3$$

Where:

X = Weight of Test portion before drying Z = Weight of Test portion after drying

2.4.3 Determination of Ash Content

The ash content was determined in accordance with ASTM D5630. A test portion of 10g was weighed out from the homogenized piece and was wrapped in a filter paper. The wrapped test portion was placed in a covered crucible, which was previously ignited and weighed (Yang et al., 2017). The crucible with its contents was introduced into a muffle furnace controlled at a temperature of 550°C for 4h and was

allowed to cool in desiccators, weighed to obtain the ash content as follows;

$$Ash\ (\%) = \left(\frac{X}{Z}\right)x100 \qquad 4$$

Where: X = weight of ash Z = weight of test portion

2.4.4 Determination of Plasticity Retention Index

The plasticity retention index was determined in accordance with ASTM D3194-17. The process involves cutting 20g test piece of the unaged (P_o) and aged (P_{30}) and then measuring the plasticity of rubber samples using a Wallace rapid plastometer (Zheng et al., 2020). The plasticity retention index was calculated using equation 5.

$$PRI\ (\%) = \left(\frac{P_{30}}{P_0}\right)x100 \qquad 5$$

Where:
P_{30} = aged sample P_o = unaged sample

2.5 Processing of Composites

Compounding of natural rubber with modified powdered filler was based on the formulation in Table 1

Table 1: Formulation in part per hundred rubber using batch factor

Ingredient	Parts per hundred rubber (phr)
Natural Rubber	100
Filler	Variable (10 - 50)
Zinc Oxide	5.0
Stearic acid	2.5
Sulphur	1.5
Mercarpto benzothiazole	1.5
sulphenamide	3.5
Tetramethyl thiuram disulphide	5.0
Paraffin Wax	

2.5.1 Compounding of Natural Rubber

The compounding of natural rubber was carried out in accordance with ASTM D4295-89 using the two-roll mill maintained at 70^0C to avoid cross-linking during mixing. The process involves preheating the rolls of a two-roll machine prior to the introduction of crumb rubber between the moving roll which rotate counter clockwisefor mastication to take place. After 5 minutes, the additives were added for effective compounding. Sulphur was added last to introduce 3-dimensional network structure into the rubber. The sequence is presented in Table 2.

a b

c d

Plate II: Two-roll Mill (b), Hydraulic Press (b), Rubber Compounding (c) and Compounded Rubber (d)

Table 2: Mixing Steps and Mixing Time in Rubber Compounding

Mixing Step	Time (min)
Rubber Mastication	3.00
Addition of Stearic	1.00
Acid	1.00
Addition of Zinc Oxide	5.00
Addition of Filler	1.00
(Buffing)	1.00
Addition of MBTS	1.00
Addition of TMTD	2.00
Addition of Paraffin	

Wax Addition of Sulphur	
Total	**15.00**

2.5.2 Cure Characteristics of Compounded Rubber

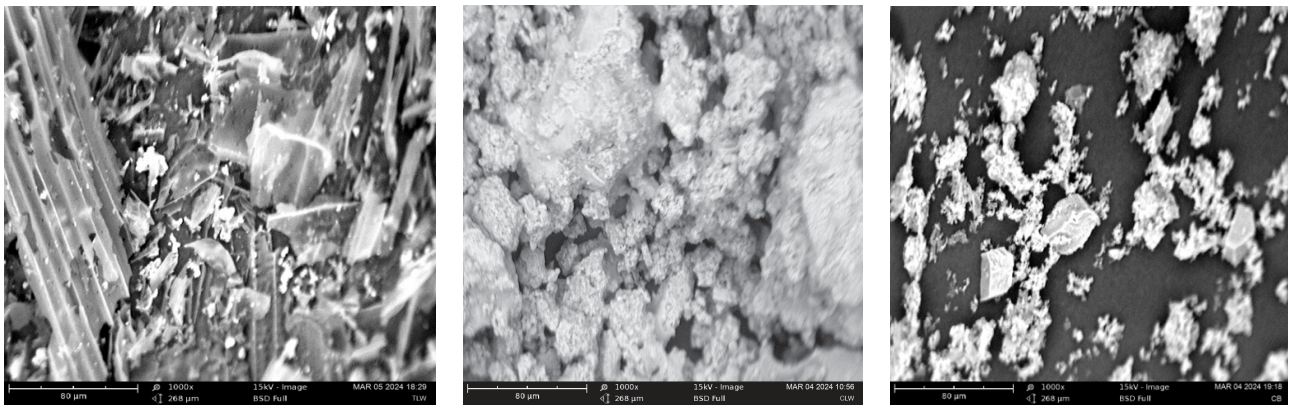
The cure characteristic was determined using Mosanto rheometer in accordance with ASTM D1415-88. The process involved cutting about 10g of the compounded unvulcanized rubber sample and placing it directly on the disc, which operates electronically. The cut test piece is then allowed to stay on the disc for about 30min. The cure time, cure temperature, scorch time, minimum and maximum modulus results of the sample were determined on the rheograph. These rheograph results were used to vulcanize the rubber samples using a hydraulic press.

3.0 Results and Discussion

3.1 Results

The results of these research findings are presented and discussed below.

3.1.1 Filler Characteristics (SEM)



Treated leather waste (a) Carbonized leather waste (b) Carbon black (c) Plate III: Micro-Graphs of the different fillers (a – c)

Table 3: Result of Natural Rubber Characteristics

Grade	NSR -10 (%)
Plasticity Retention Index	75.50
Dirt Content	0.08
Ash Content	0.65
Volatile Matter	0.72

3.1.2 Cure Characteristics of Vulcanizates

Table 4: Cure Characteristics of Vulcanizates

Filler Loading (phr)	Scorch Time, ts_2 (Mins)	Cure Time, t_{90} (Mins)	Minimum Modulus (kg-cm)	Maximum Modulus (kg-cm)	Curing Rate Index (min^{-1})
Unfilled	3.35	6.22	4.96	14.32	1.25
10	(2.59) [2.05] {1.78}	(6.04) [5.93] {4.77}	(4.10) [4.76] {5.00}	(16.70) [19.44] {20.04}	(1.27) [1.31] {1.40}
20	(2.27) [2.04] {1.65}	(5.81) [4.85] {4.79}	(4.72) [4.84] {5.17}	(19.97) [22.66] {23.53}	(1.31) [1.36] {1.45}
30	(2.15)	(5.70)	(4.80)	(22.37)	(1.37)

	[1.88] {1.59}	[4.73] {4.66}	[5.01] {5.19}	[23.17] {24.42}	[1.44] {1.52}
40	(2.08) [1.68] {1.27}	(5.64) [4.65] {4.57}	(4.88) [5.15] {5.75}	(22.41) [23.55] {24.82}	(1.45) [1.51] {1.60}
50	(2.02) [1.61] {1.19}	(5.56) [4.51] {4.45}	(5.08) [5.53] {5.97}	(25.08) [26.19] {27.95}	(1.53) [1.65] {1.74}

Key: Treated Leather Waste Filler Compounded Rubber (TLW)
Carbonized Leather Waste Filler Compounded Rubber [CLW]
Carbon Black Compounded Rubber{CB}

