Optimization of processing parameters and its effect on the mechanical properties of recycled low density polyethylene composite reinforced with *Tetracarpidium conophorum* shell particulates

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**Keywords:** recycled low density polyethylene, polymer composite, compression molding, African Walnut shell, mechanical properties

This work explored the effect of African Walnut Shell Particle (AWSP) (*Tetracarpidium conophorum*) on the properties of recycled low density polyethylene (rLDPE) composite. rLDPE/ AWSP composite were prepared via compressive moulding techniques using AWSP of sizes 300 and 600 μm respectively. Composite design of experiment and analysis of variant (ANOVA) were employed for optimization. Mechanical and morphological analysis of the composite were studied. rLDPE reinforced with AWSP of particle size 300 μm exhibited better tensile strength, modulus of rupture (MOR) and modulus of elasticity (MOE) than those of 600 μm. Morphological analysis showed that uniform distribution of the Walnut shell particulates in the microstructure of the composite is the major factor responsible for the improvement in the mechanical properties. Optimality occurred at a press temperature of 206.465 °C, press time of 10 min, press pressure of 7 MPa yielding a tensile strength of 14.082 MPa, MOR of 17.019 MPa and MOE of 755.028 MPa for 300 μm particle sized composite whereas for 600 μm size, it was achieved at press temperature of 199.993 °C, press time of 6 min, press pressure of 7 MPa giving a tensile strength of 11.252 MPa, MOR of 15.401 MPa and MOE of 459.531 MPa respectively. The result from the optimization met the standard for interior and exterior mirror casing of automobiles.

1. **Introduction**

Contemporary material requirement entails a combination of rare properties especially in materials for application in automobile, aerospace, marine and energy sector. Quite formidable array of properties like high strength to weight ratio, excellent abrasion and impact resistance, corrosion resistance among others are current requirements materials need to meet up to [1–3]. One possible way of achieving this is by replacing conventional monolithic materials with composite materials [4]. Composites are proven materials with high strength to weight ratio but cost effectiveness during production seems to be the current challenge [5].

Although polymer matrix composites have shown potentials in various areas of engineering application, most of the matrix and reinforcing materials used are synthetic and as such pose huge challenge on the environment [6–8]. The non-biodegradable nature of these materials not only makes them candidates for greenhouse gas emission but creates a waste management problem. These wastes come in the form of sachet water bags, packaging bags, water bottles among others. Similarly, one of the most abundant source of waste which also have the potential of replacing costly synthetic reinforcements in polymer matrix composites (PMCs) while improving properties like biodegradability are agricultural wastes. Rice husk, maize stalk, bread fruit shell, eggshell, tropical almond shell, groundnut shell etc have shown to have the ability to not only improve the
mechanical properties of polymers but also make them more environmentally friendly while decreasing the cost [6, 7, 9, 10]. Their renewability, low cost due to its abundance and light weight gives them an edge over synthetic filler or reinforcement materials hence the interests from researchers [9, 11–13]. Bread fruit shell as observed by [14] improved the mechanical properties of recycled low density polyethylene. Interlaminar shear strength of epoxy was enhanced due to addition of wood apple shell [15]. Shehu et al. [16] on studying the influence of particle size on mechanical properties of palm kernel shell—polyester composite observed that palm kernel shell of 300μm showcased the best combination of properties. Results from the works of [8, 17] also goes on to show how far properties and applications of agricultural waste reinforced polymer composites have gone.

African walnut (Tetracarpidium conophorum) is wild climbing plant found in forest regions of Africa and India [18]. It is mostly found in the South west states in Nigeria. It is popularly known as Ekporo by Efik and Ibibios of Cross River and Akwa Ibom, as Ukpa in Igbo, Awusa or Asala in Yoruba, Okwe in Edo and Gwandi bairi in Hausa [19]. In as much as the traditional practices believes that there are laws governing it and that if the laws are violated the plant will be wiped out from that area, there are not enough research on the plant and that’s why the values are greatly underestimated. This could make the plant go into extinction and all the benefits of the plant lost [20]. This fruit is also very reach in vitamins, minerals and calories. African Walnut shell is known for its hard shell which can be useful in tribological application. However these shells are often discarded irresponsibly and as such pose environmental problem. To reduce the hazard posed by improper utilization of these wastes (plastic and agricultural), a marriage between them is proposed which will not only yield a composite material with improved properties but will convert the so called wastes to useful engineering material and reduce the environmental impact they would have posed. This work aims at exploring the case of African Walnut shell (AWNS) and low density polyethylene from waste sachet water bags while looking at the influence of processing conditions on the properties of the composites.

