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Mechanical Properties, Morphology and Elemental Composition of Composites Produced from Thermoplastic Polymers Filled with Egg Shell

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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ABSTRACT

The aim of this research is to develop environmentally friendly, lightweight composites using egg shell, as filler in some thermoplastic polymer matrices Polypropylene (PP), High Density Polyethylene (HDPE), Acrylonitrile-Butadiene-Styrene (ABS) and Polystyrene (PS) polymer; to determine the mechanical properties of the egg shell-residue polymer composite, to find if there is any new improvement over the properties of the starting thermoplastic polymer and determine the morphology and elemental composition of the composites. Egg shell was collected from the surroundings of Ekwulumili in Nnewi-South L.G.A of Anambra State, Eastern Nigeria where they have been dumped after usage. The research was carried-out at JUNENG NIG LIMITED Enugu, Civil Engineering Department Laboratory University of Nigeria and Chemical Engineering Department Laboratory Ahmadu Bello University (ABU), Nigeria; between May 2016 and August 2018. The agro-wastes were grand into power and incorporated into the virgin thermoplastic polymers as filler at varied levels of 3%, 6%, 9%, 12% and 15%. The virgin thermoplastic polymers were used as the Control in the study. The mechanical properties of the composites produced were determined using American standard for Testing and Materials (ASTM), Standard Testing Methods; Scanning Electron Microscopy (SEM) was used to determine morphology while Energy Dispersive Spectroscopy (EDS) was used to determine the elemental composition of the composites. The results generally showed significant improvements in the mechanical properties of the egg shell

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filler composites which were largely influence by the amount of filler in the composites. Modulus of elasticity/ tensile strength on almost all the polymer matrix (HDPE, PS, PP and ABS) composites at different percentages values of the properties had better strength. The HDPE loaded with egg shell filler has MoE (Modulus of Elasticity) at 3% of 1115.50 MPa (Mega Pascal) MPa, 6% of 1581.80 MPa, 9% of 662.40 MPa, 12% of 894.34 MPa and 15% of 998.64 MPa, Control (pure HDPE) of 348.38 MPa. For PS the graphs show the result of the 9%, 6%, 12%, 15%, 3% from highest to lowest value to be 1982.60 MPa > 1255.10 MPa >1099.60 MPa > 972.22 MPa > 730.45 MPa and the Control gave 955.59 MPa. The values of PP matrix loaded were 3% (805.71 MPa) > 12% (747.18 MPa) > 9% (571.96 MPa) > 6% (514.18 MPa) > 15% (371.98 MPa), pure PP matrix of 428.20 MPa. ABS/egg shell MoE values were observed as follows: 6% (559.00 MPa) > 3% (384.66 MPa) > 12% (382.84 MPa) > 15% (372.66 MPa) > 9% (327.61 MPa) and control (160.68 MPa). The values of tensile strength for the HDPE egg shell filler composite obtained are 3% (49.02 MPa) > 6% (30.43 MPa) > 12 % (20.56 MPa) >15% (14.81 MPa) > 9% (10.69 MPa) respectively and pure HDPE matrix obtained was 7.40 MPa. For PS egg shell filler composite obtained are 9% (20.56MPa) > 12% (12.34MPa) > 6% = 15% (10.69MPa) > 3% (7.40 MPa) respectively while that of control was (12.34 MPa). PP composites at different percentage loading of egg shell filler show that the values of 3% (12.33 MPa) = 6% (12.33 MPa) > 12% (9.87 MPa) > 9% (5.75 MPa) > 15% (4.93 MPa) and the Control 8.88 MPa respectively. In ABS, the value of 6% (12.34 MPa) > 3% =12% (9.05 MPa) >15% (8,06 MPa) > 9% (7.40 MPa),and 6.58 MPa for pure ABS matrix respectively. The tensile, statistical correlation coefficient using Pearson product-moment between the Control and agro-waste fillers loading on polymer matrices used at different percentages of stress and strain indicate strong positive relationship between the variables. It is evident from the results that HDPE, PS and ABS matrices filled with egg shell composites reinforced at different percentages showed maximum flexural strength than the Control. HDPE at 12% (33.57 N/mm^2), 9% (25.43 N/mm^2), 6% (18.77 N/mm^2), 3% (16.50 N/mm^2) and 15% (16.25 N/mm^2), while control (14.92 N/mm^2). PS polymer composite, only 9% (14.32 N/mm2) value had reduced flexural strength than the Control (17.41 N/mm^2); at 6% (34.84 N/mm^2), 3% (27.35 N/mm^2), 15% (24.24 N/mm2) and 12% (18.65 N/mm2) respectively had higher values than the Control. For PP, 6% (27.35 N/mm^2) > 3% (22.37 N/mm^2) > 9% (19.90 N/mm^2) > 12% (13.72 N/mm^2) and > 15% (6.22 N/mm^2) respectively had lower values. ABS, 9% (28.60 N/mm^2) > 6% (26.67 N/mm^2) > 15% (17.50 N/mm^2) > 12% (15.65 N/mm^2) and > 3% (13.67 N/mm^2). Scanning electron microscopy (SEM) was carried out on the samples using imageJ software to estimate the average particle size of the polymer egg shell waste. In some of the composite structures, the particle of the filler material appeared to be homogeneously dispersed in the egg shell-waste/polymer composites; some appeared to be heterogeneously dispersed with voids of white patches while some form an agglomerated mass of different dimensions. The elemental compositional analysis, using Energy Dispersive Spectroscopy (EDS) had all samples contain C and N as a major element present and others as trace; Fe, Al, Mg, P, Zn, Si. This study has provided different combinations of egg shell-waste/egg shell- residue thermoplastic polymer composites which has potential application in the automobile and building construction industry.

Keywords: Egg shell; polymer matrices; composites; tensile; modulus of elasticity; flexural; percentages (3%, 6%, 9%, 12% and 15%).

1. INTRODUCTION

In the current years, composites fulfil optimal requirement criteria for several designers' materials. Composite materials are materials produced from two or more constituent materials with notably dissimilar chemical or physical properties that, when merged, create a material with properties, unlike the individual elements. The individual components remain separate and distinct within the finished structure, distinguishing composites from mixtures and solid solutions. Natural fillers are increasingly in demand across a wide range of polymer-composite materials originate from plants, crops, animals, agro-waste, or other natural sources that are renewable and biodegradable after their end-use. Several researchers have tailored their work towards defining abundant combinations of matrix/natural fillers in order to obtain new classes of composites with enhanced mechanical properties, and of lower cost. The Natural Fillers used as reinforced materials offer several environmental

advantages such as decreased dependence on non-renewable material sources, lower pollution and green house emission. Natural fibres are the most copious and renewable bio-based materials source in nature. Natural fibres are primarily based on their origins, either coming from plants, animals, or minerals. All plant fibres are composed of cellulose, while animal fibres consist of proteins (hair, silk, and wool) [1]. Natural lignocellulose fillers (flax, jute, hemp, etc.) represent an environmentally friendly alternative to conventional reinforcing fibres such as glass and carbon. Bio-fibres are used for formulation of composites because of their low cost, ease of separation, lower density, enhanced energy recovery, higher toughness, and reduced dermal and significant biodegradability [2]. Stiffness and strength are provided by natural fibres to the composites. They are easily recyclable; moreover, bio-fibres will not be fractured when processing over sharp curvatures, unlike brittle fibres, such as glass. In terms of strength per weight of the material, bio-fibres also compete perfectly when compared with conventional or traditional fibres, such as mica and glass, which are generally used for composites [1]. Natural-fibre-based packaging materials possess various benefits over synthetic packaging materials, such as stiffness, recyclability and weight ratio [3]. Current literature shown a studied-on comparing two types of fillers (RHP and talc) in preparing PP composites used a Brabender Plasti-Corder internal mixer at 180°C, which contained 0, 15, 30, 45, and 60 parts of fillers per hundred parts of polymer (php). The processability and mechanical properties of the composites with respect to the filler type and filler content were investigated. It was found that talc composites are easier to process than RHP filled polymer composites. They reported that, in terms of mechanical properties, Young's modulus and flexural modulus increased, whereas yield strength and elongation at break decreased with the increase in filler contents for both types of composites. They observed that the PP/RHP composites have lower yield strength, Young's modulus,flexuralmodulus,andhigherelongation at break than PP/talc composites [4].

The aim of this research is to develop environmentally friendly, lightweight composites using cow horn, as filler in some thermoplastic polymer matrices Polypropylene (PP), High Density Polyethylene (HDPE), Acrylonitrile-Butadiene-Styrene (ABS) and Polystyrene (PS) polymer; to determine the mechanical properties of the agro-residue polymer composite, to find if there is any new improvement over the properties of the starting thermoplastic polymer and determine the morphology and elemental composition of the composites.

2. METHODOLOGY

Egg shell was collected from the surroundings of Ekwulumili in Nnewi-South L.G.A of Anambra State, Eastern Nigeria where they have been dumped after usage. Commercial virgin polymer matrices were purchased from one of the Petrochemicals company, Nigeria. The polymeric matrices used in this research are pellets of Polypropylene (PP), High Density Polyethylene (HDPE), Acrylonitrile-Butadiene-Styrene (ABS) and Polystyrene (PS) polymer. The equipment used were Monsanto Tensiometer, weighing balance, ventilated oven, 0.2 µm mechanical sieve, Scanning Electron Microscopy (Phenom, model proX SEM), Energy Dispersive Spectroscopy (EDS) and Universal Testing Machine (UTM) 5569 A (JJ Lloyd, London, United Kingdom, capacity 1-20 KN) in accordance with ASTM D638 for tensile strength and flexural strength. Zinc Stearate was used as a protective incorporated.

Egg shell was washed with clean running water, sun dried and then was broken into pieces with mechanical grinding mill machine. The broken pieces were then ground produce fibre powder and then they were separated with 0.2µm mechanical sieve to get the particle form.

Inside a beaker 1 g NaOH was added into 99ml of distilled water to make solution. After adequate drying of the fibres for 2 to 3 hours, the fibres were soaked in the prepared NaOH solution. Soaking was carried out at different time intervals depending upon the strength of fillers/fibre required.

