Comparative Study on Creep Rate Property of Cow Horn Filler in Selected Thermoplastic Polymer Composites

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Abstract

This research is to develop environmentally friendly, lightweight composites using cow horn as filler in some thermoplastic polymer matrices High Density Polyethylene (HDPE), Polystyrene (PS), Polypropylene (PP) and Acrylonitrile-Butadiene-Styrene (ABS); to determine the creep rate properties of the cow horn-residue polymer composite, to find if there is any new improvement over the properties of the starting thermoplastic. Cow horn 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 HDPE 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.The production of coconut shell thermoplastic composite at different percentage fillers reinforcement showed bean overall higher creep rate than Control especially in HDPE, PP and ABS. Creep rate of 1.06×10^{-2} mm/mins was obtained by loading HDPE with 3% of coconut shell filler, 6% had Creep rate of 1.67×10^{-2}mm/mins, 9% had creep rate of 8.70×10^{-3} mm/mins, 12% had creep rate of 1.62×10^{-2}mm/mins and 15% had creep rate of 1.48×10^{-2}mm/mins respectively. Pure HDPE has creep rate of 1.97×10^{-2}mm/mins. PS loaded with 3% of coconut shell filler has creep rate of 1.66×10^{-2}mm/mins, 6% had creep rate of 2.43×10^{-2}mm/mins, 9% had creep rate of 2.30×10^{-2}mm/mins, 12% had creep rate of 2.52×10^{-2}mm/mins and 15% had creep rate of 1.61×10^{-2}mm/mins while the pure PS polymer has creep rate of 1.46×10^{-2}mm/mins. At 3% of coconut shell filler, the creep rate was 9.80×10^{-3}mm/mins, 6% had creep rate of 1.74×10^{-2}mm/mins, 9% had creep rate of 1.94×10^{-2}mm/mins, 12% had creep rate of 2.04×10^{-2}mm/mins and 15% had creep rate of 1.59×10^{-2}mm/mins as the pure PP polymer had creep rate of 1.89×10^{-2}mm/mins respectively. Pure ABS polymer has creep rate of 2.31×10^{-2}mm/mins, while 3% had creep rate of 1.84×10^{-2}mm/mins, 6% had creep rate of 1.96×10^{-2}mm/mins, 9% had creep rate of 1.70×10^{-2}mm/mins, 12% had creep rate of 1.70×10^{-2}mm/mins, 15% had creep

rate of $1.90 \times 10^{-2} mm/mins$ respectively. The Creep rate of polymer matrices loaded with coconut shell with exception of PS matrix composites at different percentages have stable and good behaviour of material after being subjected to high levels of stress. There was a significant improvement in creep mechanical property when different percentages of agro-wastes were incorporated in HDPE, PP, and ABS polymer matrices than the virgin polymers. The study has provided combinations of matrix/natural fillers that promote formation of new classes of composites and products with lower cost, light weight, good behaviour, high specific strength,eco-friendly nature and availability which also has potential application in the automobile and building construction industry.

Keynote: *coconut shell, composites, HDPE matrices, percentages (3%, 6%, 9%, 12% and 15%)*

1. Introduction

In the current years, composites fulfill optimal requirement criteria for several designers' materials. 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 biodegradable matrix/natural fillers in order to obtain new classes of biodegradable 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 fillers (flax, jute, hemp, cow horn, etc.) represent an environmentally friendly alternative to conventional reinforcing fibers such as glass and carbon. The advantages of natural fillers over synthetic ones are their low cost, high toughness, corrosion resistance, low density, good specific strength and reduced tool wear.

Composite can be considered as a multiphase material that exhibits a significant proportion of each or the constituent phase, in such a way that the best combination of properties is achieved. There are two parts of composite material, matrix and filler/fibre (reinforcing phase). They can be reinforced in various phases; in the form of fibres, sheets, or particles. It is surrounded in the other materials called the matrix phase. Metal, ceramic, non-metal, and polymer material can be used as reinforcing element and matrix material in development of composites. The fibres/fillers used in composites are stiffer and stronger than the matrix material (called continuous phase) which serve as load carrying members; continuous phase (matrix) of composite acts as the load transfer medium between fibres/fillers.

The aim of this research is to develop environmentally friendly, lightweight composites using coconut shell, as filler in selected thermoplastic polymer matrices; to determine the mechanical properties of the coconut shell-residue polymer composite, to find if there is any new improvement over the properties of the starting thermoplastic polymer.

2. Methodology

Coconut 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 High Density Polyethylene (HDPE), Polystyrene (PS), Polypropylene (PP) and Acrylonitrile-Butadiene-Styrene (ABS) polymer matrices were purchased from one of the Petrochemicals Company, Nigeria.The equipment used were Monsanto Tensiometer, Abrasion tester (Tabar), Weighing balance, Ventilated oven, Hammer (6.03kg), 0.2μm mechanical sieve and Universal Testing Machine (UTM) 5569A (JJ Lloyd, London, United Kingdom, capacity 1-20KN). Zinc Stearate was used as a protective incorporated.

Coconut 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 1g 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. The fillers were then taken for compression moulding and the particle sized of the filler used were 3g, 6g, 9g, 12g and 15g of cow horn fillers. The composites were prepared using the following blending formulation:

2.1 Coconut Shell/Polymer Composite Formulation

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

One hundred grams (100g) 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 HDPE matrix blended with 3g of cow horn 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 itwas 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.