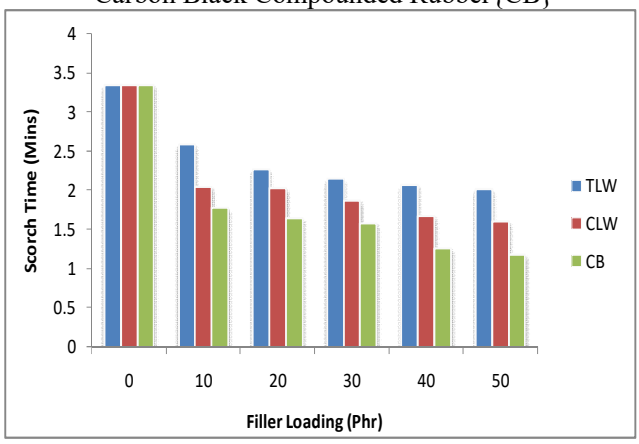


Figure 1: Scorch Time of filled Vulcanizates

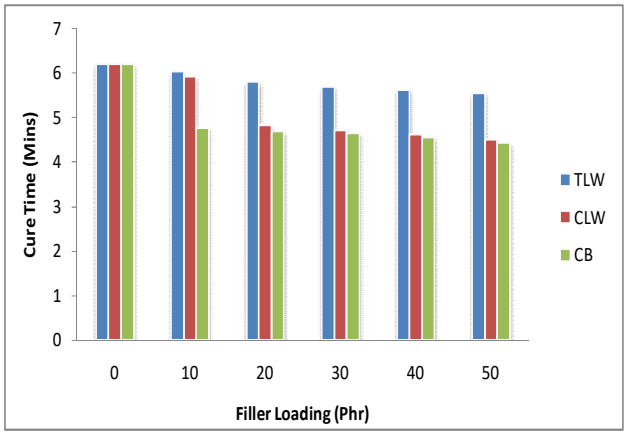


Figure 2: Cure Time of filled Vulcanizates

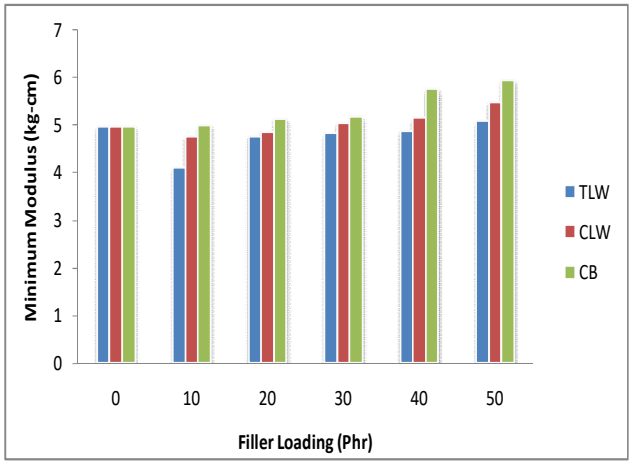


Figure 3: Minimum Modulus of filled Vulcanizates

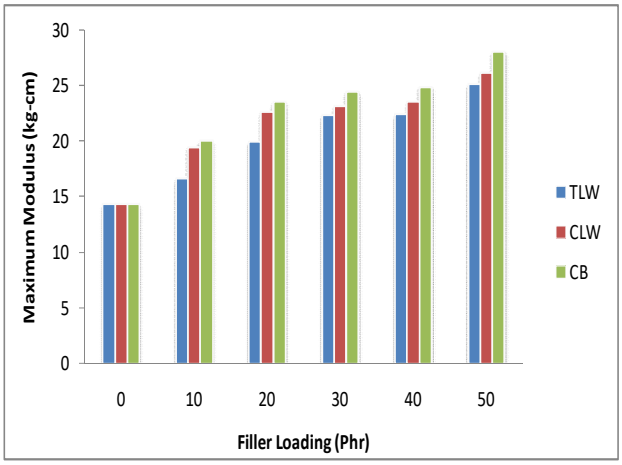


Figure 4: Maximum Modulus of filled Vulcanizates

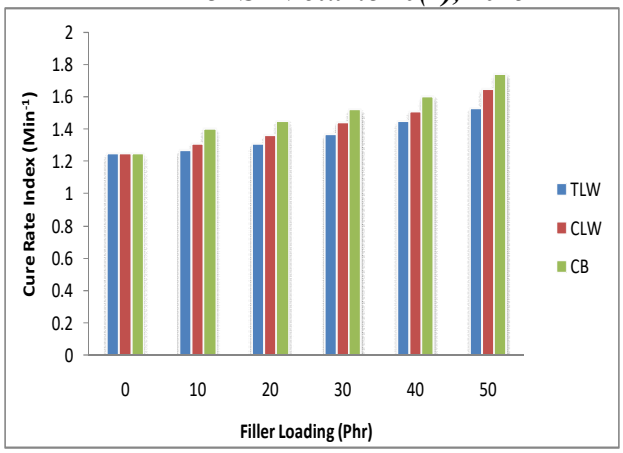


Figure 5: Cure Rate Index of filled Vulcanizates

3.2 Discussion

3.2.1 Results of Filler Characteristics

SEM micrographs in plate III (a –c) showed the morphology of the various fillers of treated leather waste (TLW), carbonized leather waste (CLW) and carbob black (CB) respectively. The progressive interphase at the transition zone of both fillers was showed. The results were interpreted in reference to ASTM C1723 (2010). The SEM morphology of the TLW powder showed a dense structure with the production of within the structure (Musa et al., 2017). However, the presence of highly define packed particles was present in the micro structure of the CLW revealing minimum pores and voids which showed that CLW will aid the interaction of filler particles in matrices and propagate adherence when incorporated in polymer matrices (Cardona et al., 2017). The micro structure of the CLW fillers showed aggregations in the packing order within the surface structure revealing tendencies to fracture surfaces which may reduce compaction when incorporated into polymer matrices. However, due to the large surface area available to network and interact with matrices, there are high tendencies that both fillers will adhere adequately with the matrices (Patnaik et al., 2010). Large surface area improves compaction and filler incorporation in polymer matrices when compared to small surface area networks (Omran et al., (2010). Stress may initiate the propagation of micro-cracks in the fillers, which further decreased the strength of vulcanizates.

3.2.2 Results of Cure Characteristics of Vulcanizates

The rheometric characteristics of the different natural rubber (NR) vulcanizates are shown in Table where minimum torgue (M_L), maximum torgue (M_H), scorch time (ts_2) and cure time (ts_{90}) respectively. The minimum torque gives an indication of the filler content in the rubber while the maximum torque in the rheograph is a measure of the cross-linking density and stiffness in the rubber matrices (Kueseng et al., 2013). In general, for all the mixes, the torque initially decreases and finally leveled-off. The initial decrease in torque was due to the softening of the rubber matrix while the increase is due to the cross-linking of the rubber (Agayev et al., 2019). The leveling- off is an indication of complete curing. It is found that the presence of fibres increases the maximum torque (Kim et al., 2015). It has been revealed that upon filler modification maximum torque increases indicating greater cross-linking due to better adhesion between the fillers and the matrices. Maximum torque value exhibited by CLW filled vulcanizates indicates maximum cross-linking. The results showed that each vulcanizate exhibited different cure characteristics due to different properties of the filler. The rough measurement of the cross-linking degree of rubber during vulcanization could be used as an indirect indication of the cross-link density of the rubber compound (Granda et al., 2016). Composites at different loadings of CLW and TLW caused a significant decrease compared with pure natural rubber. It was revealed that CLW increased curing process of natural rubber. The increment in the modulus with CB content was due to the presence of more fibrous structure which imparted more restriction to the deformation and consequently increased the vulcanizates stiffness. The larger the surface area is, the greater the interaction between the filler and rubber matrices (Zhang et al., 2010).

The structure of the CLW particles contains fibres which promoted particle dispersion in the rubber matrices. The increased dispersion lead to increased interfacial interaction and cross-linking density of both matrices The NR/CLW showed the stronger interactions between particles and natural rubber

matrix. It could be found that the scorch time and optimum cure time of vulcanizates decreased with increasing filler loading (Wang et al., 2014). At a similar filler loading, TLW exhibited longer cure time when compared to CLW and CB. One reason was that the high specific surface areas and the charges on the lattice allowed the TLW to adsorb the vulcanizing and curing agents easily. The adsorption increased as the CLW content varied from 10 phr to 50 phr. The TLW contained a large number of bound water and hydroxyl groups on the surface of which could adsorb the curatives and also caused delay of the rubber compound (Zhang et al., 2019). The scorch time and optimum cure time of TLW filled were increased possibly which absorbs the curative agents and thus reduce the active sulphurating agent.

4.0 Conclusion

This study revealed the potentials of leather industry generated buffing. The obtained data clearly reveals that leather waste (buffing) as filler materials affects the finished product final properties. Natural rubber vulcanizates filled with modified leather waste (buffing) were successfully prepared at different loadings using two-roll mill and introduced as potential value added product to the industrial community for the production of floor-mats. A comparative study performed on both treated leather waste (TLW), carbonized leather waste (CLW) and carbon black (CB) filled vulcanizates indicated improved adhesion of both CLW and TLW with natural rubber resulting in the outstanding cure characteristics properties which was revealed in the results obtained. The scorch and cure time of the composites decreased with increasing filler contents while the minimum and maximum modulus as well as cure rate index increased with increasing filler contents. However, CLW and CB filled matrices had better performance when compared to TLW filled NR compounds, which consumes more of the waste material.