The fibres were then taken for compression moulding and the particle sized of the filler used were 3 g, 6 g, 9 g, 12g and 15 g of coconut shell fillers. The composites were prepared using the following blending formulation:

2.1 Egg Shell/Polymer Composite Formulation

One hundred grams (100 g) each of polymer matrices were used as a starting material (Control) before reinforcement of various percentages such as 3%, 6%, 9%, 12% and

15% of egg shell fillers were added into the different polymer matrices used. Polymer matrices blended with particle size of the agro-wastes fillers were measured into a compression mould, for example 97g of acrylonitrile butadiene styrene matrix blended with 3g of egg shell filler was measured before subjecting the mixtures to compression moulding to produce the composites. Zinc stearate was used as protective incorporated coated into polymer matrix composite to prevent adhesion to the plastic surface and it was mixed into resin for compression moulding. Polymer matrix composite was placed between them and then the mould was closed; heat and pressure were applied to obtain a homogeneous composite. A preheating time of about 1 hour at 120°C was needed for moulding and 30 minutes for cooling to get the solid moulding. Rapid cooling (quenching) was applied at the end of holding time. After processing, specimens were cut into the desired size and shape before the characterization of the samples. Each of the experiment was carried out severally in order to obtain accurate data.

Chart 1. Weight of Polymer matrices and Agro-Wastes Filler

Weight of polymer matrices (g)	Weight of agro-wastes filler in composites (g)
100	0.0
97	3.0
94	6.0
91	9.0
88	12.0
85	15.0

2.2 Mechanical Properties

All the tests were carried out using International Standards such as American Society for Testing Materials (ASTM) standards. Universal Testing Machine (UTM) 5569A was suitable for many mechanical tests of polymer matrix composites. The composites containing 3%, 6%, 9%, 12%, 15% w/w filler each were prepared and the mechanical properties examined. The parameters determined were tensile, modulus of elasticity and flexural.

2.2.1 Tensile strength, modulus of elasticity and flexural test

Tensile strength test is a measurement of elasticity. This test was applied to observe the strength of the polymer matrix composites and it is common procedure for studying the stress–strain relationship. Flexural strength test is defined as the ability of materials to resist deformation under load or measurement of bending under pressure. This is used to measure the rigidity of the polymer matrix composites. A dog bone-shaped specimen was prepared according to International Standard (i.e. ASTM: D638) for tensile strength test and flexural strength test (i.e. ASTM: D638); the equipment used was Tensometer and each of the property samples were tested several times.

Procedure:

i. The samples were cut into a dog bone-shaped specimen according to ASTM D638 (160 × 19 × 3.2) mm (Length × Breadth × Thickness).
ii. The chucks of the tensile test were fixed on the nose pieces of the tensometer.
iii. The test pieces were inserted one at a time into the tensile chucks and locked up appropriately.
iv. While for flexural strength test; test piece was cut with respect to ASTM (300× 19 × 3.2) mm dimension.
v. The chucks of the flexural tester were fixed on the nose piece of the tensometer.
vi. The Sample were inserted into the 3-point flexural tester chamber and ensured a firm grip.
vii. The tensometer graphs for each of parament at different level were fixed to the graph drum of the machine and ensured a firm grip.
viii. The working fluid (mercury) of the machine and the load/ extension scale were properly set at zero.
ix. Gradual but continuous load through the longer handle of the machine was applied; this helped the working fluid to begin its movement.
x. At each interval, the recording pin attached to the cursor was pressed down with the left hand while the right hand was gradually loading the machine.
xi. By so doing, the load / extension property of the test piece is drawn on the graph attached to the revolving recording drum.
xii. The test piece was removed when its failure brakes occurred, then the mercury level returns back through the varida glass tube to zero level.
xiii. The true values of the loads and extension were extracted and converted into stress/ strain.

xiv. The stress / strain of the test pieces was calculated, using each of the values from the loads and extensions. Tensile strength and MoE of the test pieces were determined and measured after re-plotting the graph for Stress/ Strain.

Using ASTM D638 standard (160 ×19× 3.2) mm, that is length = 160 mm, breadth =19 mm and thickness=3.2 mm.

$$\text{Stress} = P / A_O$$

Where P is the force,

A_O is the cross-sectional area and unit is N/mm^2, 1 N/mm^2 =1 MPa.

For cross-sectional Area,

A_O = breadth × thickness (depth)

A_O= 19 × 3.2

A_O= 60.80MPa

$$\text{Strain} = (L_I - L_O) / L_O$$

$$\triangle L = X / L_O$$

Where

L_I = length after the test

L_O = initial length before the test (160 mm)

X = (Measured value) / 4

Each value from extension is the measured value and 4 is the magnification of the test pieces drawn on the graph attached to the revolving recording drum.

The graph of the Stress / Strain of the test pieces were re-plotted to determine/ measure the Tensile strength and MoE of the test pieces.

Tensile strength of each of the polymer matrix composite was calculated as maximum force divided by cross-sectional area:

$$\text{Tensile strength} = P / A_O$$

Where P is the maximum force, A_O is the cross-sectional area.

xv. While in flexural strength; using the flexural load recorded, the flexural strength of the sample was calculated using the equation below:

$$F_t = 2$$

Where

F_t = Flexural strength (N/mm^2)

P = recorded constant load (N)

L = the span length of the test piece = 300 mm

b = breadth of the test piece = 19 mm

and

d = thickness / depth of the sample = 3.2 mm

2.2.2 Morphology and elemental composition analyses

Morphology analysis using Scanning Electron Microscopy (Phenom, model proX SEM) served as an effective means for the investigation of morphology in the composite system; the Scanning Electron Microscopy (SEM) study of polymer-filler composite produced images of samples by scanning the surface with a focused beam of electrons.

Elemental Composition analysis using Energy Dispersive Spectroscopy (EDS) served as an effective means to discover the surface elemental composition and estimate their proportion at different position, consequently given an overall mapping of the sample.

3. RESULTS AND DISCUSSION

The egg shell samples results generated at different percentage fillers of agro-wastes/polymer matrix composites were presented.

3.1Tensile Strength Result for Modulus of Elasticity (MPa)

Table on Modulus of Elasticity (MoE) values for egg shell-waste/polymer matrix composite at 3%, 6%, 9%, 12% and 15% agro-waste levels.

Table 1. Modulus of Elasticity (MoE) values for egg shell-waste/polymer matrix composite

			Different percentages fillers loading				
Agro-waste	**Polymer matrices**	**Control**	**3%**	**6%**	**9%**	**12%**	**15%**
Egg shell	HDPE	348.38	1115.50	1581.80	662.40	894.34	998.64
	PS	955.59	730.45	1255.10	1982.60	1099.60	972.22
	PP	428.20	805.71	514.18	571.96	747.18	371.98
	ABS	160.68	384.66	559.00	327.61	382.84	372.66

3.2 Tensile Strength Test (MPa)

Table on Tensile strength values for egg shell/polymer matrix composite at 3%, 6%, 9%, 12% and 15% agro-waste levels.

3.3 Flexural Strength Test (N/mm^2)

Table on Flexural strength values for egg shell/polymer matrix composite at 3%, 6%, 9%, 12% and 15% agro-waste levels.

Table 2. Tensile strength values for egg shell/polymer matrix composite

			Different percentages fillers loading				
Agro-waste	**Polymer matrices**	**Control**	**3%**	**6%**	**9%**	**12%**	**15%**
Egg shell	HDPE	7.40	49.02	30.43	10.69	20.56	14.81
	PS	12.34	7.40	10.69	20.56	12.34	10.69
	PP	8.88	12.33	12.33	5.75	9.87	4.93
	ABS	6.58	9.05	12.34	7.40	9.05	8.06

Table 3. Flexural strength values for egg shell/polymer matrix composite

			Different percentages fillers loading				
Agro-waste	**Polymer matrices**	**Control**	**3%**	**6%**	**9%**	**12%**	**15%**
Egg shell	HDPE	14.92	16.50	18.77	25.43	33.57	16.25
	PS	17.41	27.35	34.84	14.32	18.65	24.24
	PP	24.27	22.37	27.35	19.90	13.72	6.22
	ABS	6.96	13.67	26.67	28.60	15.65	17.50

Pictogram on Tensile Modulus of Elasticity and Tensile Strength of Egg Shell/Polymer

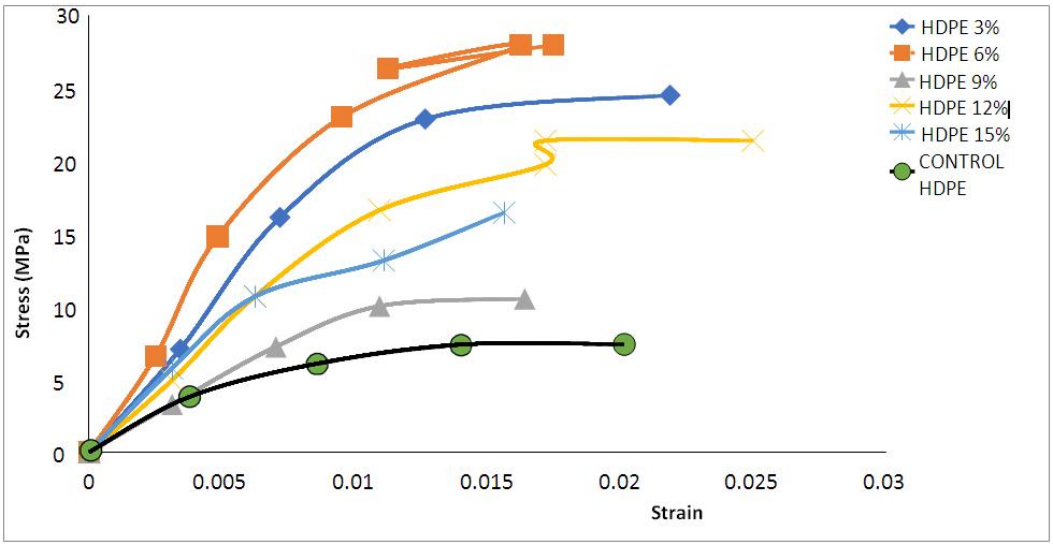


Fig. 1. 1a Stress-strain curves of the control (HDPE) and hdpe-egg shell composites at 3% - 15% filler levels