2. Materials and methods

Recycled Low density polyethylene (rLDPE) used in this work was gotten from industrial waste of Ekenedirichukwu workshop at Onitsha, Anambra State. The African Walnut Shell (AWNS) was obtained from Ose Market at Onitsha. Shown in figure 1 below are walnut seed and shell.

2.1. Preparation of African Walnut shell samples

African Walnut shells collected were soaked in water for 20 min, washed with distilled water and were sun dried to remove the moisture. Mercerization was carried out using NaOH in order to reduce its hydrophilicity, improve particulate strength and adhesion properties. The chemical treatment were done by soaking the shells in 1mol of NaOH for 1 h, and then soaking in 1 mol of acetic acid for neutralization. Finally the particles were rinsed in distilled water before sun drying. The dried African Walnut shell was crushed and ground into particles using Retsch 2800 mill Sieving was done using a set of sieves after which particulates of average particles sizes 300μm and 600μm were chosen for fabricating the composites (see figure 2).
2.2. Experimental design using central composite design (CCD)

Optimization of process parameters like weight fraction, press time, press pressure and temperature was studied using Central Composite Design (CCD). Factors were chosen based on review of similar works like [21–24] and chosen levels are presented in Table 1. Trials were generated using Design Expert software (V11.02) of which a total of 30 runs were generated. The control variables were rLDPE weight%, time, temperature and pressure were designated as A, B, C and D respectively. The low and high levels were designated as −1 and +1 respectively.

Table 1. Design factors for the polymer composite.

| Factor | Name              | Units | Type  | Minimum | Maximum | Coded Low  | Coded High | Mean   | Std. Dev. |
|--------|-------------------|-------|-------|---------|---------|------------|------------|--------|----------|
| A      | rLDPE wt%         | Numeric |       | 60.00   | 95.00   | −1 ↔ 68.75 | +1 ↔ 86.25 | 77.50  | 7.96     |
| B      | Press time        | (min)  | Numeric | 4.00    | 12.00   | −1 ↔ 6.00  | +1 ↔ 10.00 | 8.00   | 1.82     |
| C      | Press Temp.       | (°C)   | Numeric | 160.00  | 240.00  | −1 ↔ 160.00 | +1 ↔ 220.00 | 200.00 | 18.19    |
| D      | Press pressure    | (MPa)  | Numeric | 5.00    | 13.00   | −1 ↔ 7.00  | +1 ↔ 11.00 | 9.00   | 1.82     |

2.3. Preparation of composite samples

Production of the composite was carried out via compression moulding according to the experimental design shown in Table 2 above. A metallic mould of dimension 250 × 250 × 5 mm³ was made in order to get sizes of the sample which were used for different tests. For quick and easy removal of the composite board after formation, the composite mixture was wrapped in an aluminum foil smeared with grease. The mixture was formed by weighing out the needed amount of Walnut shell particles and rLDPE, then mixing them and pouring into the mold which was placed inside the compression moulding machine using conditions outlined in Table 2 (See appendix for stress-strain curves). The composite board thus formed were removed and allowed to cool to room temperature after which they were conditioned at constant room temperature and relative humidity (RH) of 68% in accordance with ASTM D618 standard.

2.4. Characterization of the composite samples

Mechanical analysis like tensile and flexural test were carried out at University of Nigeria Nsukka using a Tensometric machine M500–25CT (see Figure 3), using sample size of 160 mm × 19 mm × 3.2 mm. To understand the phases present in the African walnut and the effect of incorporating AWSP in the rLDPE matrix, x-ray diffraction was carried out using an X’pert PRO Panalytical Diffractometer. Morphology of the composite samples were studied using a scanning electron microscope (VEGA 3 TESCAN).