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Nigerian Journal of Polymer Science and Technology, 2025, Vol. 20(1), pp72-80

Received on: 18/11/2024 Revised on: 03/04/2025 Accepted: 12/05/2025

IMPACT OF POLYMER WASTE AND CLIMATE MITIGATION; A REVIEW

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Abstract

The U.S. Environmental Protection Agency (EPA) defines municipal solid waste, also referred to as solid waste, as consisting of everyday items use and throw away, such as product packaging, grass clippings, furniture, clothing bottles, food scraps, newspapers, appliances, paint, and batteries. Global waste sector emissions have grown steadily and are expected to increase in the forthcoming decades especially in developing countries because of the increases in population and GDP. It is estimated that there is a stock of 86 million tons of plastic marine debris in the worldwide ocean as of the end of 2023, with an assumption that 1.4% of global plastics produced from 1950 to 2023 has entered the ocean and has accumulated there. Some researchers suggest that by 2050 there could be more plastic than fish in the oceans by weight. In some areas there have been significant efforts to reduce the prominence of free range plastic pollution, through reducing plastic consumption, litter clean up, and promoting plastic recycling. As of 2023, the global mass of produced plastic exceeds the biomass of all land and marine animals combined. This large amount of plastic waste enters the environment, with studies suggesting that the bodies of 90% of seabirds contain plastic debris

Key: Scraps, Batteries, Stock, Debris, Emission

Polymer Wastes

Polymer wastes are unwanted or unusable materials or substances which are discarded after primary use, or worthless, defective and of no useful importance (Hammer et al., 2012). According to EPA, municipal solid waste, more commonly known as trash or garbage, is typically generated in homes, schools, hospitals, and businesses. However, due to the fact that many tribal lands are characterized as rural, remote or containing expansive boundaries, illegal dumping, burn barrels and other improper solid waste disposal continue to be a challenge. The most common Polymer waste known are plastics waste pollutants. The estimation of the past, current and future emissions as well as the mitigation potential in the waste sector has many uncertainties, the most important relating to the poor quality of activity data needed for estimation of the emissions (Jambeck et al., 2015).

Figure 1: Common Plastic Products

Plastic pollution is the accumulation of plastic objects and particles (e.g. plastic bottles, bags and microbeads) in the Earth's environment that adversely affects wildlife, wildlife habitat and humans (Jang et al., 2015). Plastics that act as pollutants are categorized by size into micro, meso or macro debris. Plastics are inexpensive and durable making them very adaptable for different uses, as a result human produce a lot of plastic. However, the chemical structure of most plastics renders them resistant to many natural processes of degradation and as a result they are slow to degrade. These two factors allow large volumes of plastic to enter the environment as mismanaged waste and for it to persist in the ecosystem (Jambeck et al., 2015). Living organisms, particularly marine animals, can be harmed either by mechanical effects such as entanglement in plastic objects, problems related to

ingestion of plastic waste or through exposure to chemicals within plastics that interfere with their physiology. Degraded plastic waste can directly affect humans through both direct consumption (i.e. in tap water), indirect consumption (by eating animals) and disruption of various hormonal mechanisms (Hammer et al., 2012). In 2019, 368 million tonnes of plastic are produced each year; 51% in Asia, where China is the world's largest producer. From the 1950s up to 2018, an estimated 6.3 billion tonnes of plastic have been produced worldwide, of which an estimated 9% has been recycled and another 12% has been incinerated [4].

a b c d

Figure 2: Some Global Problems of Plastic Wastes in the Environment (a to d)

Types and Causes of Plastic Wastes

There are three major forms of plastic that contribute to plastic pollution which include micro, macro, and mega-plastics. Mega- and micro plastics have accumulated in highest densities in the Northern Hemisphere, concentrated around urban centres and water fronts. Both mega and macro-plastics are found in packaging, footwear, and other domestic items that have been washed off of ships or discarded in landfills (Walker et al., 2018). Plastic debris are categorized as either primary or secondary. Primary plastics are in their original form when collected. Examples of these would be bottle caps, cigarette butts, and microbeads whereas secondary plastics, on the other hand, account for smaller plastics that have resulted from the degradation of primary plastics (Barnes et al., 2009). Almost all plastics are derived from materials (like ethylene and propylene) made from fossil fuels (mostly oil and gas). The process of extracting and transporting those fuels, then manufacturing plastic creates billions of tonnes of greenhouse gases. For example, 4% of the world's annual petroleum production is diverted to making plastic, and another 4% gets burned in the refining process. Recent studies have shown that plastics in the ocean decompose faster than was once thought, due to exposure to sun, rain, and other environmental conditions, resulting in the release of toxic chemicals such as bisphenol A. However, due to the increased volume of plastics in the ocean, decomposition has slowed down. The Marine Conservancy has predicted the decomposition rates of several plastic products. It is estimated that a foam plastic cup will take 50 years, a plastic beverage holder will take 400 years, a disposable nappy will take 450 years, and fishing line will take 600 years to degrade (Walker et al., 2018).

Major Plastic Polluter Countries

In 2018 approximate 513 million tonnes of plastics wind up in the oceans every year out of which the 83,1% is from the following 20 countries: China is the most mismanaged plastic waste polluter leaving in the sea the 27.7% of the world total, second Indonesia with the 10.1%, third Philippines with 5.9%, fourth Vietnam with 5.8%, fifth Sri Lanka 5.0%, sixth Thailand with 3.2%, seventh Egypt with 3.0%, eighth Malaysia with 2.9%, ninth Nigeria with 2.7%, tenth Bangladesh with 2.5%, eleventh South Africa with 2.0%, twelfth India with 1.9%, thirteenth Algeria with 1.6%, fourteenth Turkey with 1.5%, fifteenth Pakistan with 1.5%, sixteenth Brazil with 1.5%, seventeenth Myanmar with 1.4%, eighteenth Morocco with 1.0%, nineteenth North Korea with 1.0%, twentieth United States with 0.9%. The rest of world's countries combined wind up the 16.9% of the mismanaged plastic waste in the oceans, according to a study published by Jambeck et al (2015). Around 275 million tonnes of plastic waste is generated each year around the world; between 4.8 million and 12.7 million tonnes

is dumped into the sea. About 60% of the plastic waste in the ocean comes from the following top 5 countries (Jang et al., 2015).

Table 1: Plastic Pollution Generation by Top 10 Countries (Barrett et al., 2020).

Position	Country	Plastic Pollution (10^3 Tonnes Per Year)
1	China	8820
2	Indonesia	3220
3	Philippines	1880
4	Vietnam	1830
5	Sri Lanka	1590
6	Thailand	1030
7	Egypt	970
8	Malaysia	940
9	Nigeria	850
10	Bangladesh	790

All the European Union countries combined would rank eighteenth on the list.

However, the poorly-regulated incineration in those developing nations posed considerable threats to human health and the environment. Globally, researchers estimate that the production and incineration of plastic will pump more than 850 million tonnes of greenhouse gases into the atmosphere and by 2050, those emissions could rise to 2.8 billion tonnes. Alarmingly, at least 8 million tonnes of discarded plastic also enters our oceans each year, and plastic pollution at sea is on course to double by 2030 (Jang et al., 2015).

Figure 3: Plastic Wastes Deposit in Water Ways

The smaller particles (known as micro-plastics) that break off and disperse are also unwittingly ingested by marine animals, including plankton, and some of the fish we eat. The full effects of this are still being studied, but the essential premise is when micro-plastics threaten plankton populations, more carbon will re-enter the waters and atmosphere. Given that our oceans have successfully absorbed 30-50% of atmospheric carbon produced since the start of the industrial era, it's easy to see just what's at stake. And this leads us back to the plastic consumption on land that is driving this mounting plastic pollution crisis. The more plastic we make, the more fossil fuels we need, the more we exacerbate climate change (Barnes et al., 2009). The only way to address the problem is to curb the production of plastic, especially of the single-use variety, and to ramp up recycling. Reducing plastic use and waste is a key component of WWF's work. It's critical to curb greenhouse gas emissions that are exacerbating climate change, and to protect our marine environments.

Effects of Polymer Wastes

i. Effects on Environment

The distribution of plastic debris is highly variable as a result of certain factors such as wind and ocean currents, coastline geography, urban areas, and trade routes. Human population in certain areas also plays a large role in this. Plastics are more likely to be found in enclosed regions such as the Caribbean. It serves as a means of distribution of organisms to remote coasts that are not their native environments. This could potentially increase the variability and dispersal of organisms in specific areas that are less biologically diverse. Plastics can also be used as vectors for chemical contaminants such as persistent organic pollutants and heavy metals (Ang et al., 2015).

ii. Effects on Land

Plastic pollution on land poses a threat to the plants and animals including humans who are based on the land. Estimates of the amount of plastic concentration on land are between four and twenty-three times that of the ocean. The amount of plastic poised on the land is greater and more concentrated than that in the water. Mismanaged plastic waste ranges from 60 percent in East Asia and Pacific to one percent in North America. The percentage of mismanaged plastic waste reaching the ocean annually and thus becoming plastic marine debris is between one third and one half the total mismanaged waste for that year. Chlorinated plastic can release harmful chemicals into the surrounding soil, which can then seep into groundwater or other surrounding water sources and also the ecosystem of the world. This can cause serious harm to the species that drink the water (Barnes et al., 2009). However, plastic tap water pollution remains under-studied, as are the links of how pollution transfers between humans, air, water, and soil.

iii. Effect on Flooding

Volunteers clearing gutters in Ilorin, Nigeria during a volunteer sanitation day. Even when there is adequate infrastructure for sanitation, plastic pollution can prevent drainage and impede sewage flow. Plastic waste can clog storm drains, and such clogging can increase flood damage, particularly in urban areas. For example, in Bangkok flood risk increases substantially because of plastic waste clogging the already overburdened sewer system (Hammer et al., 2012).