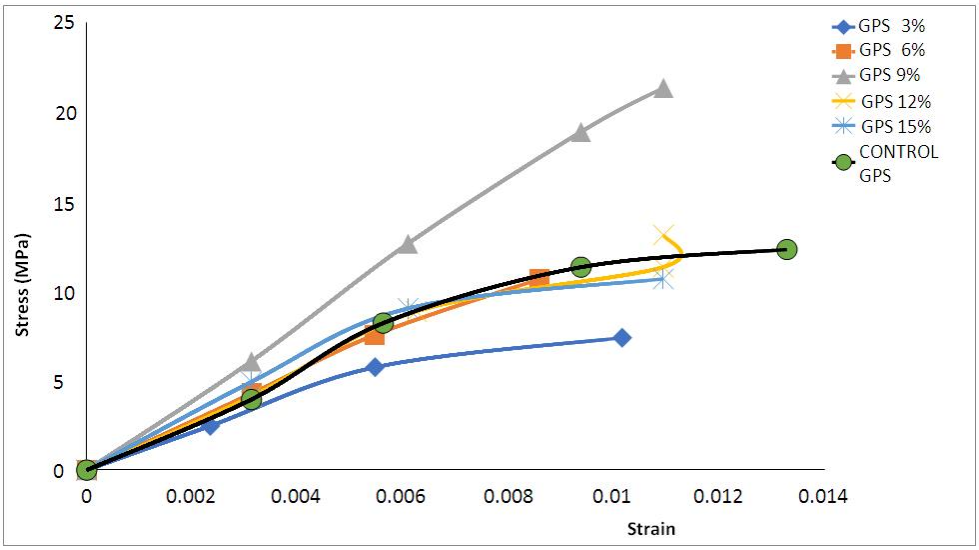


Fig. 1.1b stress-strain curves of the control (PS) and PS-egg shell composites at 3% -15% filler levels

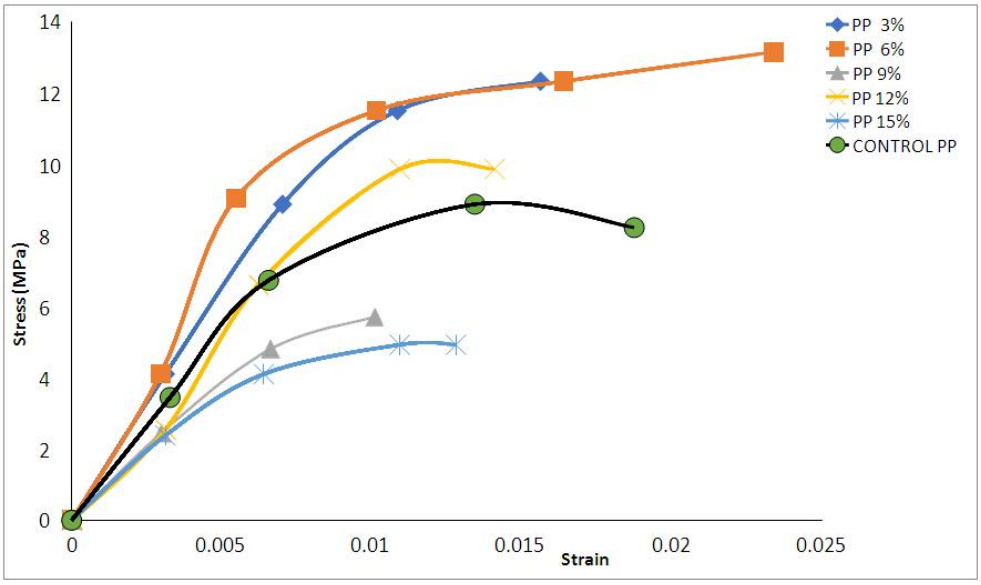


Fig. 1.1c Stress-strain curves of the control (PP) and PP-egg shell composites at 3% -15% filler levels

3.4 Modulus of Elasticity and Tensile Strength

The modulus of elasticity (Young's modulus) E is a material property that describes its stiffness and is therefore one of the most important properties of solid materials. The statistical correlation coefficient using Pearson product-moment between the control and egg shell filler loading on polymer matrices used at different percentages of stress and strain indicates a strong positive relationship between the variables. The correlations are statistically significant because their *p*-value is less than the significance level of 0.05.

The result of the egg shell filler loading reinforced on polymer matrices composites are shown in Tables 1-2 and Figs. 1.1(a) – 1.3(d; the plot of stress – strain curves for HDPE,

PS, PP and ABS reinforced with different percentages of egg shell fillers are shown. The slopes of the graph represent the modulus of elasticity (MoE) of the composites and Fig. 1.2(a-d) shows the bar chart that represents the variation of the MoE with percentage loading of egg shell filler respectively.

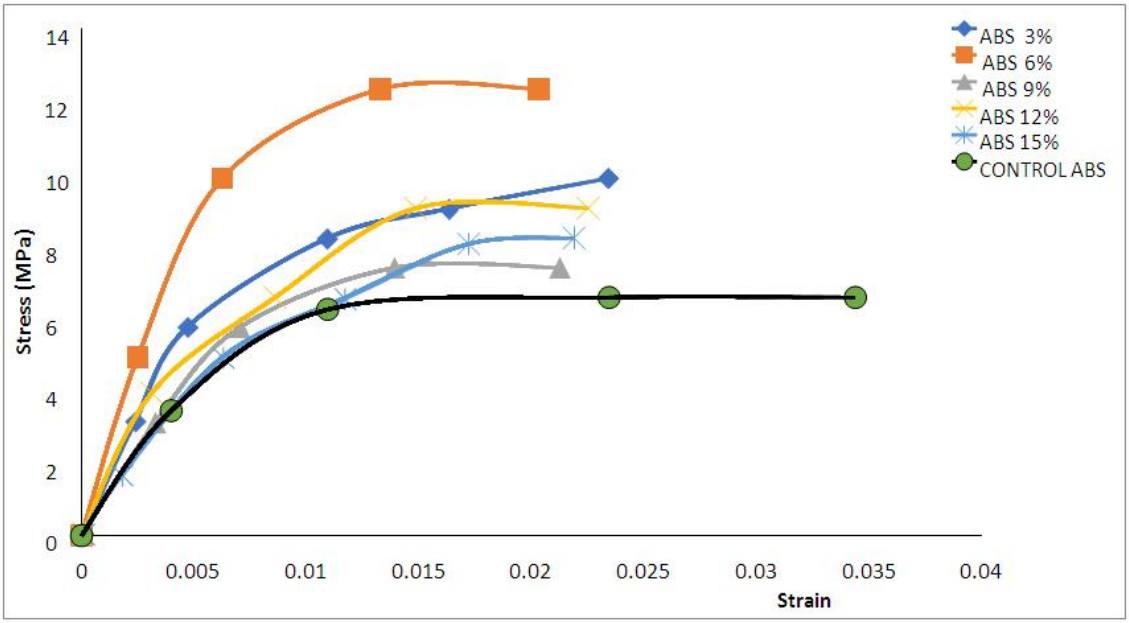


Fig. 1. 1d Stress-strain curves of the control (ABS) and ABS-egg shell composites at 3% -15% filler levels

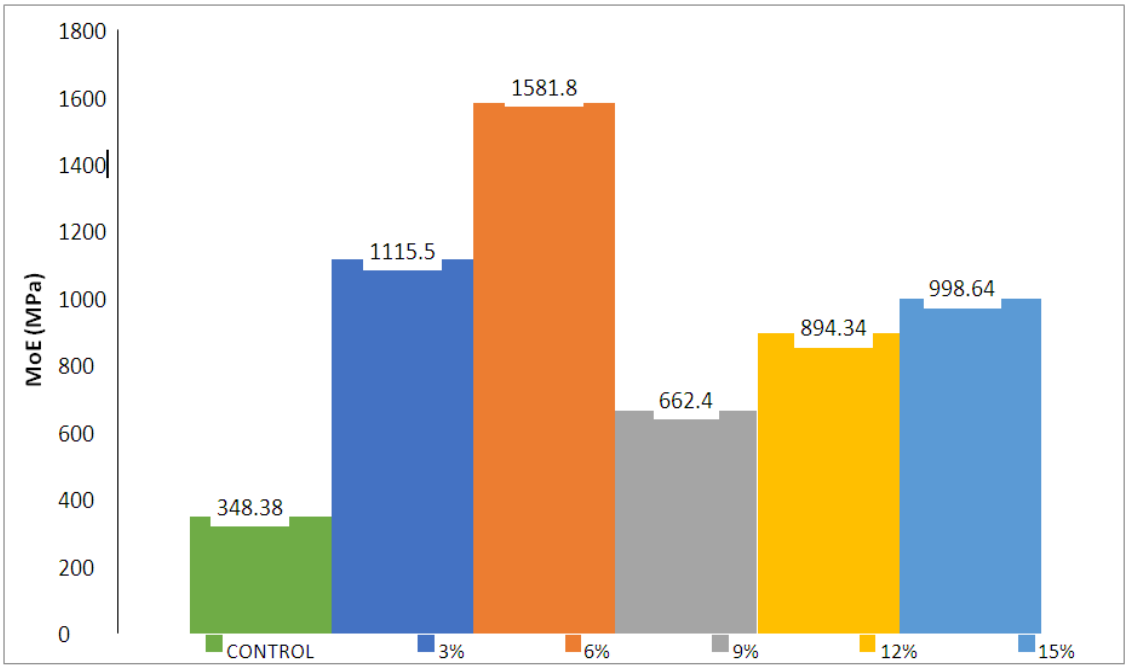


Fig 1.2a. MoE values of the control (HDPE) and HDPE-egg shell composites at 3%-15% filler levels

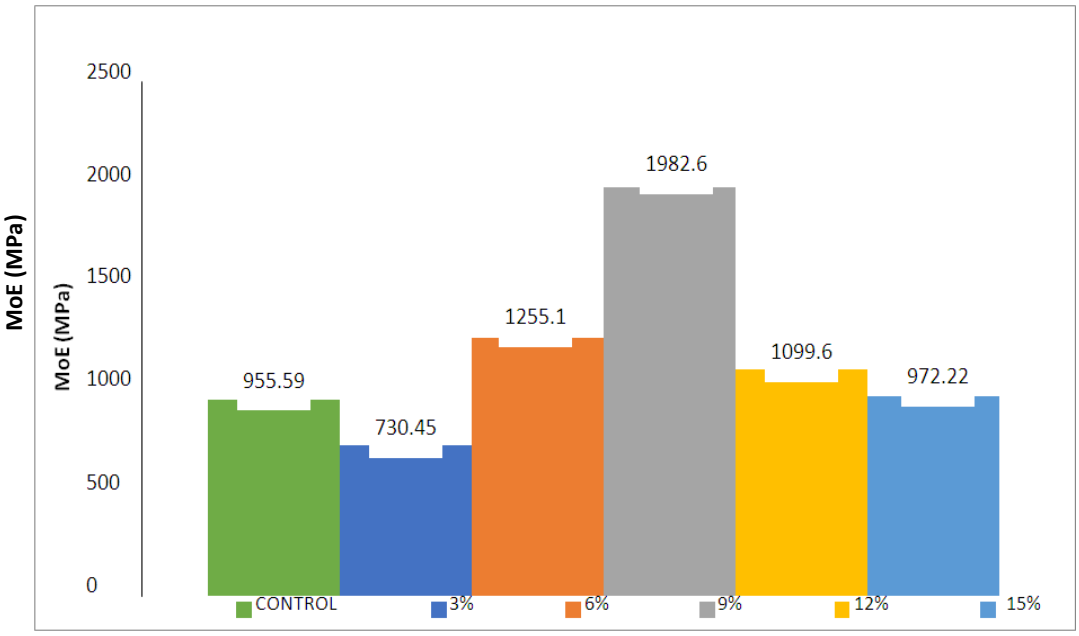


Fig. 1.2b. MoE values of the control (PS) and PS-egg shell composites at 3%-15% filler level