3. Result and discussion

3.1. X-ray diffraction

Shown in Figure 4 is the XRD spectra for walnut shell and composites with the corresponding identified phases shown in Table 3. Walnut showcased an amorphous form with no prominent peaks typical of lignocellulosic materials. Presence of element like carbon can be seen thus showing that walnut is an organic (carboneous).
Silica in the form of critobalite can also be seen as well as other hard phases like corundum, wustite, kalsilite, almandine and pyrope. Presence of these hard phases accounts for the hard nature of the shells and hardness result recorded. Kalsilite and Almandine were the most predominant phases present occurring at angle 34.82°.

Table 2. Experimental Setup for 5 level-four factorial response surface design for walnut shell particle reinforced polymer composite.

| Std | Factor 1 | Factor 2 | Factor 3 | Factor 4 | Response 1 | Response 2 | Response 3 |
|-----|----------|----------|----------|----------|------------|------------|------------|
|     | A: rLDPE (wt%) | B: Press time (min) | C: Press temp (°C) | D: Press pressure | Tensile Strength (MPa) | MOR (MPa) | MOE (MPa) |
| 1   | 68.75    | 6        | 180      | 7        | 7.78       | 9.23       | 263.68     |
| 2   | 86.25    | 6        | 180      | 7        | 7.867      | 12         | 436.85     |
| 3   | 68.75    | 10       | 180      | 7        | 11.277     | 14.07      | 672.3      |
| 4   | 86.25    | 10       | 180      | 7        | 7.061      | 14.968     | 678.21     |
| 5   | 68.75    | 6        | 220      | 7        | 11.14      | 13.6       | 548.67     |
| 6   | 86.25    | 6        | 220      | 7        | 7.09       | 15.11      | 456.144    |
| 7   | 68.75    | 10       | 220      | 7        | 15.73      | 18.01      | 831.47     |
| 8   | 86.25    | 10       | 220      | 7        | 7.274      | 16.49      | 621.74     |
| 9   | 68.75    | 6        | 180      | 11       | 10.44      | 14.476     | 321.83     |
| 10  | 86.25    | 6        | 180      | 11       | 10.046     | 14.714     | 599.58     |
| 11  | 68.75    | 10       | 180      | 11       | 10.43      | 14.098     | 444.458    |
| 12  | 86.25    | 10       | 180      | 11       | 6.4        | 12.18      | 550.63     |
| 13  | 68.75    | 6        | 220      | 11       | 14.28      | 15.55      | 575.429    |
| 14  | 86.25    | 6        | 220      | 11       | 9.45       | 14.9       | 559.577    |
| 15  | 68.75    | 10       | 220      | 11       | 14.86      | 15.639     | 633.46     |
| 16  | 86.25    | 10       | 220      | 11       | 6.886      | 12.19      | 489.85     |
| 17  | 60       | 8        | 200      | 9        | 15.7       | 12.066     | 372.537    |
| 18  | 95       | 8        | 200      | 9        | 8.1        | 10.34      | 332.034    |
| 19  | 77.5     | 4        | 200      | 9        | 9.761      | 12.98      | 387.78     |
| 20  | 77.5     | 12       | 200      | 9        | 9.44       | 14.8       | 645.76     |
| 21  | 77.5     | 8        | 160      | 9        | 8.84       | 10.59      | 534.39     |
| 22  | 77.5     | 8        | 240      | 9        | 11.31      | 13.45      | 682.21     |
| 23  | 77.5     | 8        | 200      | 5        | 7.15       | 19.33      | 710.34     |
| 24  | 77.5     | 8        | 200      | 13       | 8.74       | 20.32      | 679.99     |
| 25  | 77.5     | 8        | 200      | 9        | 10.406     | 13.47      | 500.25     |
| 26  | 77.5     | 8        | 200      | 9        | 10.479     | 14.75      | 546.47     |
| 27  | 77.5     | 8        | 200      | 9        | 10.98      | 12.98      | 481.011    |
| 28  | 77.5     | 8        | 200      | 9        | 11.27      | 13.424     | 431.962    |
| 29  | 77.5     | 8        | 200      | 9        | 10.49      | 14.01      | 476.63     |
| 30  | 77.5     | 8        | 200      | 9        | 10.67      | 13.44      | 500.1      |
with a FWHM (full width half maximum) of 0.6528. This shows that major elements in walnut shell are aluminum, silicon, iron and carbon.