Creep Test

Creep tests were carried out using International Standards such as American Society for Testing Materials (ASTM) standards. Universal Testing Machine (UTM) 5569A was suitable for the tests of polymer matrix composites. The composites containing 3%, 6%, 9%, 12%, 15% w/w filler each were prepared and the mechanical properties examined. Creep test is used in experiments to determine the efficiency, stability or the behaviour of a material when it is exposed to constant temperature and stress (the nature of stress – relaxation). The rate of deformation of a sample due to applied constant stress at a constant temperature is known as creep rate. Creep rate is the slope created by the deformation or strain versus time. It is measured in mm/min, mm/hr. or %/hr. It is a measure of the plasticity of a material at constant stress and temperature; the lower the value of creep, the better a material and vice-versa.

Procodure:

i. The material was subjected to a prolonged tensile or compressive load at constant temperature (room temperature of 25 ± 2^0C for a low stress creep curve).

ii. One tenth ($1/10^{th}$) of the tensile or compressive strength of the material was allowed to creep at chosen time interval tensile rupture occurred.

iii. A graph of the strain versus recorded time was plotted to evaluate the creep rate.

iv. The slope of the curve before the point of constant strain gave the creep rate of the material.

3. Results and Discussion

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

❖ **Creep Rate Test (mm/min) for Coconut Shell/Polymer Composites**

Table on Creep rate values for coconut shell/polymer matrices composite at 3%, 6%, 9%, 12% and 15% agro-waste levels

Table on Creep rate values for coconut Shell/polymer matrix composite

| Agro-waste	Polymer matrices	Control	Different percentages fillers loading				
			3%	6%	9%	12%	15%
	HDPE	0.020	0.011	0.017	0.009	0.016	0.015
	PS	0.015	0.017	0.024	0.023	0.025	0.016
Coconut shell	PP	0.019	0.010	0.017	0.019	0.020	0.016
	ABS	0.023	0.018	0.020	0.017	0.017	0.019