iv. Effects on Oceans and Seabirds

Marine plastic pollution is a type of marine pollution by plastics, ranging in size from large original material such as bottles and bags, down to micro-plastics formed from the fragmentation of plastic material. Marine debris is mainly discarded human rubbish which floats on, or is suspended in the ocean. About 80% of marine debris is plastic. Micro-plastics and nano-plastics result from the breakdown or photodegradation of plastic waste in surface waters, rivers or oceans (Ostle et al., 2019). It is estimated that there is a stock of 86 million tons of plastic marine debris in the worldwide ocean as of the end of 2013, assuming that 1.4% of global plastics produced from 1950 to 2013 has entered the ocean and has accumulated there. The 2017 United Nations Ocean Conference estimated that the oceans might contain more weight in plastics than fish by the year 2050. Oceans are polluted by plastic particles ranging in size from large original material such as bottles and bags, down to micro-plastics formed from the fragmentation of plastic material (Hammer et al., 2012). Aquatic life can be threatened through entanglement, suffocation, and ingestion. Fishing nets, usually made of plastic, can be left or lost in the ocean by fishermen. Known as ghost nets, these entangle fish, dolphins, sea turtles, sharks, dugongs, crocodiles, seabirds, crabs, and other creatures, restricting movement, causing starvation, laceration, infection, and, in those that need to return to the surface to breathe, suffocation (Jambeck et al., 2015).

v. Effects on Humans

Compounds that are used in manufacturing pollute the environment by releasing chemicals into the air and water. Some compounds that are used in plastics, such as phthalates, bisphenol A (BRA), polybrominated diphenyl ether (PBDE), are under close statute and might be very hurtful. Even though these compounds are unsafe, they have been used in the manufacturing of food packaging, medical devices, flooring materials, bottles, perfumes, cosmetics and much more. The large dosage of these compounds is hazardous to humans, destroying the endocrine system. BRA imitates the female's hormone called estrogen. PBD destroys and causes damage to thyroid hormones, which are vital hormone glands that play a major role in the metabolism, growth and development of the human body. Although the level of exposure to these chemicals varies depending on age and geography, most humans experience simultaneous exposure to many of these chemicals (Jang et al., 2015). Average levels of daily exposure are below the levels deemed to be unsafe, but more research needs to be done on the effects of low dose exposure on humans. A lot is unknown on how severely humans are physically affected by these chemicals. Some of the chemicals used in plastic production can cause dermatitis upon contact with human skin. In many plastics, these toxic chemicals are only used in trace amounts, but significant testing is often required to ensure that the toxic elements are contained within the plastic by inert material or polymer. Children and women during their reproduction age are at most at risk and more prone to damaging their immune as well as their reproductive system from these hormone-disrupting chemicals (Ang et al., 2015).

Waste Management Planning to Mitigate the Impact of Climate Change

Climate change is expected to produce more frequent and powerful natural disasters, which will increase the amount of disaster-related waste generated. Communities can adapt to these disasters and increase their resiliency by preparing for these disasters through pre-incident planning. Planning can expedite the removal of waste during and after an incident, which can reduce dangers of fire, personal injury and disease vectors and identify waste management opportunities and strategies. The affected are faced with challenges which include (Selke et al., 2015);

i. Larger quantities of waste resulting from the disaster.
ii. Wider variety of generated wastes at one time, including atypical wastes in greater quantities.
iii. Wider area of impact, possibly affecting more than one jurisdiction.
iv. Increased greenhouse gas (GHG) emissions from waste management activities, such as the transportation, treatment and disposal of large amounts of waste.

v. Insufficient waste management capacity to handle surges in necessary recycling, treatment and disposal.

vi. Greater chances of waste management facilities being impacted by the disaster, resulting in possible decrease to existing capacity for generated wastes and reduction of available waste management options.

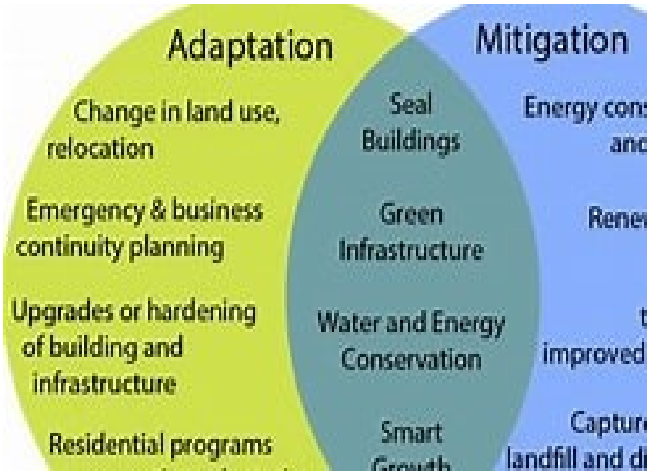

Figure 4: Global Implications of Polymer Wastes on Climate Change

According to the EPA, waste prevention and recycling-jointly referred to as waste reduction are potent strategies for reducing greenhouse gases. There are many co-benefits of implementing waste management plans in Indian Country beyond greenhouse gas reduction. These co-benefits include a healthier airshed, reduced illegal dumping, and community beautification. What tribes can do: The four main tenets of waste reduction are reduced, reuse, recycle and compos. For waste that cannot be prevented, tribes can provide recycling, garbage pickup, and self-haul options as safe and healthy means to managing waste disposal. Waste reduction is a powerful tool for mitigating greenhouse gas emissions from the municipal waste sector. Integrated waste management plans (IWMPs) are an effective means of implementing important waste reduction strategies within communities (Hammer et al., 2012). EPAs Office of Resource Conservation and Recovery (ORCR) has developed a brochure to assist tribes, titled 3 Steps to Developing Tribal Integrated Waste Management Plan (IWMP). Again, in addition to greenhouse gas mitigation from waste reduction, there are many benefits to developing and implementing IWMPs. ORCR identifies several of these benefits (Thompson et al., 2009):

i. Lowers operating costs for waste management
ii. Increases program efficiency
iii. Reduces the use of open dumps
iv. Improves protection of human health & the environment

Adapting to the Waste-related Impacts of Climate Change (Walker et al., 2018)

Of the almost 3 million tonnes of plastic that Australia produces each year, 95% is discarded after a single use. Less than 12% is recycled, which leaves a staggering amount to be disposed of - in landfills or incinerated. We used to rely on countries like China, Myanmar and Cambodia to handle our waste plastic. Although energy and water reduction efforts are critical to reducing our impact on the environment, waste reduction is just as important.

a Identifying Strategies to Expedite Removal of Disaster-Related Waste During a Disaster

i. Reduces dangers of fire, personal injury and disease vectors
ii. Limits number of times waste is handled during cleanup
iii. Increases probability that waste will be separated into different waste streams, instead of co-mingled into large piles of waste, which facilitates reuse, recycling, treatment and proper disposal of different waste streams

b Reuse and Recycling Program to Enhanced Scaled up to Handle Disaster-Related Wastes

i. Maximizes reuse and recycling opportunities available to the community within and across jurisdictional lines during a disaster
ii. Maintains a robust and viable reuse and recycling infrastructure, such as recycling facilities and end markets for reused and recycled products
iii. Encourages green building programs

c Opportunities for Source Reduction and Hazard Mitigation Before Disaster Occurs

i. Decreases the total amount of waste that may be generated (e.g., by raising minimum floor/foundation elevations in low-lying areas or updating building code requirements so that more resilient building materials and strategies that increase a buildings capacity to withstand greater wind, rain or snow loads are incorporated into building design and construction)
ii. Eliminates the generation of potentially problematic wastes (e.g., retrofitting PCB transformers to reduce PCB-contaminated wastes)

Climate Mitigation

The term mitigation refers to efforts to cut or prevent the emission of greenhouse gases - limiting the magnitude of future warming. It may also encompass attempts to remove greenhouse gases from the atmosphere (Van-Minnen et al., 2008). Climate change mitigation consists of actions to limit global warming and its related effects. This involves reductions in human emissions of greenhouse gases (GHGs) as well as activities that reduce their concentration in the atmosphere. It is one of the ways to respond to climate change, along with adaptation. Mitigation of climate change may also be achieved by changes in agriculture, reforestation and forest preservation and improved waste management. Methane emissions, which have a high short-term impact, can be targeted by reductions in cattle and more generally by reducing meat consumption (Boysen et al., 2017).