Incorporation of AWSP of particle size 300 μm to rLDPE matrix led to the development of a semi-crystalline composite materials as shown in figure 4. Major peaks occurred at 18.8443, 21.8481, 24.2422 and 38.2184° corresponding to allotropes of silica (cristobalite and tridymite), magnetite, chladniite and minrecordite. From the spectrum, it can be seen that silica is a major component which is in agreement with observed phases in XRD of walnut shell. Calcium in carbonate form can also be seen in the form of minrecordite CaZn\((\text{CO}_3)_2\) as well as in phosphate in the form of Na\(_2\)CaMg\(_6\)\((\text{PO}_4)_3\) (see table 3). This accounts for hard nature of walnut shells. Presence of hard phases also improves the mechanical and wear properties of the composite. Consequently, incorporation of walnut shells in recycled low density polyethylene improved crystallinity of the composite as can be seen with the presence of prominent peaks.

![Figure 4. XRD Spectra of African Walnut shell and composites.](image)

Table 3. Identified phase patterns for African Walnut shell and composites.

| Visible Ref. Code | Score | Compound Name | Displacement [°2θ.] | Scale Factor | Chemical Formula |
|-------------------|-------|---------------|---------------------|--------------|-----------------|
| * 06-0675 | 18 | Bort | 0.000 | 0.077 | C |
| * 84-0302 | 14 | W. Plistite | 0.000 | 0.047 | Fe\(_{90}\)O |
| 82-1235 | 14 | Cristobalite | 0.000 | 0.400 | SiO\(_2\) |
| 77-2135 | 12 | Corundum | 0.000 | 0.143 | Al\(_2\)O |
| 83-1220 | 12 | Kalsite | 0.000 | 0.219 | KAlSiO\(_4\) |
| 74-2029 | 11 | Almandine | 0.000 | 0.176 | Al\(_2\)Fe\(_3\)(SiO\(_4\)) |
| 86-0152 | 13 | Pyrope, syn | 0.000 | 0.473 | Mg\(_2\)Al(SiO\(_3\)) |

Identified phase patterns for rLDPE/AWSP polymer composite for 300 μm particle size.

| Visible Ref. Code | Score | Compound Name | Displacement [°2θ.] | Scale Factor | Chemical Formula |
|-------------------|-------|---------------|---------------------|--------------|-----------------|
| 76-0941 | 43 | Cristobalite low | 0.000 | 0.901 | SiO\(_2\) |
| 89-0950 | 36 | Magnetite | 0.000 | 0.331 | Fe\(_2\)O |
| 03-0227 | 27 | Tridymite, (heated) | 0.000 | 0.376 | SiO\(_2\) |
| 47-1763 | 31 | Chladniite | 0.000 | 0.192 | Na\(_2\)CaMg\(_6\)(PO\(_4\)) |
| 35-0667 | 19 | Minecordite | 0.000 | 0.129 | CaZn(PO\(_4\)) |

Observed phase patterns for rLDPE/AWSP polymer composite for 600 μm particle size.

| Visible Ref. Code | Score | Compound Name | Displacement [°2θ.] | Scale Factor | Chemical Formula |
|-------------------|-------|---------------|---------------------|--------------|-----------------|
| 77-0438 | 37 | Spinel | 0.000 | 0.040 | MgAl\(_2\)O |
| 89-0950 | 35 | Magnetite | 0.000 | 0.015 | Fe\(_2\)O |
| 76-0941 | 32 | Cristobalite low | 0.000 | 0.653 | SiO\(_2\) |
| 01-0378 | 20 | Tridymite | 0.000 | 0.197 | SiO\(_2\) |
| 47-1763 | 20 | Chladniite | 0.000 | 0.077 | Na\(_2\)CaMg\(_6\)(PO\(_4\)) |
| 72-1651 | 11 | Calcite | 0.000 | 0.011 | CaCO\(_3\) |
| 37-0451 | 24 | Natrite | 0.000 | 0.044 | Na\(_2\)CO\(_3\) |