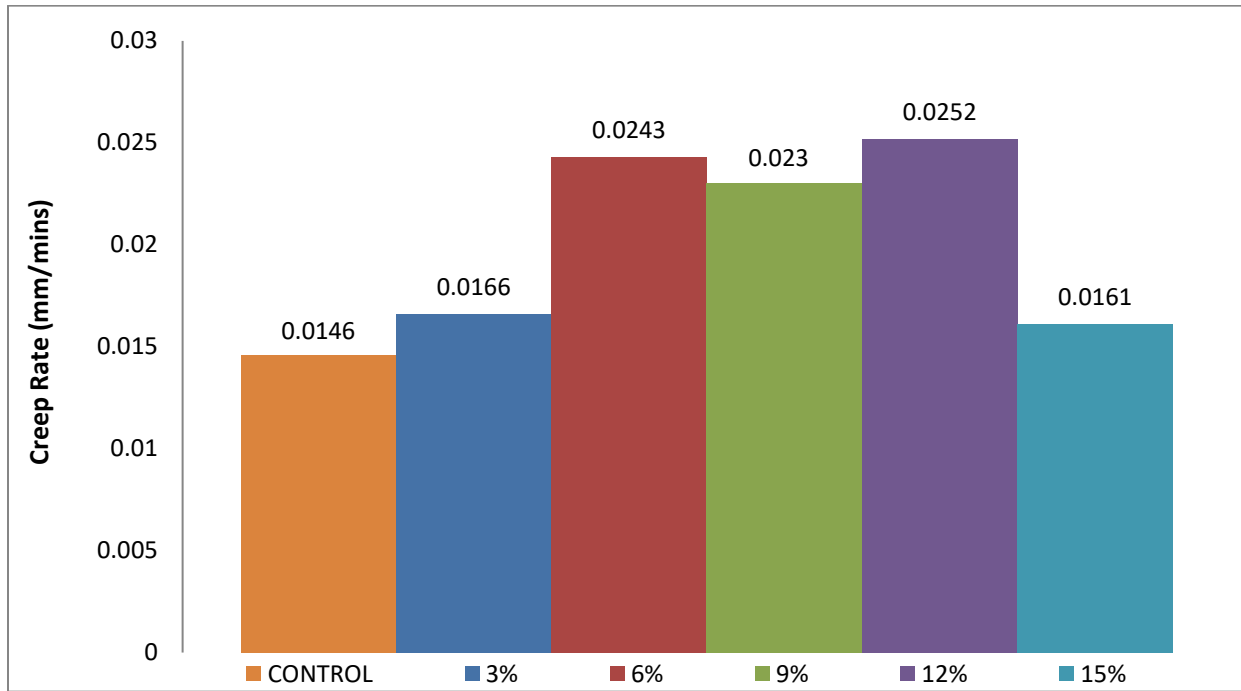**Pictogram on Creep Rate of Agro-Waste/Polymer Composite**
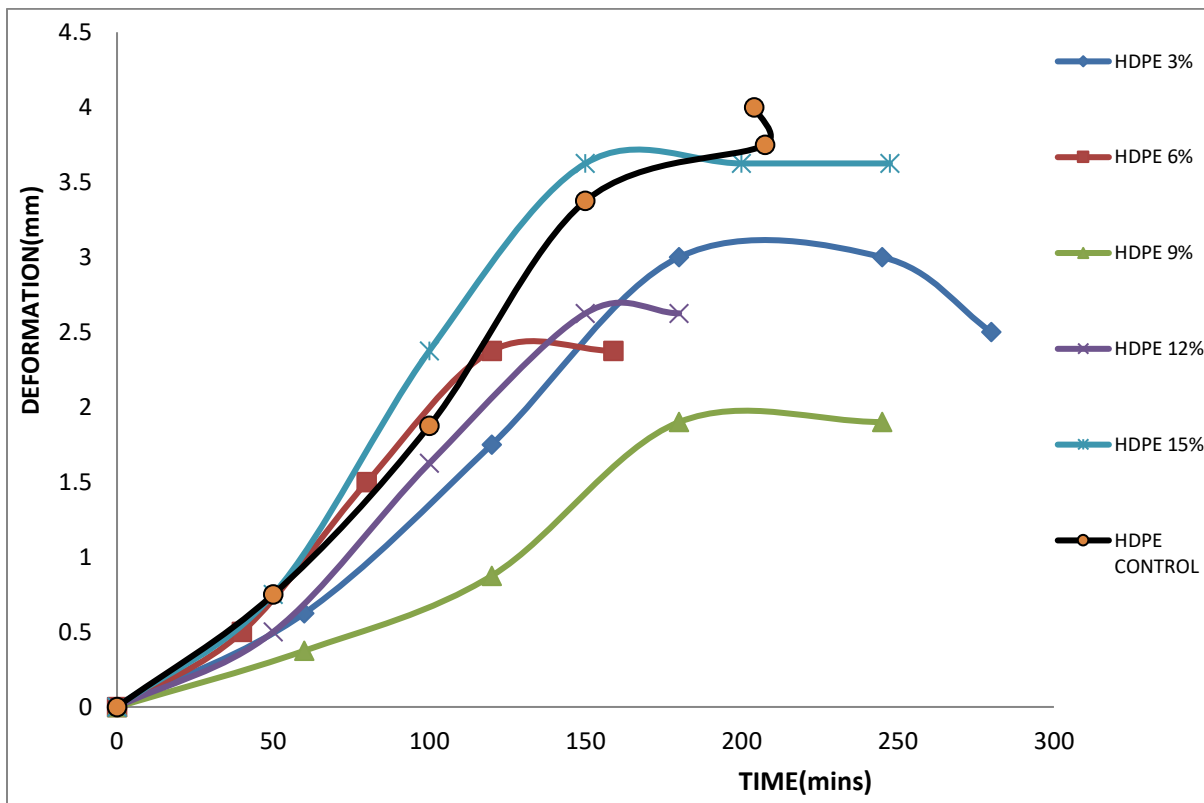
Fig 1a Deformation Curves of the Control (HDPE) and HDPE-Coconut Shell Composites at 3%-15% Filler Levels
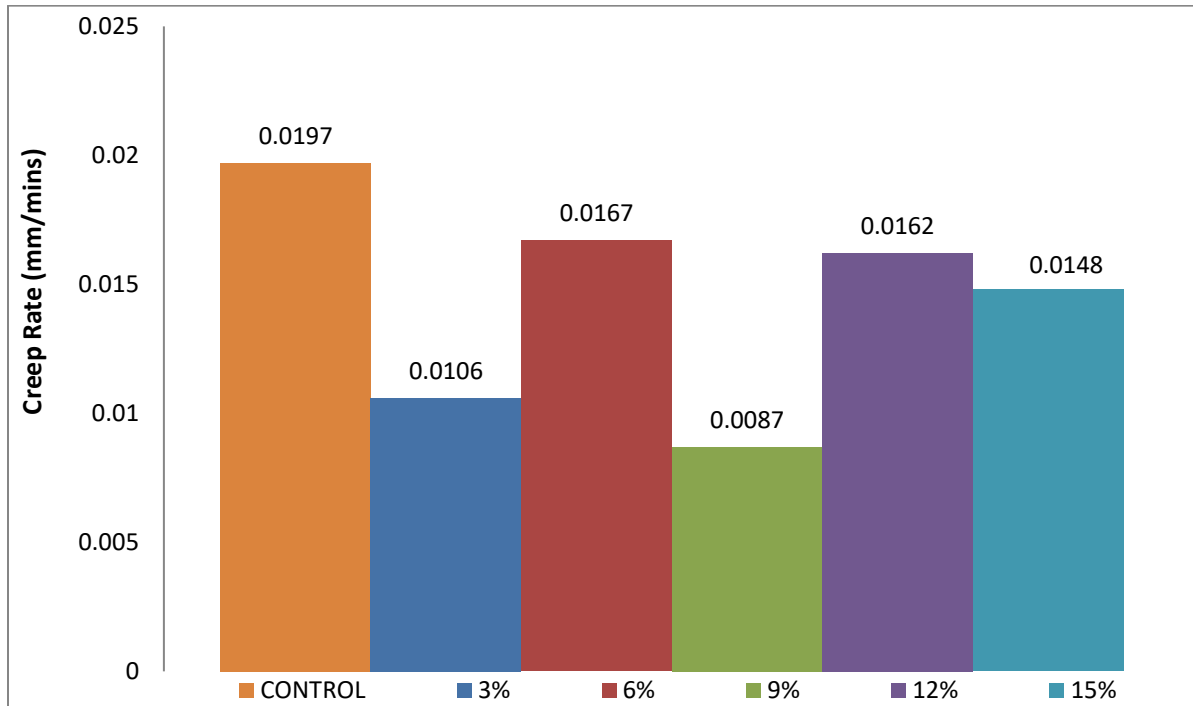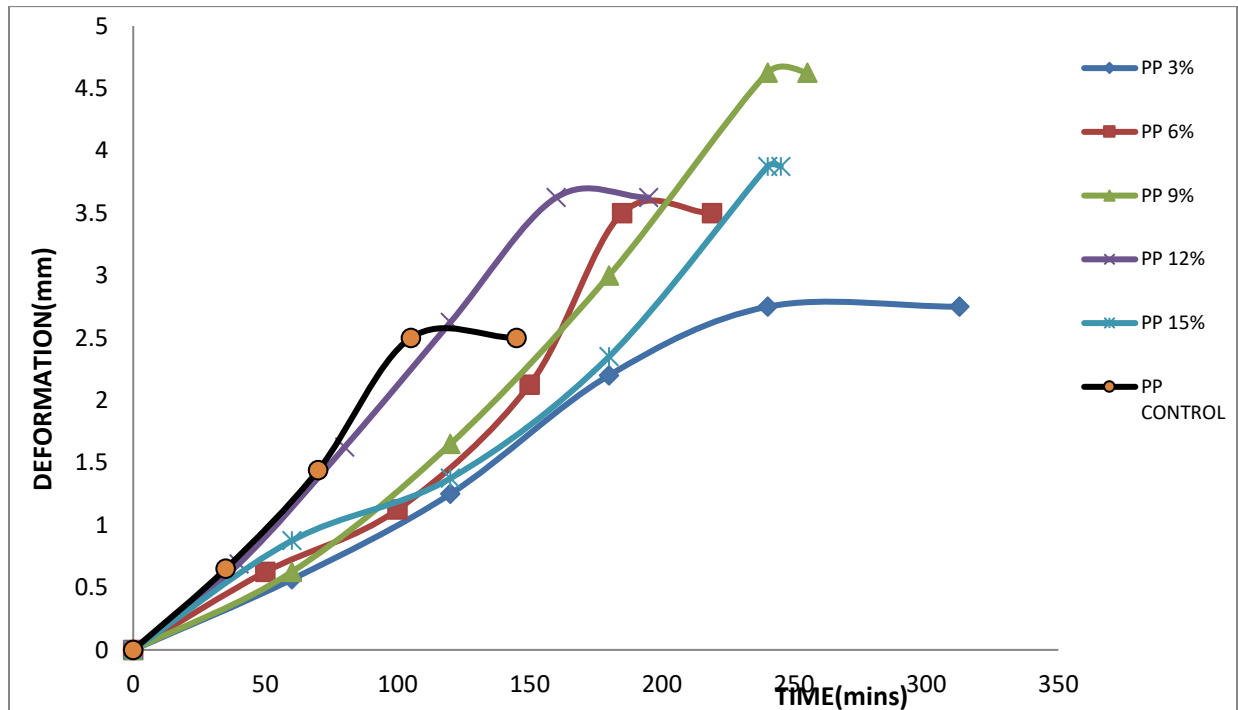