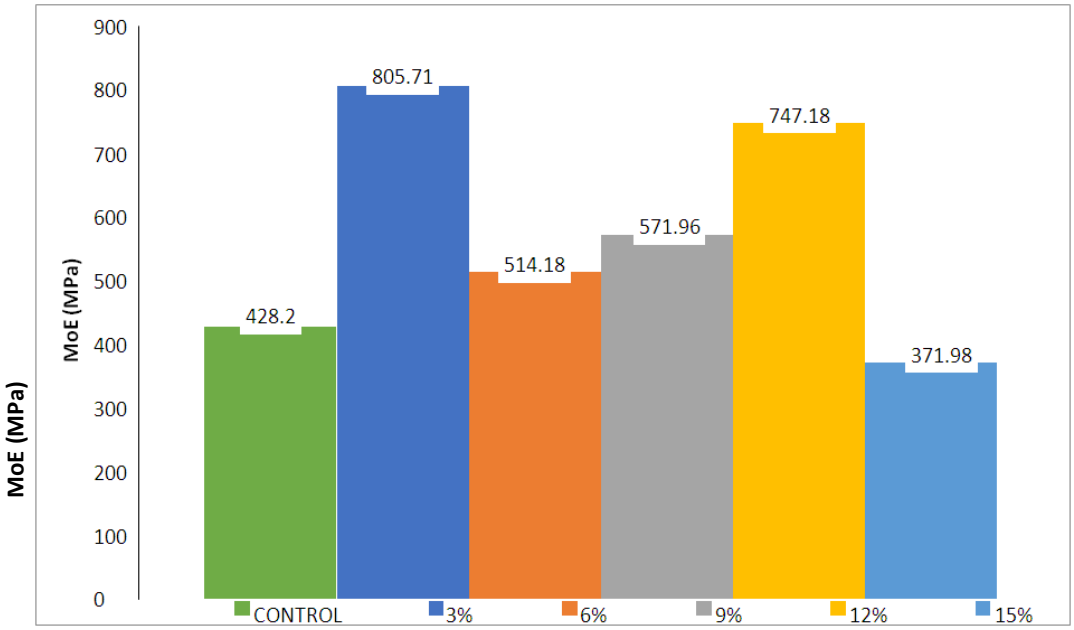


Fig 1.2c. Values of the control (PP) and PP-egg shell composites at 3%-15% filler levels MoE

3.4.1 HDPE matrix for MoE

The HDPE loaded with 3% of egg shell filler has MoE of 1115.50 MPa, 6% has MoE of 1581.80 MPa, 9% has MoE of 662.40 MPa, 12% has MoE of 894.34 MPa and 15% of egg shell filler has MoE of 998.64 MPa, when compared with the Control (pure HDPE) of 348.38 MPa. It is evident that the incorporation of egg shell at all levels filler to HDPE polymer matrix reinforced the polymer by the increase its MoE; there were increase in stiffness of HDPE/egg shell composites and this in turn increased the brittleness of the composites; although improve of stiffness in the composites is desirable but brittlenessisundesirable.

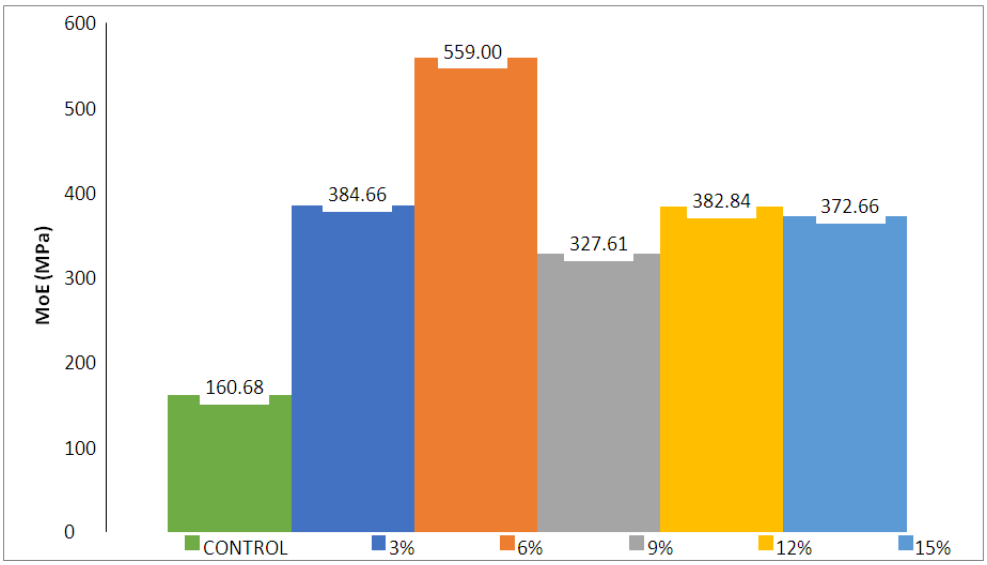


Fig. 1. 2d. MoE values of the control (ABS) and ABS-Egg Shell Composites at 3%-15% Filler levels

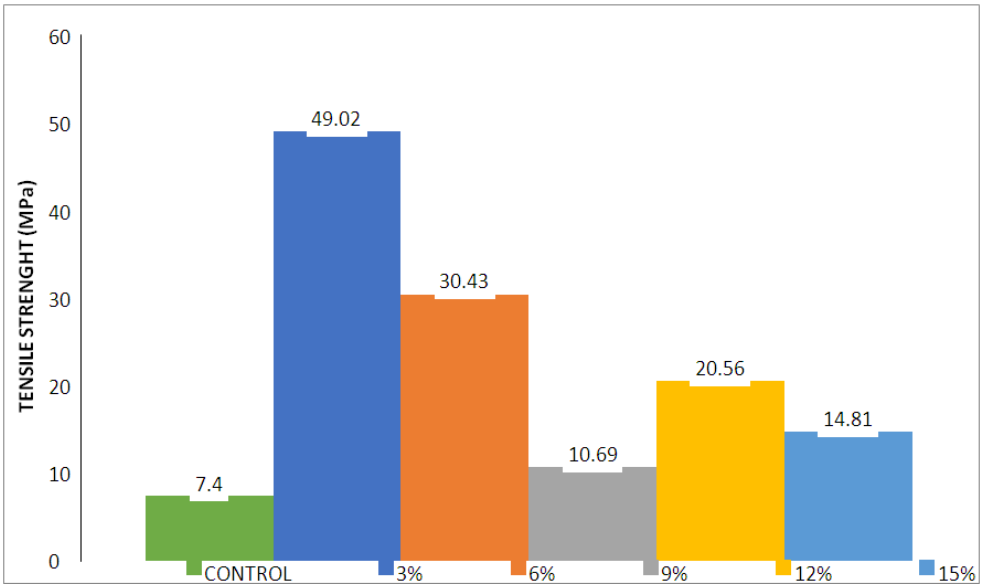


Fig. 1. 3a Tensile strength values of the control (HDPE) and HDPE-egg shell composites at 3%-15% filler levels

3.4.2 PS matrix for MoE

For PS the graphs show the result of the 9%, 6%, 12%, 15%, 3% from highest to lowest value to be1982.60 MPa > 1255.10 MPa >1099.60 MPa > 972.22 MPa > 730.45 MPa and the Control gave 955.59 MPa. It is evident that reinforcing PS with egg shell filler at 6%, 9%, 12% and 15% of egg shell filler led to increase in the MoE which ultimately increased the brittle tendency of the polymer composites. This suggests that 3% egg shell filler is not sufficient to cause reinforcement of the PS matrix.

3.4.3 PP matrix for MoE

The values of the MoE of the composites obtained from the slopes of the curve of PP matrix loaded were 3% (805.71 MPa) > 12%

(747.18 MPa) > 9% (571.96 MPa) > 6% (514.18 MPa) > 15% (371.98 MPa). When compared with MoE of pure PP matrix of 428.20 MPa, it was observed that composite formed with 3% of egg shell filler has the highest MoE which decreases as the percentage of the egg shell filler increases although there was no specific pattern of decrease. MoE of the composite formed with 15% of egg shell filler was the least as its value is far much below the Control. The decrease in MoE at higher concentration may be due to poor interfacial bonding between the particles of the egg shell filler and the polymer matrix which leads to creation of partially separated micro – spaces (voids) which obstruct stress propagation between the egg shell filler and the polymer matrix [5].