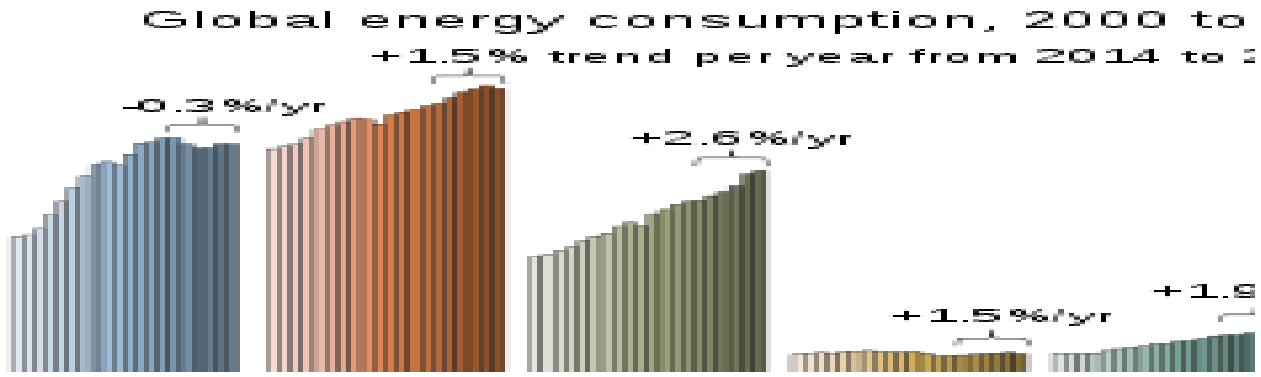

Figure 5: Global Energy Consumption

Drivers of Global Warming

GHG emissions are measured in CO_2 determined by their global warming potential (GWP), which depends on their lifetime in the atmosphere. Estimations largely depend on the ability of oceans and land sinks to absorb these gases. Short-lived climate pollutants (SLCPs) including methane, hydrofluorocarbons (HFCs), tropospheric ozone and black carbon persist in the atmosphere for a period ranging from days to 15 years as compared to carbon dioxide which can remain in the atmosphere for millennia. Reducing SLCP emissions can cut the ongoing rate of global warming by almost half and reduce the projected Arctic warming by two-thirds (Boysen et al., 2017).

i. Carbon dioxide (CO_2)

Fossil fuel: oil, gas and coal (89%) are the major driver of anthropogenic global warming with annual emissions

i. Cement production (4%) is estimated at 1.42 GtCO
ii. Land-use change (LUC) is the imbalance of deforestation and reforestation. Estimations are very uncertain at 4.5 GtCO

iii. Wildfires alone cause annual emissions of about 7 GtCO
iv. Non-energy use of fuels, carbon losses in coke ovens, and flaring in crude oil production
2 mostly by fossil fuel (72%)

ii. Methane (CH_4)

Methane has a high immediate impact with a 5-year global warming potential of up to 100. For methane, a reduction of about 30% below current emission levels would lead to a stabilization in its atmospheric concentration (Jang et al., 2015).

i. Fossil fuels (32%), again, account for most of the methane emissions including coal mining (12% of methane total), gas distribution and leakages (11%) as well as gas venting in oil production (9%).
ii. Livestock (28%) with cattle (21%) as the dominant source, followed by buffalo (3%), sheep (2%), and goats (1.5%).
iii. Human waste and wastewater (21%): When biomass waste in landfills and organic substances in domestic and industrial wastewater is decomposed by bacteria in anaerobic conditions, substantial amounts of methane are generated.
iv. Rice cultivation (10%) on flooded rice fields is another agricultural source, where anaerobic decomposition of organic material produces methane [13].

iii. Nitrous Oxide (N_2O)

N_2O has a high GWP and significant Ozone Depleting Potential (ODP). It is estimated that the global warming potential of N_2O over 100 years is 265 times greater than CO_2. For N_2O, a reduction of more than 50% would be required for a stabilization (Van-Minnen et al., 2008).

i. Most emissions (56%) by agriculture, especially meat production: cattle (droppings on pasture), fertilizers, animal manure.
ii. Combustion of fossil fuels (18%) and bio fuels.
iii. Industrial production of adipic acid and nitric acid.

iv. F-Gases

Fluorinated gases include hydrofluorocarbons (HFC), perfluorocarbons (PFC), and sulphur hexafluoride (SF6). They are used by switchgear in the power sector, semi-conductor manufacture, aluminium production and a large unknown source of SF6. Continued phase down of manufacture and use of hydrofluorocarbons (HFCs) under the Kigali Amendment to the Montreal Protocol will help reduce HFC emissions and concurrently improve the energy efficiency of appliances that use HFCs like air conditioners, freezers and other refrigeration devices (Lai et al., 2004).

v. Black carbon

Black carbon is formed through the incomplete combustion of fossil fuels, biofuel, and biomass. It is not a greenhouse gas but a climate forcing agent. Black carbon can absorb sunlight and reduce albedo when deposited on snow and ice. Indirect heating can be caused by the interaction with clouds. Black carbon stays in the atmosphere for only several days to weeks. Emissions may be mitigated by upgrading coke ovens, installing particulate filters on diesel-based engines and minimizing open burning of biomass (Pimentel et al., 2005).

Climate change in Nigeria

To mitigate the adverse effect of climate change, not only did Nigeria sign the Paris agreement to reduce emission, in its national climate pledge, the Nigerian government has promised to work towards ending gas flaring by 2030. In order to achieve this goal, the government established a Gas Flare Commercialisation Programme to encourage investment in practices that reduce gas flaring. Also, the federal government has approved a new National Forest Policy which is aimed at protecting ecosystems while enhancing social development. Effort is also being made to stimulate the adoption of climate-smart agriculture and the planting of trees (Pimentel et al., 2005). One of the outcomes of the UNFCC Copenhagen Climate Conference was the Copenhagen Accord, in which developed countries promised to provide US$30 million between 2010 and 2012 of new and additional resources. The European Commission has requested its member states to define what they understand to be additional, and researchers at the

Overseas Development Institute have found four main understandings (Howe et al., 2019):

i. Climate finance classified as aid, but additional to (over and above) the '0.7%' ODA target;
ii. Increase on previous year's Official Development Assistance (ODA) spent on climate change mitigation;
iii. Rising ODA levels that include climate change finance but where it is limited to a specified percentage; and
iv. Increase in climate finance not connected to ODAm (Anderson et al., 2012).

Links between Polymer Waste and Climate Mitigation (Prestonet al., 2011)

The earth's climate system is changing in response to increasing concentrations of greenhouse gases (GHG). GHGs are emitted through a variety of human activities including electricity production, transportation, agriculture, and industry. Reducing and recycling solid waste can help to curb the emission of greenhouse gases in some important ways (Jambeck et al., 2015).

i. Emissions from extraction of resources: Trees, minerals, oil and other basic components of materials we use must be extracted from the environment. The extraction process and resulting depletion of resources releases GHGs and disrupts the ecosystem.
ii. Transportation of goods and materials: Raw materials must be transported to processing and manufacturing facilities. Most finished goods include excessive packaging, which has several stages of extraction and transportation (Van den Berg et al., 2020).
iii. Manufacturing emissions: The production of goods and materials also has associated emissions. This can be direct emissions output from the manufacturing facility itself, or indirect output through the energy it uses.
iv. Landfill methane: As some materials degrade in the anaerobic environment of a landfill, methane is released. Methane is a potent GHG, with as high as 72 times the impact on warming the climate than CO_2. In California, landfills are one of the top five sources of GHG emissions.
v. Emissions from incineration: Even with emission controls, some GHG and other air pollutants are produced from these processes. Energy recovery capabilities at these facilities can help to negate climate impact (Van den Berg et al., 2020).
vi. Ocean pollution: Litter, particularly single-use plastic items, and polluted runoff enter our oceans, damaging its ecosystem. Healthy oceans are critical to maintaining a healthy climate, and acidification and warming ocean temperature may amplify overall warming.
vii. Destruction of forests: Trees cut down for the production of paper-based products can no longer filter our air or sequester carbon. We must preserve elements of our ecosystem that mitigate climate change.

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Nigerian Journal of Polymer Science and Technology, 2025, Vol. 20(1), pp81-90
Received on: 11/10/2024 Revised on: 07/05/2025 Accepted: 25/05/2025

RECYCLING OF LOW - DENSITY POLYETHYLENE (WATER SACHET) FILM AS FILLER FOR THE PRODUCTION OF POLYURETHANE IN COLD CHAIN SUPPLY MANAGEMENT.

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ABSTRACT
The aim of this study is to investigate the potentials of incorporating recycled low-density polypropylene (PE) sachet water film as a sustainable filler in the manufacture of flexible polyurethane (PU) foam materials that could enhance cold chain management systems. Different formulations of PU foam were tested, focusing on the effects of PE on key mechanical properties. All formulations were mixed for 15 seconds, ensuring a consistent process, though cream time (13.6-17.2 seconds) and rise time (108-124 seconds) varied across compositions. The foam densities ranged from 21.64 to 26.44 kg/m³, with higher PE content generally increasing density and Mechanical properties influenced by the PE content. Compression strength rose with higher PE but remained within the National Institute of Standards (NIS) limit of 10 kg/cm². However, flexural strength, tensile strength, force per unit area, and elongation decreased as PE content increased, indicating a trade-off between cost-efficiency and mechanical performance. Despite these changes, all formulations showed homogeneous morphology under Scanning Electron Microscopy, suggesting consistent material quality. The presented work indicates that PE can be efficiently introduced as a filler for flexible PU foams, hereby improving the foam performance, lowering production costs, and reducing the environmental impact of the indiscriminate disposal that is redirected by reusing these waste materials. However, higher PE percentages tend to lower the mechanical performance of the foam, indicating a need for optimized compositions.