Fig 1b Creep Rate Values of the Control (HDPE) and HDPE-Coconut Shell Composites at 3%-15% Filler Levels
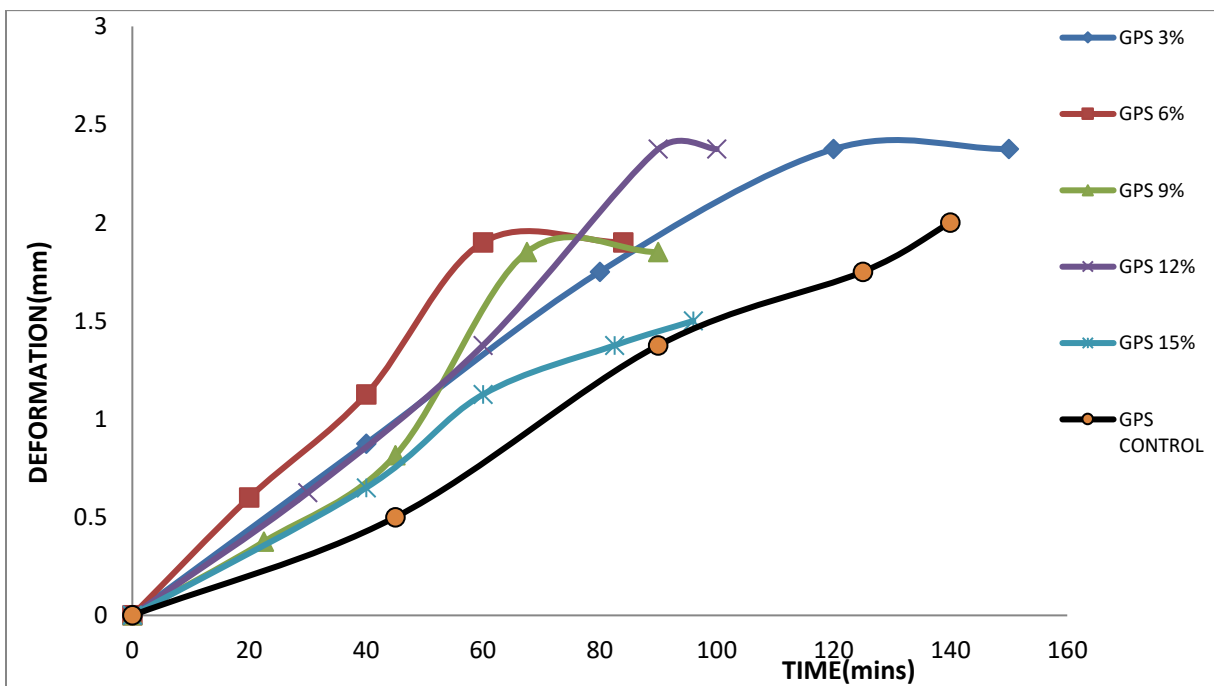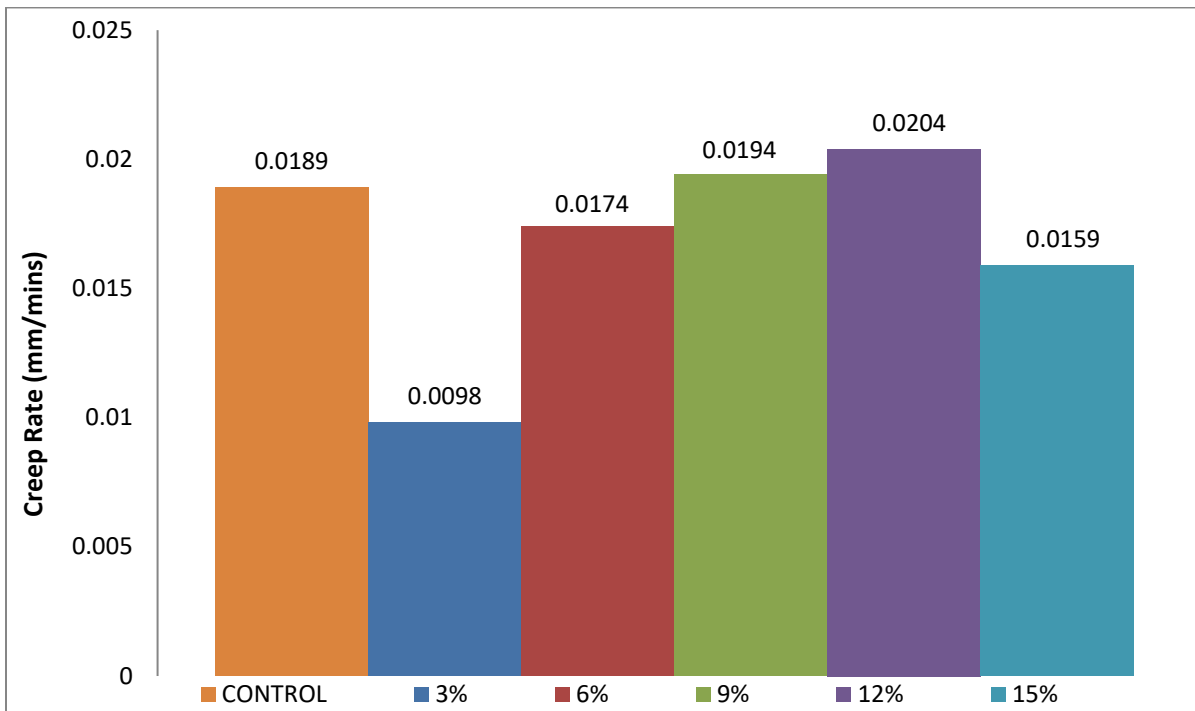
Fig 2a Deformation Curves of the Control (PS) and PS-Coconut Shell Composites at 3%-15% Filler Levels