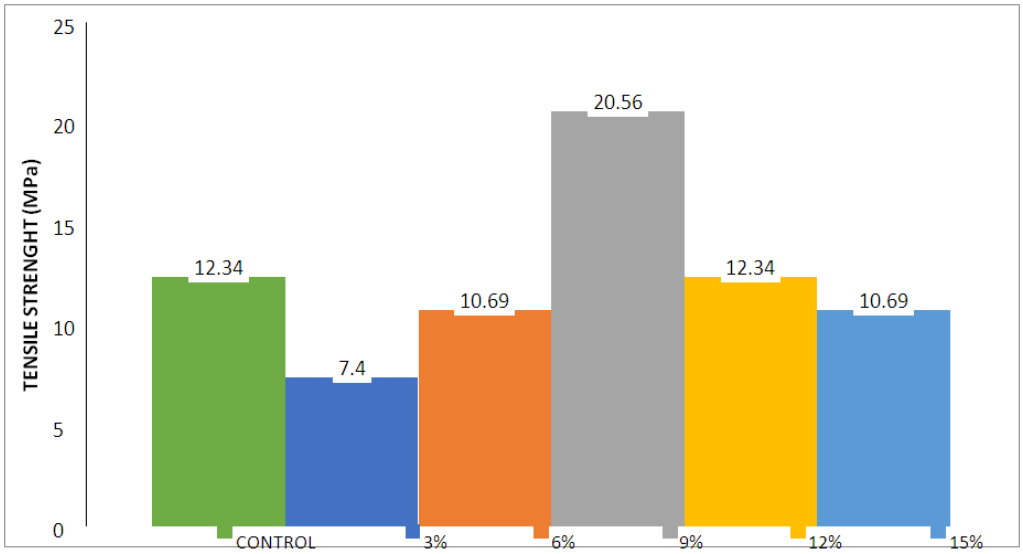


Fig 1.3b. Tensile Strength Values of the control (PS) and ps-egg shell composites at 3%-15% filler levels

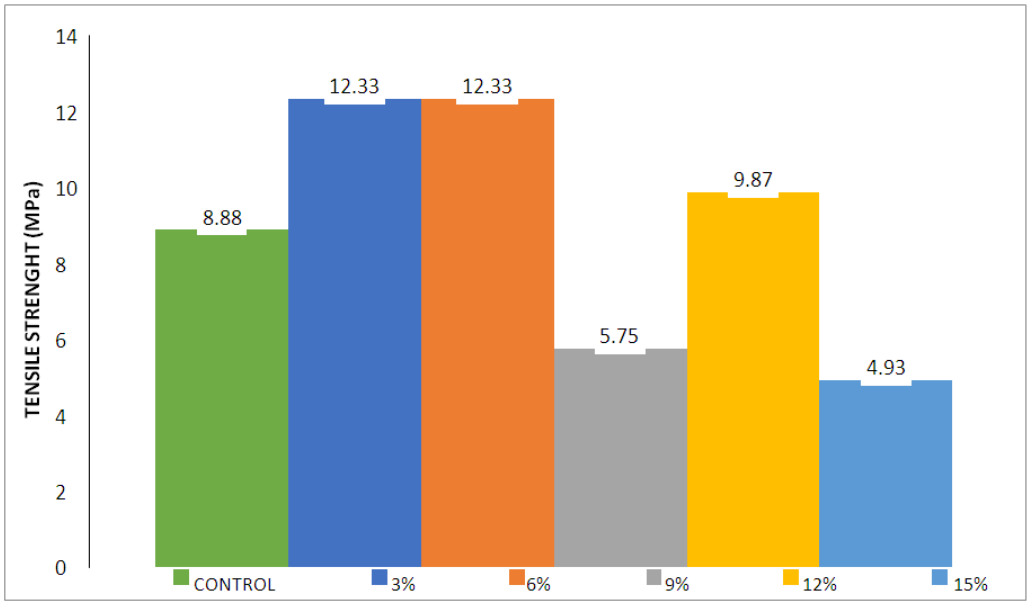


Fig 1. 3c.Tensile strength values of the control (PP) and PP-egg shell composites at 3%-15% filler levels

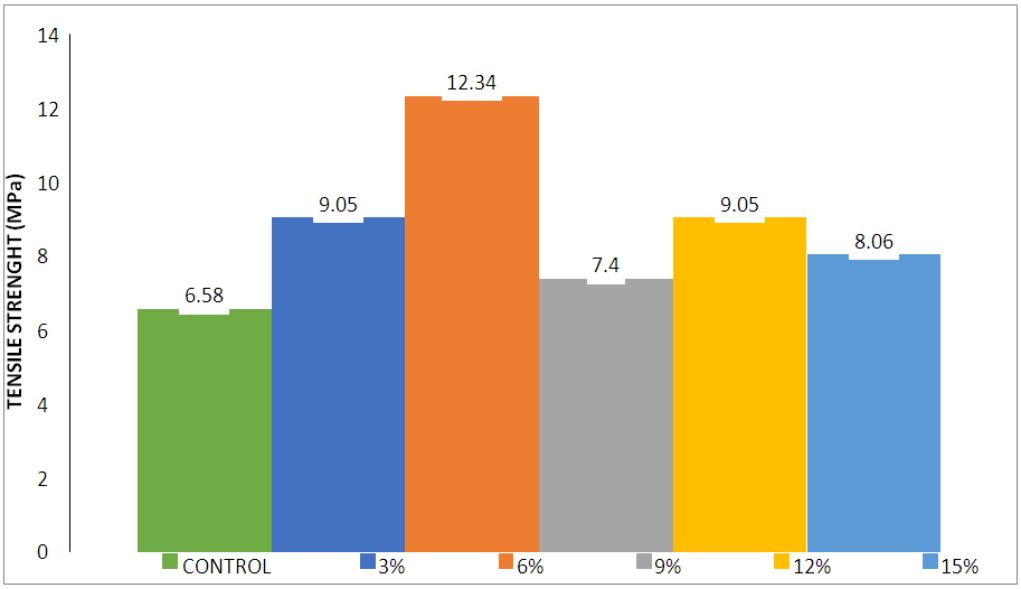


Fig. 1. 3d. Tensile strength values of the control (ABS) and ABS-egg shell composites at 3%-15% filler levels

Pictogram on Flexural Strength of Egg Shell/Polymer Composite

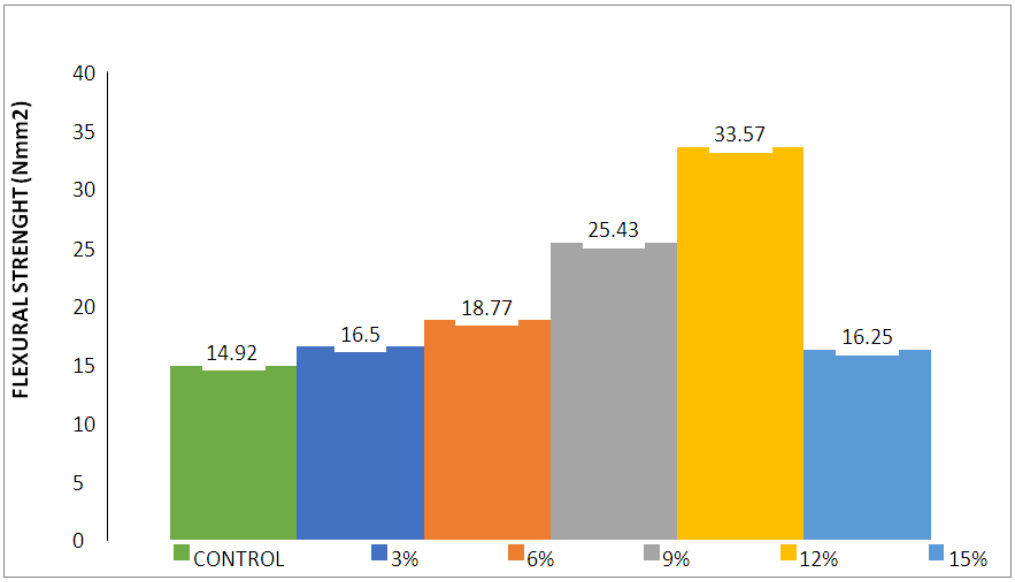


Fig. 2a. Flexural strength values of the control (HDPE) and HDPE-Egg shell composites at 3%-15% filler levels

3.4.4 ABS matrix for MoE

ABS/egg shell MoE values were observed as follows: 6% (559.00 MPa) > 3% (384.66 MPa) > 12% (382.84 MPa) > 15% (372.66 MPa) > 9% (327.61 MPa). Generally, these increases in MoE of the ABS matrix were observed in all of the egg shell levels when compared with the control (160.68 MPa), showing significant influence of egg shell filler on the MoE of ABS matrix. The highest MoE of 559.00 MPa at 6% filler loading which is about 370% increase shows that there was homogeneous dispersion of the filler within the polymer matrix at relatively

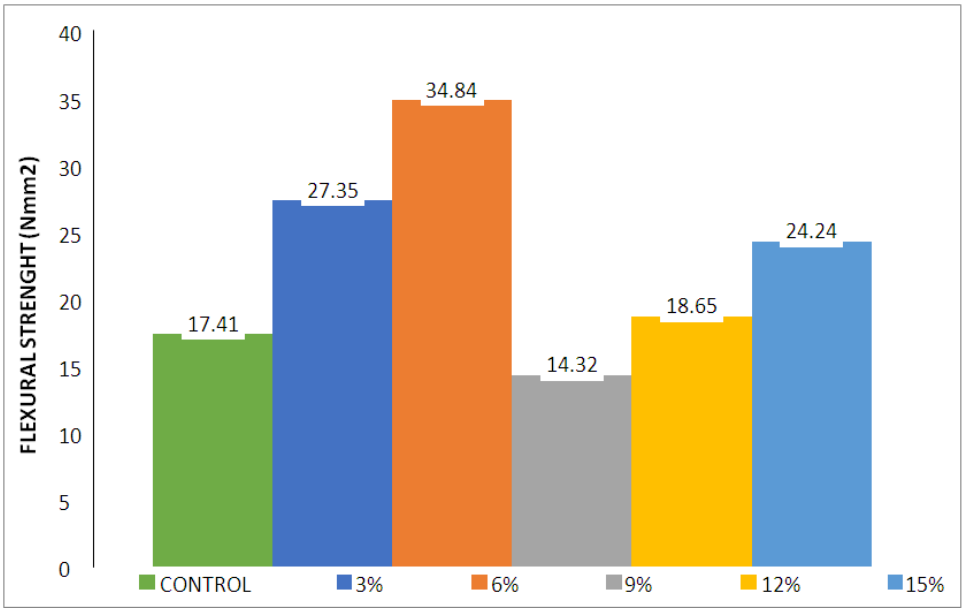


Fig. 2b. Flexural strength values of the control (PS) and PS-Egg shell composites at 3%-15% filler levels