Figure 4. XRD Spectra of African Walnut shell and composites.
Comparatively, the XRD spectrum for the walnut shell particulate—recycled low density polyethylene composite for 600 μm also showed the presence of silica in different forms which is in agreement with the observation for 300 μm. Silica (cristobalite and tridymite) also had the highest intensity showing highest percentage in the composite. Carbonates of calcium and sodium in the form of calcite and natrite can be observed with magnetite and chladnite; all which are phases which were seen in the spectrum for that 300 μm size. However compared to the XRD spectrum for the composite reinforced with 300 μm particle size, peaks at 36.3704, 38.1315 and 39.8874 were more prominent which can be attributed to the difference in particle size. The composite was observed to be more crystalline as can be seen by the number of observed peaks as shown in table 3.

3.2. Microstructural analysis
Microstructural examination of the composites carried out via scanning electron microscope can be shown in figures 5(a) and (b) below. Figure 5(a) shows the morphology of 300 μm particle sized walnut shell-rLDPE composite. The particulates are fairly uniformly distributed with good interfacial bonding, though there are some clusters in the composite. Excellent interfacial adhesion is a precedent for good mechanical properties. The micrograph for the 600μm particulate size walnut shell/rLDPE composite as shown in figure 5(b) also revealed a fairly distributed particulates in the rLDPE matrix. However, agglomerated particles of the reinforcement can also be seen to which the decreased observed mechanical properties can be attributed. The larger particle-sized walnut shell particulate showcased poorer interfacial bonding and might have acted as a crack initiator and propagator in the recycled low density polyethylene matrix.

3.3. Mechanical properties
Optimized result from the experimental design setup for tensile strength, modulus of elasticity and modulus of rupture is shown in tables 4 and 5 corresponding to 300 μm and 600 μm size. In determining the optimum combination of parameters, quadratic model in the form of Analysis of Variance (ANOVA) was employed because it has the highest order polynomial with significant additional terms and an un-aliased model.

3.3.1. Tensile strength
Fitted quadratic polynomial model based on ANOVA for the tensile behavior of the composite is shown in table 6 below. Fitness of selected model, level of significance of individual terms as well as degree of interaction of responses was determined via statistical analysis of variance (ANOVA). From table 6, lack of fit value of 1.74 was obtained. Lack of fit compares the residual with the pure error value. Pure error shows the extent of accuracy of the predicted equation. Cor Total (corrected total) shows variability in the individual observations about the mean [25]. A model F-value of 43.52 with P-value of <0.0001 indicating significance at 95% confidence level was observed for the model. The p-value (probability of error value) shows the level of significance of each regression coefficient as well as the interaction effect of each cross product. A value less than 0.0500 shows significance. The fitted model presented an R² of 0.9760 and standard deviation of 0.4919 signifying 97.60% variability. Only 3
factors (rLDPE wt%, Press Time and Press Temp.) were significant (statistically important) for increase in tensile strength of the composite at confidence level of 95%. Precision and reliability of the values were high as portrayed by the low Coefficient of variation value (5.53%). The lack of fit test with p-value of 0.8625 indicates that the model fitted to the experimental data. Predicted R-Squared of 0.9158 is in agrees with the Adjusted R-Squared of 0.9535, with a difference less than 0.2 and R² values approximately equal to 1 With an Adeq Precision value 24.8614, the model can be used to navigate the design space since a value greater than 4 is appropriate.

Examination of the residuals to confirm the appropriateness of the model used was done. The variation between the observed and predicted response residual is shown by the residual. The plot of predicted versus actual (figure 6), normal plot of residual (figure 7) and residual versus run (figure 8) were used to examine the effects. The plots seem to show decent correlation between the observed and predicted values with no variation of the constant variance which is similar to the observation of [26].