Fig 2b Creep Rate Values of the Control (PS) and PS-Coconut Shell Composites at 3%-15% Filler Levels

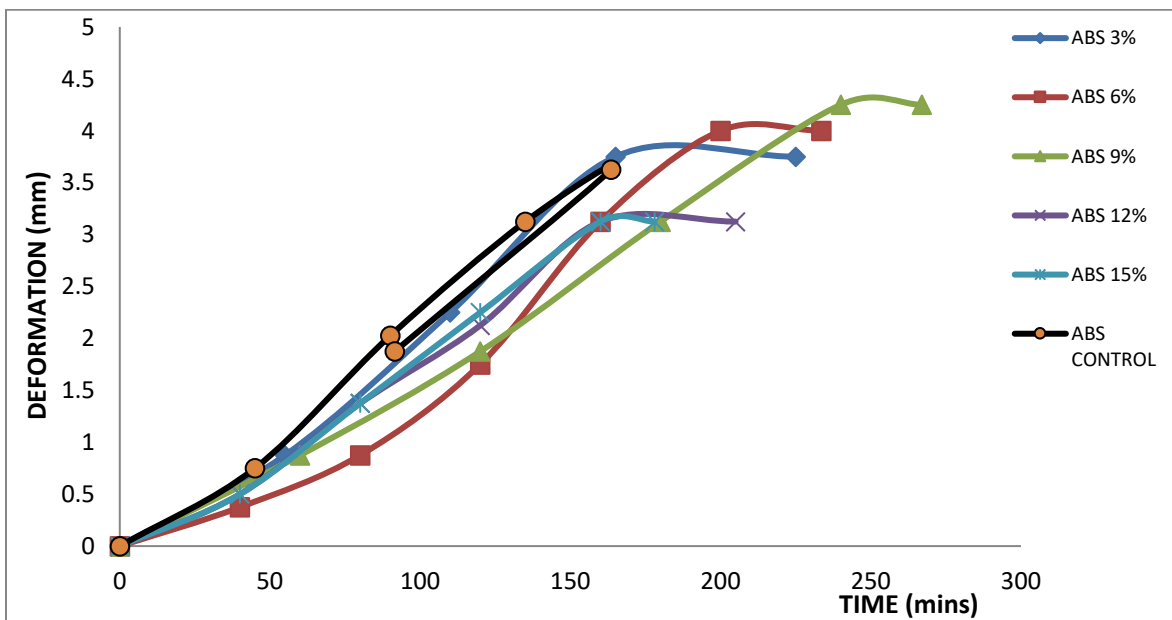**Fig 3a Deformation Curves of the Control (PP) and PP-Coconut Shell Composites at 3%-15% Filler Levels**
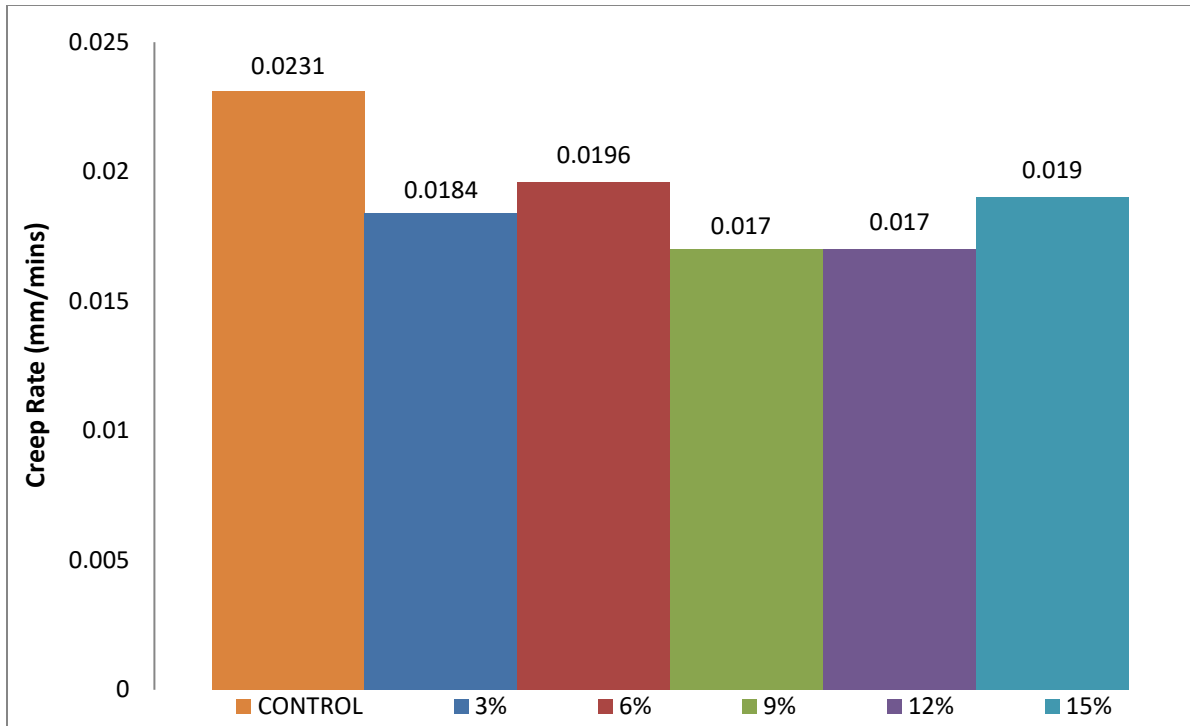