Keywords: Polyurethane Foam, Low Density Polyethylene (LDPE), Water Sachet Film, Filler, Cold Chain.

1. INTRODUCTION

Certain additive materials have been used to impart foam plastics with cushioning and load bearing properties. Such additives include fillers either as bulk or reinforcing fillers. Fillers are substances added to other materials (plastics, composites and other materials) to lower consumption of the more expensive binder material or to improve some properties of the base material. In production of flexible polyurethane foams, fillers are used to modify the morphology and mechanical properties of the material. Predominantly, fillers are introduced to reduce the overall cost of the products, however the desired integrity in quality are sustained or improved upon as in case of extenders. (Dalen, 2014). Among over twenty most important fillers, calcite ($CaCO_3$) holds the largest market volume and is mainly used in plastic sectors. Other fillers include dolomite ($CaMg(CO_3)_2$), kaolin and talc.

Fillers are used in flexible urethane foams to reduce their flammability, increase the bulk and structural reinforcement. Fillers used in foam formulations are mainly inorganic in nature that needs vigorous agitation to produce a stable suspension. Inorganic solid materials used in filled foam formulations include; hydrated alumina, carbonates, silicates, silica, glass fibers, and barium sulfate. Historically, inorganic fillers such as barium sulfate and calcium carbonate have been used in flexible slab stock foams to achieve increased density and/or load bearing, and to reduce cost. Normal concentrations range from 20 to 150 parts per hundred parts polyols. The use of inorganic fillers has several disadvantages including difficulty of preparing and maintaining the dispersion; problems with removal of entrapped air; difficulty of mixing and pumping and extruding the filler/polyol slurry; the loss of the foam physical properties; difficulty of processing on all types of foam machinery, due to their abrasive nature, resulting in increased wear on machinery components.

Polyurethane foams (PURs) are generally obtained by poly-addition reaction between polyols, isocyanates and suitable blowing agents. Several additives (catalysts, surfactant and flame retardants) are added in order to tune the final characteristics of the product (Coccia, 2021). The mechanical and functional properties of the foams are strongly affected by the nature of polyols and isocyanate precursors as well as by the distribution of the soft and hard segments of PURs (Carriço, 2016; Coccia, 2021; Wendels, 2021).

Polyurethanes (PUR) are classified as polymeric materials, which are produced in a polyaddition reaction of multifunctional isocyanates with polyols. PUR materials may be obtained in the form of solid or foamed products with desired properties. Currently, PUR is produced on a large industrial scale and widely used in daily life due to their various and universal properties. (Ibrahim et al.; 2015, Aleksander et al., 2017) PUR most often are used in the furniture, automotive, footwear, construction, and refrigeration industries. There are multiple applications in which they appear in the form of foamed materials as flexible, viscoelastic, semi-rigid, and rigid foams. (Tejas, 2015; Prociak, 2016). Additionally, the local demand for cold chain products which includes essential food items (From the farm to the dining table) and drugs in the form of vaccines (From the research labs to the drug administration), it is firmly required that the items of interest must be stored at specified temperatures in order to ensure the shelf life of these very important commodities. This became more relevant especially in the advent of Covid -19 pandemic and the realities surrounding the demands for other vaccines in the fight against malaria, monkey pox, Anti-rabies, Lasa-fever and the likes as laid out by the Centre for Disease Control vaccine storage and Handling toolkit, March 2024. The integrity of the aforementioned products is linked to a sustained cold chain delivery as amplified in World Health Organization Unit 4: Cold Chain and logistics management, which has a large bearing on the paddings and laggings derived from desired polyurethanes products. (polyurethanes.org). The recycling of polyethylene films from pure water sachet water as a desirable filler in production of polyurethanes is a major step in the forward direction in resolving the impact of indiscriminately disposed LDPE pure water sachet film. The menace cursed by these littering films includes the blockage of drainages and water ways that results in enhancing destructive floods and the development of stagnant ponds that serve as habitat for breeding undesirable organisms that are vectors to malaria, cholera and other parasites. Our environment and our health are positively impacted by the innovation of this

research as supported by Singh et al., 2017. Any Patent from the outcome of the findings herein is a viable economic venture. One of the several targets for the product engineered is in the manufacture of enhanced customized units for cold chain management supply system. In recent times, the movement of items such as food, drugs, especially vaccines that require storage at low temperatures in order to retain product integrity has become increasingly unavoidable globally. To this end the World Health Organization in collaboration with Pan American Health Organization makes every effort to ensure that supplies such as drugs and vaccines supplies, provide the expected benefits when an individual gets immunized, it is required that epidemiologist and health staff are equipped to provide potent supply for protecting the recipient against the targeted disease(s). In this respect, the focus of the Immunization program should be built around a minimum of five pillars: (1) Countries are advised to use good quality refrigeration equipment (2) Health staff involved in managing vaccines should be trained (3) Cold Chain and supply chain operations should be evaluated (4) Research and development should be carried out in the area of cold chain technology with respect to soft and hard wares (5) The management capacity and skills to support all operations linked to cold chain and supply chain needs to be improved to accommodate new products. (PAHO & WHO, Cold Chain 2025)

2. MATERIALS AND METHODS

2.1 SAMPLE COLLECTION

Industrial chemicals such as: polymer polyol (PPO), conventional polyol (CPO), toluene di-isocyanate (TDI) (80/20), stannous octanoate, dimethyl ethanolamine, polysilicone methylene dichloride, and $CaCO_3$ were products of Korean Fire Chemicals Ltd., BASF and Dupont, and were graciously provided by Vitafoam Nig. Plc, Jos Mega Factory. Sachet water film was collected, washed and dried, and was pulverized at Destiny Recycling Company Kwan Jos Plateau State.

2.2 SAMPLE TREATMENTS

Low density polyethylene (LDPE) based water sachet films were recycled into polymer powder by thermochemical treatment. Varying weights of sachet films were dissolved in automotive gas oil (AGO) at elevated temperature, followed by quenching in an ice-bath stainless steel container to determine optimum powder yield and particle size distribution. Sieve analysis of powder was carried out into different particle sizes and consequently to eliminate lumps.

2.3 FOAM FORMULATION

One-shot technique of urethane foam formulation was used (Richter, 1974). The ingredients were measured accurately using syringes, micro-syringes, pipettes and measuring cylinders into moulds of dimensions (21.5cm x 13.7cm x 14.5cm), using the recipes on Table 1. The components were thoroughly stirred and TDI added with continuous stirring until the systems creamed. The foams were then allowed to rise undisturbed and left to cure 24 hours after which physico- mechanical properties were determined.

Table 1: Formulation's ratio of PUFs

Sample Identity	0%	5.0%	7.5%	10%	12.5%	15%
CPO (g)	200	200	200	200	200	200
$CaCO_3$ or PE (g)	0	10	15	20	25	30
Silicone (g)	1.80	1.80	1.80	1.80	1.80	1.80
Amine (g)	0.40	0.40	0.40	0.40	0.40	0.40
Stannous (g)	0.38	0.38	0.38	0.38	0.38	0.38
Water (g)	8.64	8.64	8.64	8.64	8.64	8.64
TDI (g)	110.96	110.96	110.96	110.96	110.96	110.96

2.4 PHYSICAL PROPERTIES

Some of the polyurethane foam's physical properties were found in a rather simple fashion. Densities for each type of foam were found using a scale and a set of calipers in accordance with ASTM D3574-95, "Standard Test Methods for Flexible Cellular Materials – Slab, Bonded, and Molded Urethane Foams," Test A. There were three samples weighed and measured for each type of foam and an average density was determined. The density for each type of polyurethane foam tested is listed in Table I.

2.5 MICROSTRUCTURE DETERMINATION

The samples were cut gently into thin wafers using a fine blade. These wafers were later mounted on a stub and coated with silver paint at the edges. The silver paint is used to provide a conductive path from the surface of the coated sample to the stub, which then goes off to an electrical ground. Later the sample was placed in an oven at 150°F for 5–20 min for drying the paint. Since the samples are non-conductive, either sputter or carbon coating was employed. Then the samples were put under the scanning electron microscope for analysis. Two scanning electron microscopes were used: an AMRAY 1600 with an accelerating voltage of 20 kV and a Hitachi S-4700 FESEM with an accelerating voltage of 5 kV.