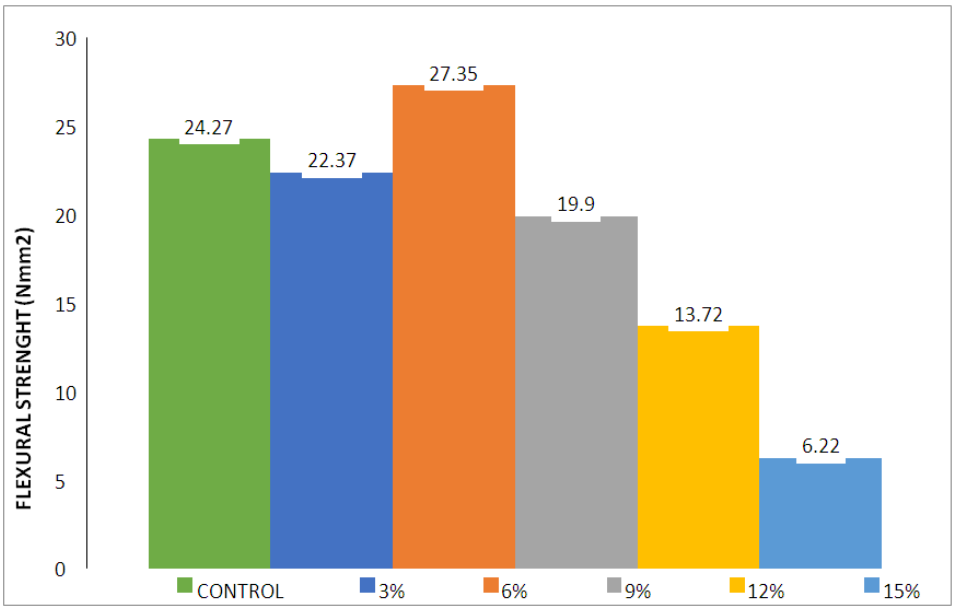


Fig. 2c. Flexural strength values of the control (PP) and PP-Egg shell composites at 3%-15% filler levels

lower percentage of egg shell filler. Also it is worthy to note that increase above 6% of the egg shell filler leads to decrease in MoE of the ABS polymer matrix, which suggests that 6% is the optimum egg shell filler level for reinforcement consequently, any further increase in the filler level results in no reinforcing effect as seen in the decreased MoE values for 9%- 15%.

3.5 Tensile Strength

Table 2 and Fig. 1.3(a-d) show the data and bar chart that represent the variation of tensile

strength of HDPE, PS, PP and ABS composites loaded with 3%, 6%, 9%, 12% and 15% of egg shell filler respectively.

3.5.1 HDPE matrix for tensile strength

The values of tensile strength for the HDPE egg shell filler composite obtained are 3% (49.02 MPa) > 6% (30.43 MPa) > 12 % (20.56 MPa) >15% (14.81 MPa) > 9% (10.69 MPa) respectively and pure HDPE matrix obtained was 7.40 MPa. There is an improvement of the tensile strength due to addition of egg shell filler. Highest value of tensile strength for the HDPE egg shell composite was obtained when 3% of the filler material was added to the polymer. This suggests good dispersion of egg shell filler within the matrix of the polymer which leads to strong interfacial bonding between the particles of the egg shell filler and the polymer.

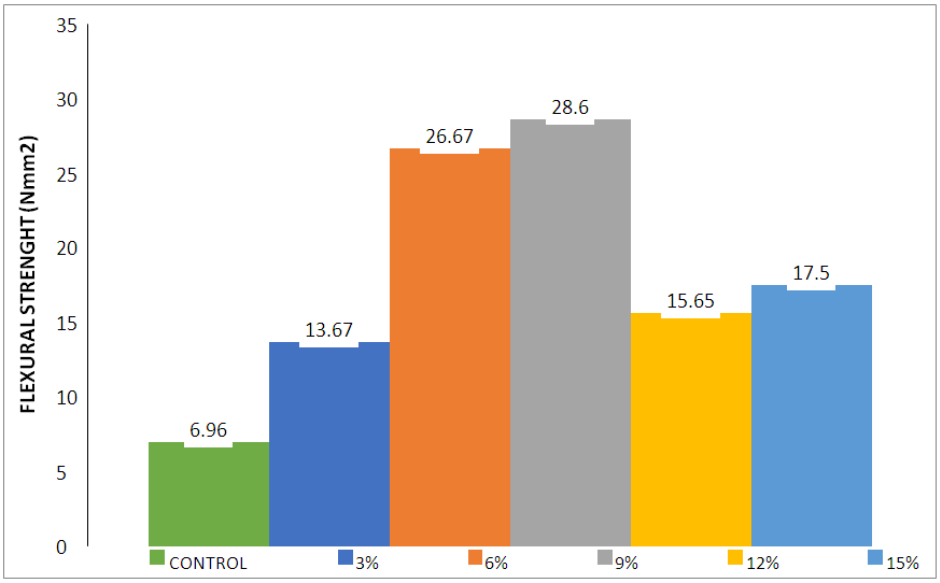


Fig. 2d. Flexural Strength Values of the Control (ABS) and ABS-Egg Shell Composites at 3%-15% Filler Levels