Fig 3b Creep Rate Values of the Control (PP) and PP-Coconut Shell Composites at 3%-15% Filler Levels

Fig 4a Deformation Curves of the Control (ABS) and ABS-Coconut Shell Composites at 3%-15% Filler Levels

Fig 4b Creep Rate Values of the Control (ABS) and ABS-Coconut Shell Composites at 3%-15% Filler Levels

3.1 Polymer Matrix Reinforced with Cow Horn Filler

Table; Figure 1(a), 2(a) 3 (a) and 4(a) showed the data and graph of deformation (creep strain) against time for HDPE, PS, PP and ABS cow horn composites. The slope of the curve gives the creep rate of the polymer composites. Generally, the curves showed primary creep and few regions of secondary creep with no evidence of tertiary creep (i.e. rupture). The comparison for the creep rate for different percentages of cow horn filler in HDPE, PS, PP and ABS polymer matrices are presented in Figure 1(b), 2(b) 3(b) and 4(b).

3.1.1 HDPE Matrix

Creep rate of $1.06 \times 10^{-2} \, mm/mins$ was obtained by loading HDPE with 3% of coconut shell filler, 6% had Creep rate of $1.67 \times 10^{-2} mm/mins$, 9% had creep rate of $8.70 \times 10^{-3} \, mm/mins$, 12% had creep rate of $1.62 \times 10^{-2} mm/mins$ and 15% had creep rate of $1.48 \times 10^{-2} mm/mins$ respectively. Pure HDPE has creep rate of $1.97 \times 10^{-2} mm/mins$. The results showed that creep rate of the HDPE polymer composites formed by 3%, 6%, 9%, 12% and 15% coconut shell filler have lower values than that of the pure polymer matrix and this implies that the creep behaviour was improved by 46.19%, 15.23%, 55.84%, 17.77% and 28.87% due to the presence of 3%, 6%, 9%, 12% and 15% coconut shell within the polymer matrix. This also

shows that creep behaviour of HDPE improved as it was loaded with different coconut shell filler composite with 9% of coconut shell filler having the best creep rate improvement of 55.84%.

3.1.2 PS Matrix

PS loaded with 3% of coconut shell filler has creep rate of $1.66 \times 10^{-2} mm/mins$, 6% had creep rate of $2.43 \times 10^{-2} mm/mins$, 9% had creep rate of $2.30 \times 10^{-2} mm/mins$, 12% had creep rate of $2.52 \times 10^{-2} mm/mins$ and 15% had creep rate of $1.61 \times 10^{-2} mm/mins$ while the pure PS polymer has creep rate of $1.46 \times 10^{-2} mm/mins$. The result confirmed that the incorporation of different percentages of coconut shell filler into PS do not improve creep behaviour of PS matrix rather worsen it.