2.6 TENSION TEST

The purpose of conducting a tension test was to determine the tensile strength of each type of polyurethane foam. This test also gives an elastic modulus for the foam in tension. The procedure for tension testing was in accordance with ASTM D3574-95, "Standard Test Methods for Flexible Cellular Materials – Slab, Bonded, and Molded Urethane Foams," Test E. Test specimen dimensions are shown in the ASTM standard. A special large extension clip gage of 25-mm gage length was used in the middle of the specimen to measure the elongation during the tension tests.

2.7 COMPRESSION TEST

The purpose of conducting a compression test was to determine a compressive stress-strain relationship for the different types of reinforced polyurethane foam. Three samples of each type of foam were tested to give an average and to show the repeatability of data. This test also gives the compressive elastic modulus. The procedure for the compression test was in accordance with ASTM D3574-95, "Standard Test Methods for Flexible Cellular Materials – Slabs, Bonded, and Molded Urethane Foams," Test C. Pieces were cut from a polyurethane foam plate with a width and a length of 20.0-mm (0.787-inch). Two of the pieces were placed together to make a 25.4-mm (1.0 inch) thick specimen, and then tested as directed by the standard. There were

three specimens tested. Each specimen was preflexed twice by compressing it 75 to 80% of its original thickness, in this case about 5 mm. The specimen was then relaxed for 6 min. Then the specimen was compressed to about 25% of its thickness at a rate of 0.83 mm/s (0.033 in/s)

3 RESULTS AND DISCUSSION RESULTS

Table 2: Density of various reinforced polyurethane foam

PUFs	Mixed Time (s)	Cream Time (s)	Rise Time (s)	Density (kg/m^3)
0% $CaCO_3$	15	14.8	111	21.64
5% $CaCO_3$	15	13.6	120	25.76
5% PE	15	15.4	108	24.28
10% PE	15	16.5	124	25.27
15% PE	15	16.8	114	25.36
20%	15	17.2	109	26.44

Table 3: Mechanical properties of various reinforced polyurethane foam.

PUFs	Compression (kg/cm^2)	NIS Value for Compression (kg/cm^2) (Max)	Flexural Strenght (kg/cm^2)	Tensil Strain (N/mm^2)	Tensil Stress (N/mm²)	Elongation (N/mm²)
0% $CaCO_3$	9.0	10	41.7	2.431	33.806	3.646
5% $CaCO_3$	10.7	10	37.9	1.595	22.512	2.306
5% PE	10.9	10	34.9	1.50	21.50	2.05.
10% PE	11.9	10	28.4	1.46	20.37	1.98
15% PE	12.0	10	12.18	1.37	18.76	1.55
20% PE	12.0	10	12.1	0.9	16.59	0.60