Model equation generated by Design Expert (V11.0.2) after eliminating insignificant coefficients terms (p—value >0.05) is shown below

\[
\text{Tensile Strength} = -78.74483 + 0.113361A + 1.33906B + 0.807519C \\
+ 1.01856D + 0.031000A \times B - 0.001843A \times C - 0.014594B \\
\times C - 0.078698B^2 - 0.001387C^2
\] 

(1)

Table 4. Optimization limits for the AWNSP composite for particle size of 300 micron.

| Number | rLDPE | Press time | Press Temp. | Press pressure | Tensile Strength | MOR | MOE | Desirability |
|--------|-------|------------|-------------|----------------|-----------------|-----|-----|-------------|
| 1      | 68.750 | 10.000     | 206.465     | 7.000          | 14.082          | 17.019 | 755.028 | 0.720  | Selected |
| 2      | 68.753 | 10.000     | 206.148     | 7.000          | 14.049          | 16.995 | 753.261 | 0.720  |
| 3      | 68.750 | 10.000     | 206.811     | 7.000          | 14.116          | 17.045 | 757.001 | 0.720  |
| 4      | 68.861 | 10.000     | 206.587     | 7.000          | 14.045          | 17.039 | 755.602 | 0.720  |
| 5      | 68.750 | 10.000     | 206.308     | 7.007          | 14.070          | 16.993 | 753.404 | 0.720  |
| 6      | 68.751 | 10.000     | 207.341     | 7.001          | 14.170          | 17.084 | 759.955 | 0.720  |
| 7      | 68.750 | 10.000     | 207.521     | 7.000          | 14.187          | 17.099 | 761.091 | 0.720  |
| 8      | 69.008 | 10.000     | 206.405     | 7.000          | 13.962          | 17.040 | 754.411 | 0.720  |
| 9      | 68.926 | 9.994      | 206.366     | 7.000          | 13.990          | 17.022 | 753.740 | 0.719  |
| 10     | 68.751 | 10.000     | 205.072     | 7.000          | 13.942          | 16.911 | 747.324 | 0.719  |

Table 5. Optimization limits for the AWNSP composite for particle size of 600 micron.

| Number | rLDPE | Press time | Press Temp. | Press pressure | Tensile Strength | MOR | MOE | Desirability |
|--------|-------|------------|-------------|----------------|-----------------|-----|-----|-------------|
| 1      | 68.750 | 6.000      | 199.993     | 7.021          | 11.252          | 15.401 | 459.531 | 0.804  | Selected |
| 2      | 68.750 | 6.000      | 200.000     | 7.021          | 11.266          | 15.374 | 458.800 | 0.803  |
| 3      | 68.778 | 6.021      | 200.000     | 7.000          | 11.241          | 15.382 | 458.828 | 0.803  |
| 4      | 68.750 | 6.000      | 200.000     | 7.039          | 11.277          | 15.350 | 458.152 | 0.802  |
| 5      | 68.856 | 6.000      | 200.000     | 7.000          | 11.225          | 15.369 | 459.087 | 0.802  |
| 6      | 68.841 | 6.000      | 200.000     | 7.036          | 11.251          | 15.325 | 457.874 | 0.801  |
| 7      | 68.750 | 6.086      | 199.997     | 7.001          | 11.236          | 15.354 | 457.082 | 0.799  |
| 8      | 69.018 | 6.000      | 200.000     | 7.000          | 11.182          | 15.318 | 458.358 | 0.799  |
| 9      | 68.750 | 6.029      | 201.699     | 7.000          | 11.331          | 15.609 | 466.150 | 0.796  |
| 10     | 68.750 | 6.000      | 202.251     | 7.001          | 11.364          | 15.697 | 469.401 | 0.796  |

Table 6. Statistical analysis of Variance (ANOVA) for the fitted Quadratic Model for Tensile Strength.