3.1.3 PP Matrix

PP shows the bar chart for comparison of creep rate of PP matrix loaded with different percentages of coconut shell filler. At 3% of coconut shell filler, the creep rate was $9.80 \times 10^{-3} mm/mins$, 6% had creep rate of $1.74 \times 10^{-2} mm/mins$, 9% had creep rate of $1.94 \times 10^{-2} mm/mins$, 12% had creep rate of $2.04 \times 10^{-2} mm/mins$ and 15% had creep rate of $1.59 \times 10^{-2} mm/mins$ as the pure PP polymer had creep rate of $1.89 \times 10^{-2} mm/mins$ respectively. These results revealed that loading PP with 3%, 6%, and 15% improved the creep behaviour of PP by 48.15 %, 7.94% and 15.87% respectively. This indicates also that PP composite with 3% coconut shell filler loading has the best creep behaviour.

3.1.4 ABS Matrix

In ABS, pure ABS polymer has creep rate of $2.31 \times 10^{-2} mm/mins$, while 3% had creep rate of $1.84 \times 10^{-2} mm/mins$, 6% had creep rate of $1.96 \times 10^{-2} mm/mins$, 9% had creep rate of $1.70 \times 10^{-2} mm/mins$, 12% had creep rate of $1.70 \times 10^{-2} mm/mins$, 15% had creep rate of $1.90 \times 10^{-2} mm/mins$ respectively. From the results, it can be seen that loading ABS matrix with 3%, 6%, 9%, 12% and 15% of coconut shell filler led to slight improvement of the creep behaviour of ABS matrix. The composites formed have improvements of 20.35%, 15.15%, 26.41%, 26.41% and 17.75% respectively. This suggests that composites formed with 9% and 12% of coconut shell filler loading had the best creep behaviours.

4. Conclusion

In recent years, the agro-waste fibres/fillers have attracted substantial importance among other materials as reinforcement agents in polymer/filler composites. The attractive features of natural fibres/fillers are their low cost, light weight, high specific modulus, stability and good behaviour of the materials, eco-friendly nature,

availability and sustainability. This work presents the production of composites from cow horn/thermoplastic polymer composites as fillers at different percentages of reinforcement in High-Density Polyethylene (HDPE), Polystyrene (PS) Polypropylene (PP) and Acrylonitrile-Butadiene-Styrene (ABS). Different filler loadings of 3%, 6%, 9% 12% and 15% were used to produce the composites. The creep rates of composites were determined in order to gain insight into the effect of filler content on the mechanical properties of the formulated composites.The production of coconut shell thermoplastic composite at different percentage fillers reinforcement showed bean overall higher creep rate than Control especially in HDPE, PP and ABS.Creep rate of $1.06 \times 10^{-2} \, mm/mins$ was obtained by loading HDPE with 3% of coconut shell filler, 6% had Creep rate of $1.67 \times 10^{-2} mm/mins$, 9% had creep rate of $8.70 \times 10^{-3} \, mm/mins$, 12% had creep rate of $1.62 \times 10^{-2} mm/mins$ and 15% had creep rate of $1.48 \times 10^{-2} mm/mins$ respectively. Pure HDPE has creep rate of $1.97 \times 10^{-2} mm/mins$. The results showed that creep rate of the HDPE polymer composites formed by 3%, 6%, 9%, 12% and 15% coconut shell filler have lower values than that of the pure polymer matrix and this implies that the creep behaviour was improved by 46.19%, 15.23%, 55.84%, 17.77% and 28.87% due to the presence of 3%, 6%, 9%, 12% and 15% coconut shell within the polymer matrix. PS loaded with 3% of coconut shell filler has creep rate of $1.66 \times 10^{-2} mm/mins$, 6% had creep rate of $2.43 \times 10^{-2} mm/mins$, 9% had creep rate of $2.30 \times 10^{-2} mm/mins$, 12% had creep rate of $2.52 \times 10^{-2} mm/mins$ and 15% had creep rate of $1.61 \times 10^{-2} mm/mins$ while the pure PS polymer has creep rate of $1.46 \times 10^{-2} mm/mins$. The result confirmed that the incorporation of different percentages of coconut shell filler into PS do not improve creep behaviour of PS matrix rather worsen it.At 3% of coconut shell filler, the creep rate was $9.80 \times 10^{-3} mm/mins$, 6% had creep rate of $1.74 \times 10^{-2} mm/mins$, 9% had creep rate of $1.94 \times 10^{-2} mm/mins$, 12% had creep rate of $2.04 \times 10^{-2} mm/mins$ and 15% had creep rate of $1.59 \times 10^{-2} mm/mins$ as the pure PP polymer had creep rate of $1.89 \times 10^{-2} mm/mins$ respectively. PP results revealed that loading PP with 3%, 6%, and 15% improved the creep behaviour of PP by 48.15 %, 7.94% and 15.87% respectively. Pure ABS polymer has creep rate of $2.31 \times 10^{-2} mm/mins$, while 3% had creep rate of $1.84 \times 10^{-2} mm/mins$, 6% had creep rate of $1.96 \times 10^{-2} mm/mins$, 9% had creep rate of $1.70 \times 10^{-2} mm/mins$, 12% had creep rate of $1.70 \times 10^{-2} mm/mins$, 15% had creep rate of $1.90 \times 10^{-2} mm/mins$ respectively. From the results, it can be seen that loading ABS matrix with 3%, 6%, 9%, 12% and 15% of coconut shell filler led to slight improvement of the creep behaviour of ABS matrix. It can be seen that loading ABS matrix with 3%, 6%, 9%, 12% and 15% of coconut shell filler led to slight improvement of the creep behaviour of ABS matrix. The composites formed have improvements of 20.35%, 15.15%, 26.41%, 26.41% and 17.75% respectively.The Creep rate of polymer

matrices loaded with coconut shell with exception of PS matrix composites at different percentages have stable and good behaviour of material after being subjected to high levels of stress (that is, high temperatures to change its form in relation to time of an object) than the Control. The lower the value of creep rates of a polymer composite, the better the polymer composites.There was a significant improvement in creep mechanical property when different percentages of agro-wastes were incorporated in HDPE, PP, and ABS polymer matrices than the virgin polymers. The reason being that filler particles which act as load carrying members, not only helped to stiffen the composite, but improved nature of stress relaxation of the materials and overall load distribution.The study has provided combinations of matrix/natural fillers that promote formation of new classes of composites and products with lower cost, light weight, good behaviour, high specific strength,eco-friendly nature and availability which also has potential application in the automobile and building construction industry.