Surface Morphology of Egg Shell/Polymer Composites

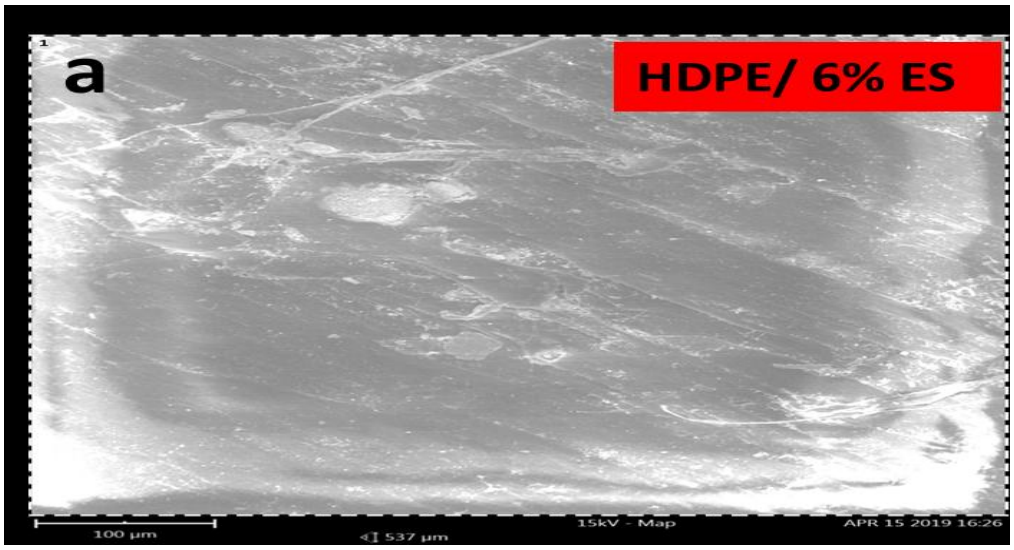


Fig. 3a. SEM micrograph of HDPE loaded with 6% Egg shell filler

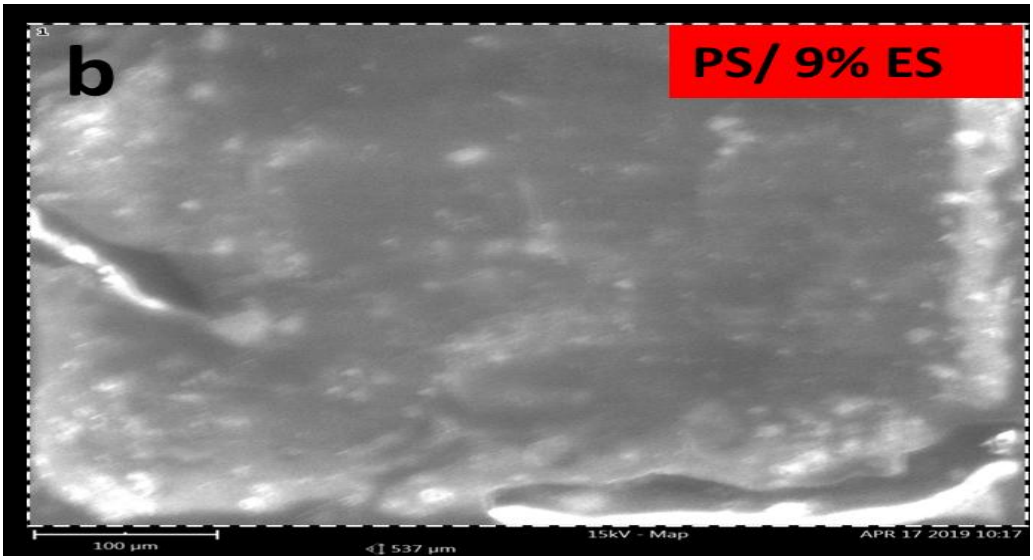


Fig. 3b. SEM micrograph of PS loaded with 9% Egg shell filler

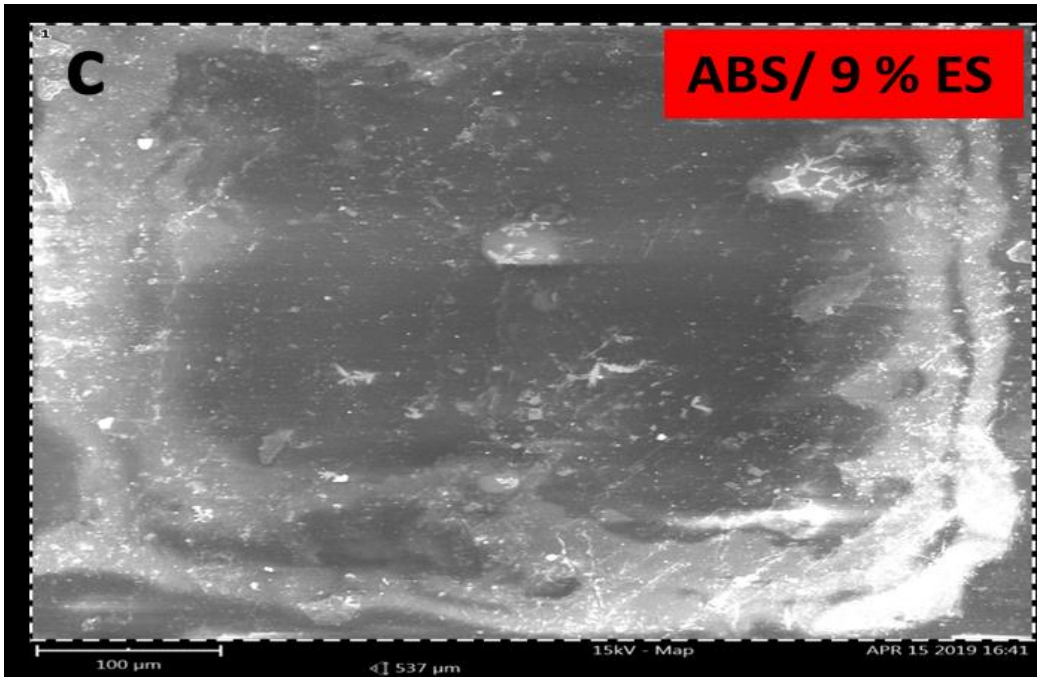


Fig. 3c. SEM micrograph of ABS loaded with 9% Egg shell filler

Elemental Composition of Egg Shell/Polymer Composites

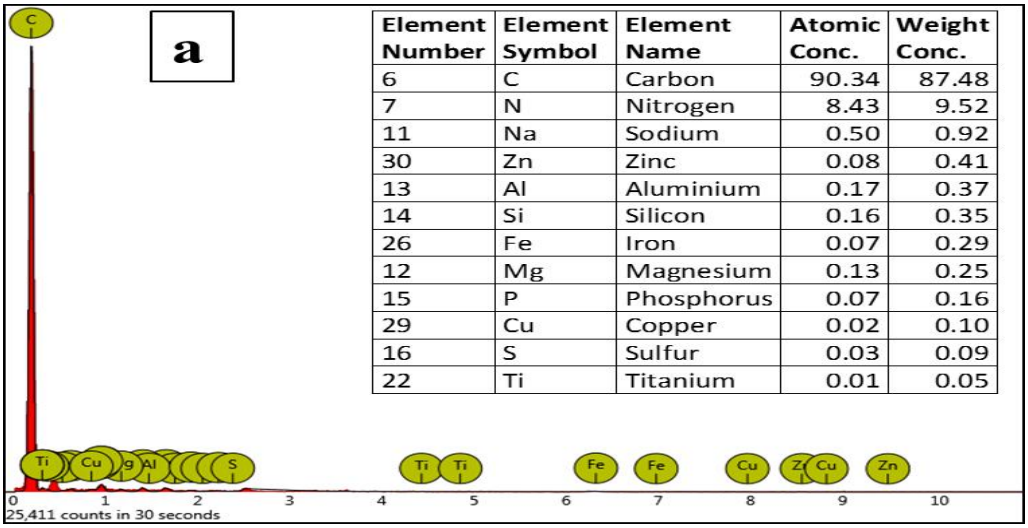
3.5.2 PS matrix for tensile strength

The values of tensile strength for the PS egg shell filler composite obtained are 9% (20.56 MPa) > 12% (12.34 MPa) > 6% = 15% (10.69 MPa) > 3% (7.40 MPa) respectively while that of control was (12.34 MPa). The result shows that incorporation of egg shell filler in the PS matrix has not been reasonably satisfactory as no particular pattern of increment or reduction of the tensile strength was observed. The only improvements in the tensile strength were observed for composites formed with 9% and 12% of egg shell filler while decrease in

tensile strength were observed for composites formed with 3%, 6% and 15 % of egg shell filler.

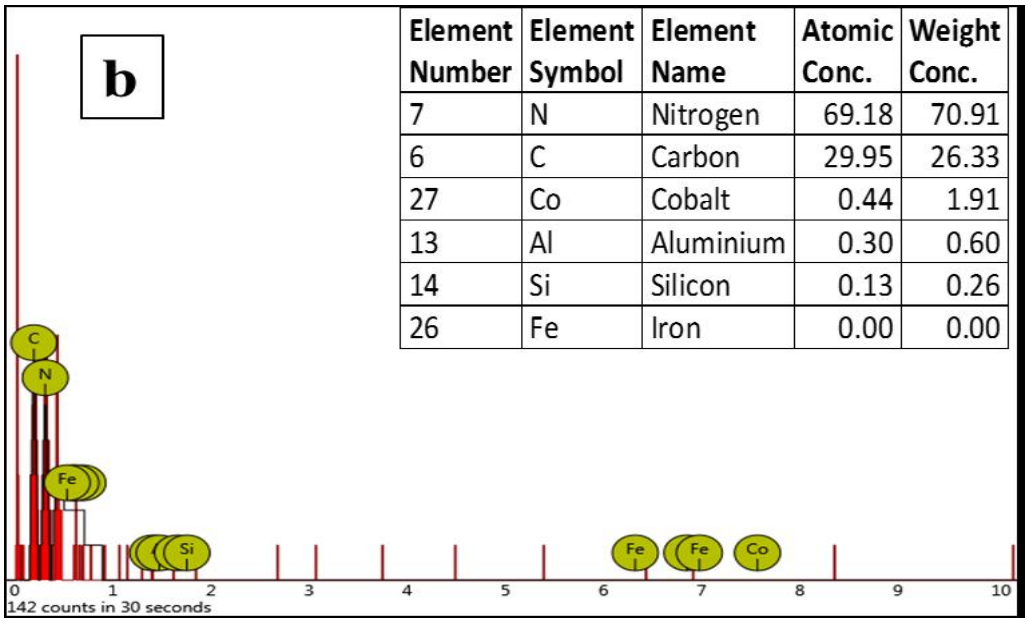
3.5.3 PP matrix for tensile strength

The comparison of tensile strength of PP composites at different percentage loading of egg shell filler show that the values of 3% (12.33 MPa) = 6% (12.33 MPa) >12% (9.87MPa) > 9% (5.75 MPa) > 15% (4.93 MPa) and the Control 8.88 MPa respectively. There are increases in the values of the tensile strength of PP matrix when loaded with 3%, 6% and 12% of egg shell filler. Decrease in tensile strength was observed for PP matrix loaded with 9 % and 15% egg shell filler. The increase in tensile strength observed in 3%, 6% and 12% egg shell filler loading may be due to homogenous dispersion of egg shell filler particles into the polymer matrix which leads to strong interfacial bonding between the egg shell and PP particles which results in good adhesion of the egg shell filler on the polymer matrix.



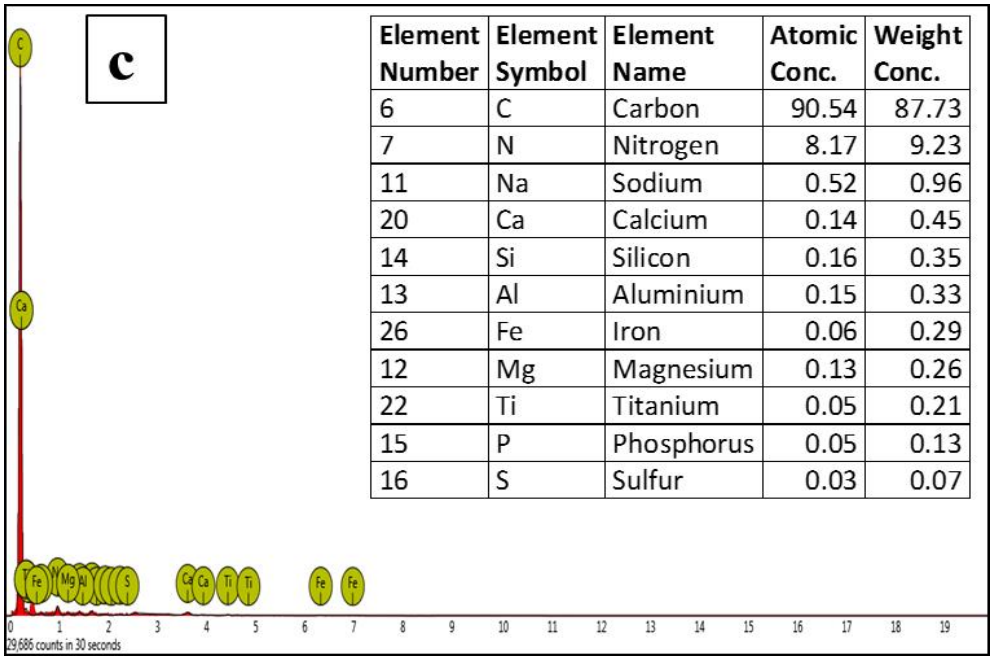
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	90.34	87.48
7	N	Nitrogen	8.43	9.52
11	Na	Sodium	0.50	0.92
30	Zn	Zinc	0.08	0.41
13	Al	Aluminium	0.17	0.37
14	Si	Silicon	0.16	0.35
26	Fe	Iron	0.07	0.29
12	Mg	Magnesium	0.13	0.25
15	P	Phosphorus	0.07	0.16
29	Cu	Copper	0.02	0.10
16	S	Sulfur	0.03	0.09
22	Ti	Titanium	0.01	0.05

Fig. 4a. EDS spectra on elemental composition of HDPE loaded with 6% egg shell



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
7	N	Nitrogen	69.18	70.91
6	C	Carbon	29.95	26.33
27	Co	Cobalt	0.44	1.91
13	Al	Aluminium	0.30	0.60
14	Si	Silicon	0.13	0.26
26	Fe	Iron	0.00	0.00

Fig. 4b. EDS spectra on elemental composition of PS loaded with 9% egg shell



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	90.54	87.73
7	N	Nitrogen	8.17	9.23
11	Na	Sodium	0.52	0.96
20	Ca	Calcium	0.14	0.45
14	Si	Silicon	0.16	0.35
13	Al	Aluminium	0.15	0.33
26	Fe	Iron	0.06	0.29
12	Mg	Magnesium	0.13	0.26
22	Ti	Titanium	0.05	0.21
15	P	Phosphorus	0.05	0.13
16	S	Sulfur	0.03	0.07

Fig. 4c. EDS spectra on elemental composition of ABS loaded with 9% egg shell

3.5.4 ABS matrix for tensile strength

In ABS, the chart for comparison of tensile strength of the ABS polymer matrix and its egg shell filler composites show the value of 6% (12.34MPa) > 3% =12% (9.05 MPa) >15% (8,06MPa) > 9% (7.40MPa), and 6.58 MPa for pure ABS matrix respectively. All the tensile strengths obtained for the composites are higher than the tensile strength of pure ABS matrix. This shows that improvement in the tensile strength of ABS occurs when it is reinforced with egg shell filler.

3.6 Flexural Strength

The flexural strength of different percentages of egg shell in a polymer composite of HDPE, PS, PP and ABS is shown in Table 3 and Fig. 2(a-d).