| Source          | Sum of Squares | Degree of freedom | Mean Square | F-value | p-value |
|-----------------|----------------|-------------------|-------------|---------|---------|
| Model           | 147.41         | 14                | 10.53       | 43.52   | <0.0001 |
| Residual        | 3.63           | 15                | 0.2419      |         |         |
| Lack of Fit     | 1.74           | 10                | 0.1735      | 0.4582  | 0.8625  |
| Pure Error      | 1.89           | 5                 | 0.3787      |         |         |
| Cor Total       | 151.04         | 29                |             |         |         |
| Std. Dev.       | 0.4919         | R²                | 0.9760      |         |         |
| Mean            | 8.89           | Adjusted R²       | 0.9535      |         |         |
| C.V.%           | 5.53           | Predicted R²      | 0.9158      |         |         |
| Adeq Precision  |                |                   | 24.8614     |         |         |
Where $A = rLDPE\ wt\%$, $B = Press\ Time\ (minutes)$, $C = Press\ Temperature\ (^\circ\ C)$ and $D = .\ Press\ Pressure\ (MPa)\n
Figures 9(a) and (b)–11(a) and (b) show the interaction plot for the weight fraction of $rLDPE$, press time, press temperature and press pressure with tensile strength for $300\ \mu m$ and $600\ \mu m$ respectively. From figures 9(a) and (b) where a plot of press time and $rLDPE$ weight keeping press temperature and press pressure constant, an improvement in tensile strength of the composite as the weight fraction of the filler increases and decrease as the $rLDPE$ wt% increases. Polymer composites with smaller particle size ($300\ \mu m$) of AWSP shows higher tensile strength than the ones of larger particle size ($600\ \mu m$) (figures 9(b)–(b)). This type of behavior could be due to better dispersion and improved adhesion between the $rLDPE$ matrix and finer AWN shell powder as a result of higher aspect ratio associated with the finer particles. Similar result was observed by [27] while investigating the behavior of Linear Low Density Polyethylene Filled Oyster Shell Powder composite. Nwanonenyi et al [24] also reported an increase in tensile strength with increase in filler weight and filler size. It could also be seen from figures 9(a) and (b) that increase in press time increases the tensile strength of the composite. This is due to improved bonding via compaction as a result of longer pressing. Figures 11(a) and (b) shows the effect of press temperature and press time at a constant wt% $rLDPE$ of 77.5 and constant pressure of 9 MPa on the tensile strength of the composite for $300\ \mu m$ and $600\ \mu m$ respectively. It can be seen that the tensile strength increases with increase in press time. This could be due to the fact that there is enough time for the
compaction of the composite. Figure 10(a) shows that increased temperature and molding time has positive influence on the tensile strength.

3.3.2. Modulus of elasticity (MOE)
Table 7 shows the analysis of variance (ANOVA) for fitted quadratic polynomial model for modulus of elasticity (MPa). The significance of the model was verified by F-value of 53.68 and was equilibrated by the p-value of <0.050 indicating a significance at 95% confidence level. An R² value of 0.9804 and a predicted R² value of 0.9317 with a difference of 0.2 shows that the model has a variability of 98.04%. A low value of Coefficient of variation of 3.86% also shows the significance of the model (degree of precision and reliability of the values). A high adeq. Precision value of 38.2432 was also recorded. Three main model factors (A) Resin, (B) Pressure, and (D) Time), interaction terms (AB, AC, AD, BC, BD,) and the quadratic term (D²) were all found to be statistically significant for increase in MOE of the composite at confidence level of 95%. Model equation for the modulus of elasticity is given as

\[
\text{Modulus of Elasticity (MOE)} = -2806.48703 + 40.66542A + 96.81686B - 235.11452D - 0.982132A \times B - 0.269621A \times C + 1.49328A \times D - 0.807861B \times C + 14.02705B \times D - 0.131580C \times D + 2.74253D^2
\] (2)
3D-contour plot of the parameters and MOE of composites is shown in figures 12(a) and (b), 13(a) and (b) and 14(a) and (b). From figures 12(a) and (b) which shows the influence of press time, rLDPE weight fraction on the MOE at constant temperature and pressure for the composites of different particle sizes (300 μm and 600 μm respectively), modulus of elasticity of the composites increased with increases in filler content and decreased with increase in particle size of the filler. Thus it followed the same trend as that of tensile strength. This
observation climaxes the fact that the introduction of fillers into a polymeric material increases the stiffness of the composites \cite{28, 29}. According to the work done by \cite{30} on snail shell powder and talc reinforced polymer composite, the snail shell powder help to enhance the modulus of elasticity on the composites.