References

1. Cheng, Q., Wang, J., Wen, J., Liu, C., Jiang, K., Li, Q. and Fan, S. (2010).'Carbon nanotube/epoxy composites fabricated by resin transfer moulding. Carbon 48(1):260–266.

2. Choi, N. W., Mori, I. and Ohama Y. (2006), "Development of Rice Husks Plastic Composite for Building Materials," Journal of Waste Management, 26(2): 189-194.

3. Crespo, J. E., Sánchez, L. D., García and López J. (2008), "Study of the Mechanical and MorphologicalProperties of Plasticized PVC Composites Containing Rice Husk Fillers," Journal of Reinforced Plastics and Composites, 27 (3): 229-243.

4. Ewansila, C. J., Ebhoaye, J. E., Asia, I. O., Ekebafe, L. O. and Ehigie, C. (2012).Proximate and minerial composition of coconut (Cocos Nucifera) shell. International Journal of Pure and Applied Science and Technology, 13(1):53 – 56.

5. Faruk, O., Bledzki, A.K., Fink, H-P, Sain, M. (2010).'Biocomposites reinforced with natural fibers: Prog Polym Sci 37:1552–1596.

6. Fono – Toma, R. S. and Koya, O. A. (2013). Characterization of pulverized palm kernel shell for sustainable waste diversification. International Journal of Scientific and Engineering Research, 4(4): 6 – 10.

7. Iftekhar, A. and Prakash, A. M. (2010), "Mechanical Properties of Fly Ash Filled High Density Polyethylene," Journal of Minerals & Minerals Characterization & Engineering, 9 (3): 183-198.

8. *Ikumapayi, O. M. and Akinlabi, E. T., (2018). Composition, characteristics and socioeconomic benefits of palm kernel shell exploitation: an overview. Journal of Environmental Science and Technology, 11: 220 – 232.*

9. *Leman, A. S., Shahidan, S., Senin, M. S. and Hannan, N. I. R. R., (2016). A preliminary study or chemical and physical properties of coconut shell powder as a filler in concrete. Conference series: Material Science and Engineering, 160, 012059: 1 – 7.*

10. *Ofor H.O (2021)," Mechanical Properties, Morphology and Elemental Composition of composites produced from Thermoplastic Polymers Filled with Egg Shell". International Research Journal of Pure and Applied Chemistry, 22(1), 59-78*

11. *Ofor H.O (2021)," Physico-Mechanical Properties of composites Produced from Thermoplastic Polymers Filled with Egg Shell". Chemical Science International Journal, 28-45.*

12. *Ofor H.O and Ojiako E.N (2019)," The Effect of Cow Horn as Filler on the Physico-Mechanical Property in Polymeric Matrices Composite". Journal of Basic Physical Research. 9 (1) 81-90.*

13. *Ofor H.O and Ojiako E.N (2019)," The Effect of Egg Shell as Filler on Creep Mechanical Property in Thermoplastic Polymer Matrices Composite". ANACHEM Journal 9 (1) 1630-1644.*

14. *Ofor H.O and Ojiako E.N (2019)," The Effect of Palm Kernel Shell as Filler on the Physico-Mechanical Property in Polymeric Matrices Composite". Journal of Basic Physical Research. 9 (1) 71-80.*

15. *Ojiako E.N, O for H.O and Nwadiogwu J.O (2019)," The Effect of Palm Kernel Shell as Filler on the Physico-Mechanical Property in Polymeric Matrices Composite". COOU Journal of Physical Sciences. 2 (2) 101-128.*

16. *Sapuan, SM, Pua F., El-Shekeil Y. and AL-Oqla FM (2013). 'Mechanical properties of soil buried kenaf fibre reinforced thermoplastic polyurethane composites. Mater Des 50:467–470.*

17. *Simone, M., Rosa, L., Evelise, F. S., Carlos, A. F. and Sonia M. B. N. (2009), "Studies on the Properties of Rice Husk Filled Polypropylene Composites—Effect of Maleate Polypropylene," Journal of Material Science, 12 (3): 333-338*

18. *Thakur, V., Singha, A. and Thakur, M. (2012). 'Biopolymers based green composites: Mechanical, thermal and physico-chemical characterization'. J Polym Environ 20(2):412–421.*

19. *Timothy, T., Ryan, M., Lisa, C., Christiana, W., and Caroline, B. (2008), "Development and Characteristics of New Materials Base on Plastic Waste and Agro Fibre," Business Media, 43(26): 4057-4068.*

20. *UNCEP, "Governing Council Ministerial Environment Forum, during Its 25th Session in February," 2009.*

21. *Yusriah, L., Sapuan, S., Zainudin, E.S. and Mariatti, M. (2014). Characterization of physical, mechanical, thermal and morphological properties of agro-waste betel nut (Areca catechu) husk fibre. J Clean Prod 72:174–180.*