3.6.1 HDPE matrix

The result of HDPE shows that all the values at different percentages are greater than that of the Control, indicating the importance of the reinforcement with egg shell filler; 12% (33.57 N/mm^2), 9% (25.43 N/mm^2), 6% (18.77 N/mm^2), 3% (16.50 N/mm^2) and 15% (16.25 N/mm^2), while control (14.92 N/mm^2). These are in line with the other researchers' report that natural fillers reinforced HDPE matrix composite give a greater flexural strength and have an advantage when used in the production applications [6].

3.6.2 PS matrix

On PS polymer composite, only 9% (14.32 N/mm^2) value had reduced flexural strength than the Control (17.41 N/mm^2) whereas at 6% (34.84 N/mm^2), 3% (27.35 N/mm^2), 15% (24.24 N/mm^2) and 12% (18.65 N/mm^2) respectively had higher values than the Control. The highest flexural strength was at 6% (34.84 N/mm^2).

3.6.3 PP matrix

For PP, the percentage filler that had values greater than the Control is 6% (27.35 N/mm^2).The other percentages at 3% (22.37 N/mm^2) > 9% (19.90 N/mm^2) > 12% (13.72 N/mm^2) and > 15% (6.22 N/mm^2) respectively had lower values.

3.6.4 ABS matrix

ABS polymer composite, the different percentages filler loading showed increased values of flexural strength than the Control, thus 9% (28.60 N/mm^2), 6% (26.67 N/mm^2) > 15% (17.50 N/mm^2) > 12% (15.65 N/mm^2) and > 3% (13.67 N/mm^2) respectively.

It could be seen that HDPE and ABS matrices reinforced with egg shell at different percentages

of egg shell had higher flexural strength. The increased composites' stiffness depends on the nature of the filler, filler content, and the uniformity of the filler dispersion. These observations are supported by (3), who concluded that good filler dispersion in the composite system could be confirmed by observing the linear increase in the composite's strength.

3.7 Surface Morphology of Polymer/Egg Shell Composite

Scanning Electron Microscopy (SEM) serves as an effective means for the investigation of morphology of the composite system. According to (8), the SEM study of polymer filler composite helps in determining the distribution (dispersiveness) and compatibility between the filler and polymer matrix. In general, all the surfaces of the polymer composites are smooth with the particles appearing to be compact. In some of the composite structure, the particle of the filler material appeared to be homogeneously dispersed in the polymer matrix while some appeared to have formed an agglomerated mass of different dimensions. ImageJ software was used to estimate the average particle size of the polymer/agro – waste composite. Fig. 3(a – c) show the micrograph images of HDPE, PS and ABS prepared with loading of 6%, 9% and 9% egg shell (ES) filler respectively. The estimated particle sizes from the micrographs of HDPE/ 6% ES, PS/ 9% ES and ABS/ 9% ES obtained using ImageJ software were , and .

3.7.1 HDPE/Egg shell composite

Fig. 3(a) shows the micrograph of HDPE matrix with 6% which revealed two phases in the polymer, the phase due to homogeneous dispersion of the filler material into the polymer matrix and the other phase due to heterogeneous dispersion of filler material. This might be due to weak bonding that leads to poor interfacial interactions between the particles of the two systems that formed the composite.

3.7.2 PS/Egg shell composite

Fig. 3(b) shows the micrograph image of PS with 9% of egg shell filler. The polymer composite shows formation of homogeneously dispersed composite within some part of the micrograph and heterogeneous dispersed parts as well due to weak bonding between the polymer matrix and the egg shell filler.

3.7.3 ABS/Egg shell composite

Fig. 3(c) shows the micrograph of ABS with 9% palm egg shell filler. The micrograph shows heterogeneous surface with some small portions being voids. These voids formed are due to weak adhesion between the polymer and the egg shell filler.

3.8 Elemental Composition of Polymer/Egg Shell Composite

Energy Dispersive Spectroscopy (EDS) relies on an interaction of some source of X-ray excitation on polymer filler composite. EDS helps to discover the surface elemental composition and estimate their proportion at different position, consequently giving an overall mapping of polymer filler composite.

Fig. 4(a – c) show the Energy Dispersive Spectroscopy (EDS) spectra and elemental composition of the HDPE/ES, PS/ES and ABS/ES composites.

3.8.1 HDPE/Egg shell composite

Fig. 4(a) shows that the composite is composed of carbon and nitrogen as major elements present. Carbon has a weight percentage of 87.48% which corresponds to 90.34% atomic concentration while Nitrogen has a percentage weight of 9.52% corresponding to 8.43% of atomic concentration. Traces of other elements appeared in small amounts.

3.8.2 PS/Egg shell composite

Fig. 4(b) revealed the presence of carbon and nitrogen as the major elements; carbon has weight percentage value of 26.33% corresponding to 29.95% atomic concentration while nitrogen has percentage weight of 70.91% which corresponds to 69.18% atomic concentration.

3.8.3 ABS/Egg shell composite

Fig. 4(c) reveals the presence of carbon and nitrogen as main elements. Carbon represents 87.73% weight of the composite and nitrogen

represents 9.23% and corresponds to atomic concentrations of 90.54% and 8.17% respectively. There are traces of other elements as shown in Fig. 4(c).

The elemental composition of the polymer/egg shell filler composites contain five common elements namely, carbon (C), nitrogen (N), iron (Fe), aluminum (Al), silicon (Si). Other elements present in some of the samples are sodium (Na), phosphorus (P), magnesium (Mg), sulphur (S), titanium (Ti), zinc (Zn), copper (Cu), cobalt (Co) and calcium (Ca). The presence of these elements (mostly the metals) in the fabricated polymer composites is because of the loading of the polymer with different amounts of egg shell filler materials. These elements observed in small quantities correspond to the composition of egg shell filler. The compositional result of egg shell is in line with the results previously obtained by [7,8,2,1,9].

4. CONCLUSION

There was a significant improvement in tensile strength, tensile modulus and flexural strength of the blend egg shell filler composites which were influenced by the amount of filler in the composites. The HDPE loaded with egg shell filler has MoE (Modulus of Elasticity) at 3% of 1115.50 MPa (Mega Pascal) MPa, 6% of 1581.80 MPa, 9% of 662.40 MPa, 12% of 894.34 MPa and 15% of 998.64 MPa, Control (pure HDPE) of 348.38 MPa. For PS the graphs show the result of the 9%, 6%, 12%, 15%, 3% from highest to lowest value to be 1982.60 MPa > 1255.10 MPa >1099.60 MPa > 972.22 MPa > 730.45 MPa and the Control gave 955.59 MPa. The values of PP matrix loaded were 3% (805.71 MPa) > 12% (747.18 MPa) > 9% (571.96 MPa) > 6% (514.18 MPa) > 15% (371.98 MPa), pure PP matrix of 428.20 MPa. ABS/egg shell MoE values were observed as follows: 6% (559.00 MPa) > 3% (384.66 MPa) > 12% (382.84 MPa) > 15% (372.66 MPa) > 9% (327.61 MPa) and control (160.68 MPa). The values of tensile strength for the HDPE egg shell filler composite obtained are 3% (49.02 MPa) > 6% (30.43 MPa) > 12 % (20.56 MPa) >15% (14.81 MPa) > 9% (10.69 MPa) respectively and pure HDPE matrix obtained was 7.40 MPa. For PS egg shell filler composite obtained are 9% (20.56 MPa) > 12% (12.34 MPa) > 6% = 15% (10.69 MPa) > 3% (7.40 MPa) respectively while that of control was (12.34 MPa). PP composites at different percentage loading of egg shell filler show that the values of 3% (12.33 MPa) = 6% (12.33 MPa) >12% (9.87 MPa) >9% (5.75 MPa) > 15% (4.93 MPa) and the Control 8.88 MPa respectively. In ABS, the value of 6% (12.34 MPa) > 3% =12% (9.05 MPa) >15% (8,06 MPa) > 9% (7.40 MPa), and 6.58 MPa for pure ABS matrix respectively. The tensile, statistical correlation coefficient using Pearson product-moment between the Control and agro-waste fillers loading on polymer matrices used at different percentages of stress and strain indicate strong positive relationship between the variables. It is evident from the results that HDPE, PS and ABS matrices filled with egg shell composites reinforced at different percentages showed maximum flexural strength than the Control. HDPE at 12% (33.57 N/mm2), 9% (25.43 N/mm2), 6% (18.77 N/mm2), 3% (16.50 N/mm2) and 15% (16.25 N/mm2), while control (14.92 N/mm2).PS polymer composite, only 9% (14.32 N/mm2) value had reduced flexural strength than the Control (17.41 N/mm2); at 6% (34.84 N/mm2), 3% (27.35 N/mm2), 15% (24.24N/mm2) and 12% (18.65 N/mm2) respectively had higher values than the Control. For PP, 6% (27.35 N/mm2) > 3% (22.37 N/mm2) > 9% (19.90N/mm2) > 12% (13.72 N/mm2) and > 15% (6.22 N/mm2) respectively had lower values. ABS, 9% (28.60 N/mm2) > 6% (26.67 N/mm2) > 15% (17.50 N/mm2) > 12% (15.65 N/mm2) and > 3% (13.67 N/mm2). There's often an optimum filler level for improved mechanical properties. It could be concluded that in most of the composites, the filler had good degree of interaction with the polymer as indicated by the test data obtained from the agro-waste thermoplastic polymer composites. This was due to the dispersion of the filler particles which acted as load carrying members, not only helping to stiffen the composite, but improved bending, flexibility and overall load distribution. HDPE, PS and ABS matrices filled with egg shell composites reinforced at different percentages showed maximum flexural strength than the Control. Scanning electron microscopy (SEM) using imageJ software was carried out on the samples to estimate the average particle size of the polymer egg shell waste. In some of the composite structures, the particle of the filler material appeared to be homogeneously dispersed in the egg shell-waste/polymer composites; some appeared to be heterogeneously dispersed with voids of white patches while some form an agglomerated mass of different dimensions. The elemental compositional analysis, using Energy Dispersive Spectroscopy (EDS) had all samples contain C and N as a major element present and others as trace; Fe, Al, Mg, P, Zn, Si. This study has

provided different combinations of egg shell-waste/egg shell-residue thermoplastic polymer composites which has potential application in the automobile and building construction industry. The utilization of agro-waste products in Nigeria and its degradation would help solve the problem of environmental pollution threat which they pose. Finally, the whole project would serve as a means of turning waste to wealth by utilizing agro-waste products in developing low cost polymer composites to serve a number of interesting applications.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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