Figures 13 (a) and (b) show the plot for the influence of press temperature, rLDPE weight fraction on the modulus of elasticity with press time and pressure being constant for composites with fillers of particle size 300 \( \mu \text{m} \) and 600 \( \mu \text{m} \) respectively. An improvement in MOE can be seen as press temperature and rLDPE filler weight increases, High temperature guarantees uniform melt and proper mixing.

The interaction between press pressure and press temperature for the composites of different particle sizes (300 \( \mu \text{m} \) and 600 \( \mu \text{m} \) respectively) is shown in figures 14 (a) and (b). At lower temperature and pressure, a decline in MOE can be observed. Inadequate pressure and low temperature makes proper compaction unfeasible hence the decrease in MOE. However as the press pressure and press temperature increases the MOR increases, apparently there was enough temperature and pressure for the compaction thereby stiffening up the composite. From the Statistical plot in figures 13 and 14, it can be seen that high pressing temperatures, low press pressure, long pressing time and high resin content favor increase in MOE, hence are the most significant factors for MOE of the Walnut Shell composite.

3.3.3. Modulus of rupture (MOR)

Flexural behavior of rLDPE/AWSP composite also known as modulus of rupture is shown in tables 4 and 5 above. ANOVA used to determine the level of significance is shown in table 8 below. It can be seen that F-value of
87.04 with a p-value < 0.0001 was obtained indicating up to 95% significance since the equilibrated p-value for 95% significance is 0.05. The model as fitted presents an R- square of 0.9878 and standard deviation of 0.4413 with the weight fraction of rLDPE and press time being significant factors although other interaction terms were also found to be significant. The Predicted R-Squared value of 0.9449 is in reasonable agreement with the Adjusted R-Squared of 0.9765 thus indicating fitness between data and model.
Model equation based on p-value less than 0.05 is shown below

\[
\text{Modulus of Rupture (MOR)} = -94.82457 + 0.403431A + 3.92110B \\
- 0.005749A \times B - 0.028431B \times C + 0.407250B \times D \\
- 0.015475C \times D + 0.003184A^2 - 0.102281B^2 \\
- 0.000459C^2 + 0.144906D^2
\] (3)

From figures 15(a) and (b) and 16(a) and (b) which shows the plot of different parameters for the composites of different particle sizes (300 \( \mu \)m and 600 \( \mu \)m respectively). It can be seen that at higher filler content and lower particle size of filler, an enhancement in the modulus of rupture occurs. The may be due to the rigidity and inflexibility as a result of more uniform dispersal of the filler in the polymer matrix, which invariably hinders the chain movement of the molecules during deformation. This is in agreement with the work done by [31] on the influence of natural fibers and particulates on flexural properties of polymer composites. This is also similar to the result gotten by [30]. This type of increase in MOR was also reported by [32]. It could also be seen that the MOR of 300 \( \mu \)m is higher than that of 600 \( \mu \)m, this could be because the finer particle bonds better than the coarser particle in this case 600 \( \mu \)m.

4. Conclusion

In the present research optimization of process parameter for the producing composite from AWNS was successfully carried out by Central Composite Design (CCD) of which model equations for predicting tensile strength, modulus of elasticity and modulus of rupture were generated. Weight fraction of rLDPE, press time, press temperature and pressure as well as particle size of the filler influenced the mechanical properties of the composite. An increment in the mechanical properties of the composites with increasing parameters and particle weight was observed with optimal properties occurring at intermediate processing conditions. Optimization using the CCD design of experiment showed the optimum values of the composite occurred at press temperature of 206.465 °C, press time of 10 min, press pressure of 7 MPa yielding a tensile strength of 14.082 MPa, MOR of 17.019 MPa and MOE of 755.028 MPa for 300 \( \mu \)m particle size whereas for 600 \( \mu \)m size, optimality was achieved at press temperature of 199.993 °C, press time of 6 min, press pressure of 7 MPa giving a tensile strength of 11.252 MPa, MOR of 15.401 MPa and MOE of 459.531 MPa.

Acknowledgments

The authors wish to acknowledge the technical staff of Department of Metallurgical and Materials Engineering, Nnamdi Azikiwe University, Awka, Nigeria.
Appendix A

Stress—strain curves for samples shown in table 2.
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