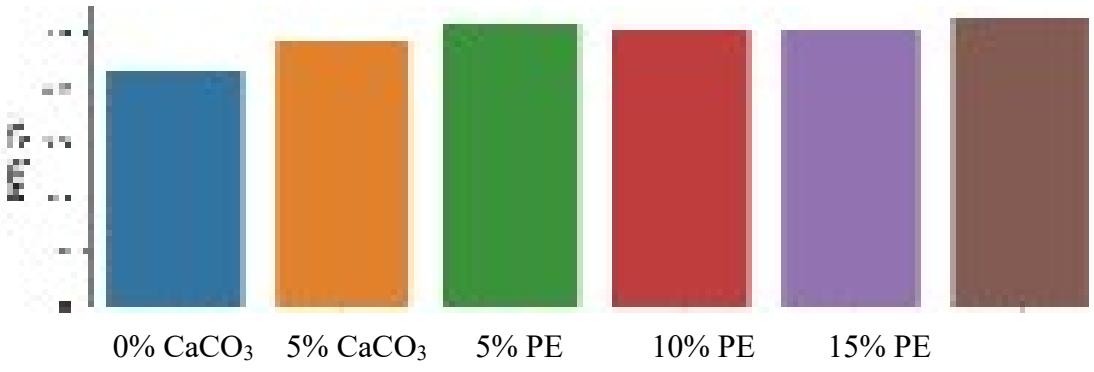

Figure 1: Density of PUFs

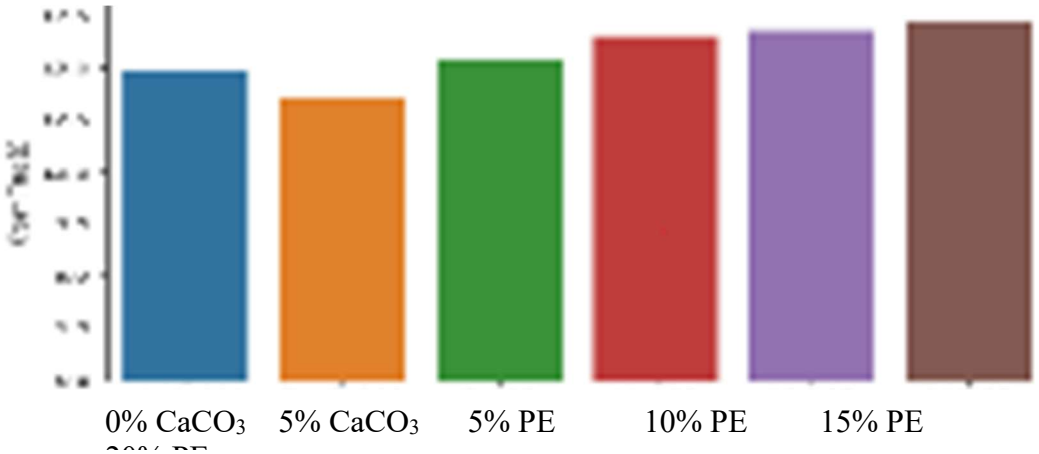

Figure 2: Cream Time of PUFs

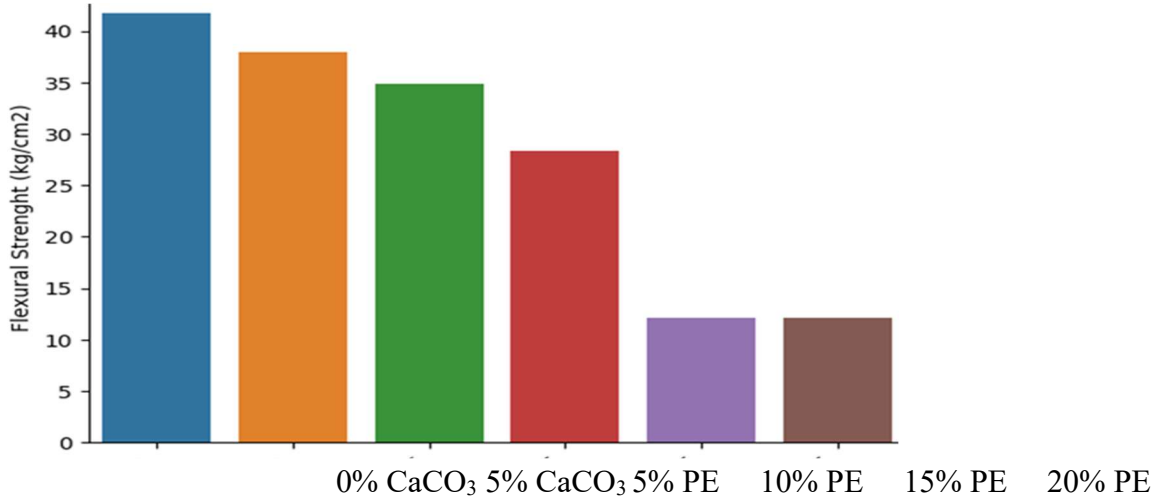

Figure 3: Flexural Strength of PUFs

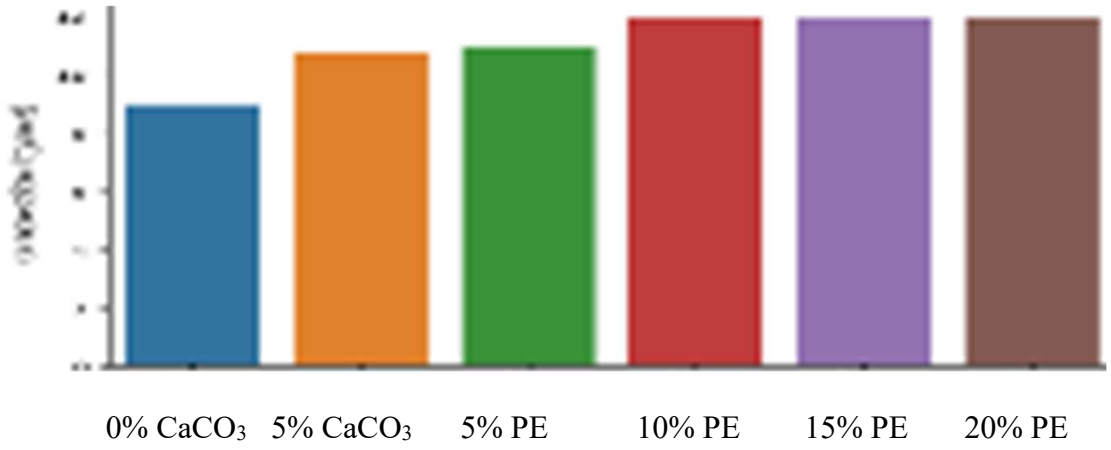

Figure 4: Compression of PUFs

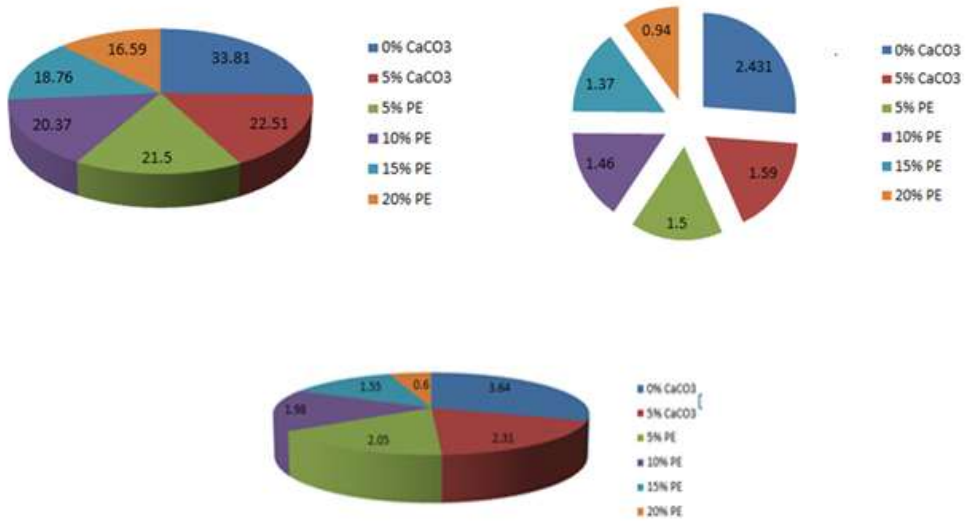

Figure 5: (a) Tensile Stress of PUFS, (b) Tensile Strain of PUFs and (c) Elongation of PUFs

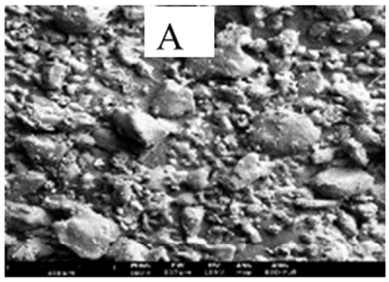

Plate 1: A – 0% Filler

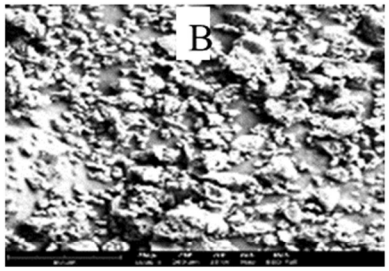

Plate 2: B – 5% $CaCO_3$

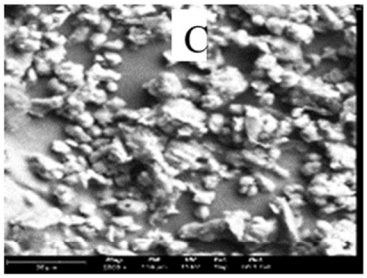

Plate 3: C – 5% PE

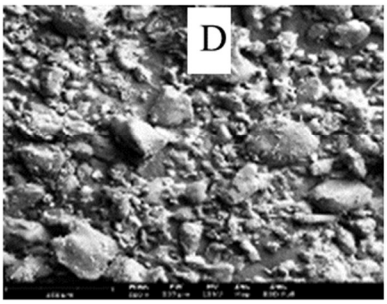

Plate 4: D - 10% PE

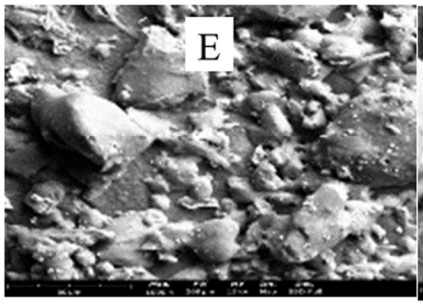

Plate 5: E - 15% PE

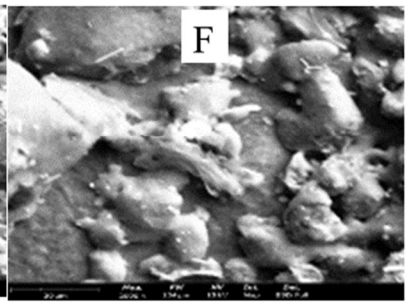

Plate 6: F - 20% PE

3.1 DISCUSSION

Table 1 provides data on various polyurethane foams (PUFs) with different compositions, specifically varying percentages of calcium carbonate ($CaCO_3$) and polyethylene (PE).

Various forms of polyurethane foam, describing their ingredients. The duration for blending the foam components. In all instances, it remains consistent at 15 seconds, implying a uniform mixing time for the foams. The time it takes for the foam to reach a creamy consistency after mixing. It varies for different formulations, with values ranging from 13.6 to 17.2 seconds. The time it takes for the foam to rise after reaching the creamy consistency. It also varies across different formulations, with values ranging from 108 to 124 seconds. The density of the formed polyurethane foam, measured in kilograms per cubic meter (kg/m^3). The density varies across different formulations, with values ranging from 21.64 to 26.44 kg/m^3. The filler did not show any significant effect on density of the flexible foams. This relates to a study by Javni (2002), in which micro – silica filler was used.

Table 2 shows how changing the composition of the polyurethane foam affects its cream time, rise time, and final density. For example, increasing the percentage of polyethylene (PE) generally results in a slightly higher density, and there are variations in the cream time and rise time as well. The consistent mixed time suggests a standardized mixing process across all formulations.

The kg/cm^2 measurement of the polyurethane foam determines its compression strength, indicating the highest level of perplexity and burstiness. It represents the maximum load the material can withstand under compressive forces. As the percentage of PE increases, the compression strength tends to increase. The maximum value allowed for compression strength according to the National Institute of Standards (NIS). In this case, the value is consistently 10 kg/cm2 for all formulations. Latinwo et al., (2010) suggested that the increase in the hardness of the foam by nano and micro fillers is due mainly to the random dispersion of the fillers into the polyurethane matrix. The interaction between the filler particles and the polymer matrix as a result of intercalation of the polymer chains into the filler galleries influence the chemical structures of the polymer chains. The strength of the material when subjected to bending or flexural forces. It decreases with an increase in the percentage of PE in the formulation. The ability of the material to withstand stretching or tensile forces. It generally decreases with an increase in the percentage of PE. This relate to a study by Zukowska et al., (2022), which ground tire rubber (GTR) was used as filler in flexible polyurethane foams, which shows it can be efficiently applied as a filler for flexible PU foams, which could simultaneously enhance their performance. The force per unit area applied to the material during tensile testing. It shows a decreasing trend as the percentage of PE increases. The measure of how much a material can stretch or deform before breaking. It decreases with an increase in the percentage of PE. the table indicates how changing the composition of the polyurethane foam affects its compression strength, flexural strength, tensile properties, and elongation. Generally, higher percentages of polyethylene (PE) result in lower mechanical properties for these specific foam formulations. They all have homogenous morphology.

4 CONCLUSION AND RECOMMENDATIONS

4.1 CONCLUSION

The use of water sachet waste film powder as filler in polyurethane foam production has proven to be an efficient in the production of polyurethane foams and it presents an environmentally friendly way of disposal of this waste, and it will go a long way in addressing the menace generated by the littering of these waste films. The soil fertility degradation as a result of the poor aeration and poor water penetration caused by these materials will be redirected thereby, improving compost for agriculture by separation of the waste films from other municipal solid wastes which are biodegradable.

Notably, the recycling LDPE into powder for the production of flexible polyurethane Foam can contribute to resource conservation. It allows for the reuse of plastic material, reducing the demand for new raw materials. Also, the services of people for the collection, sorting and cleaning of the wastes will be needed and as such, job opportunities will be created

It is worthy to state that the material generated is readily explorable for the production of insulators and packaging products in cold chain boxes and appliances that will enhance cold chain supply.

4.2 RECOMMENDATION

Further study should be carried out in combining *LDPE sachet water* with other types of polymers to investigate if it could provide a more effective and improved foam formulations suitable for conformations and templates that would present avenue for cold chain supply

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