Effects of breadfruit seed hull ash particles on microstructures and properties of recycled low density polyethylene/breadfruit seed hull ash composites

C.U. Atuanya\textsuperscript{a,}, S.C. Nwaigbo\textsuperscript{b} and P.K. Igbokwe\textsuperscript{c}

\textsuperscript{a} Department of Metallurgical and Materials Engineering, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria.
\textsuperscript{b} Department of Mechanical Engineering, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria.
\textsuperscript{c} Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria.

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\textbf{Abstract.} Renewable resources such as natural fillers in reinforced materials, with their new range of applications, represent an important basis for fulfilling the ecological objective of creating environmental friendly materials. A study on composites, using breadfruit seed hull ash particles (BFHAP) as a reinforcing material and recycled low-density polyethylene (RLDPE) as a novel matrix, has been undertaken. The composites were produced by varying the breadfruit seed hull ash particles from 5-25 wt\% and the properties studied using mechanical tests and microstructural analysis. The results show that there was a uniform distribution of the breadfruit seed hull ash particles in the microstructure of RLDPE composites, which is a major factor responsible for improvement in mechanical properties.

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1. Introduction

Polymer composite materials are used in a wide range of structural applications in aerospace, construction and automotive industries due to their lightweight and high specific stiffness and strength [1]. A variety of materials are used, ranging from lower performance glass fibre/polyester used in small sail boats and domestic products, to high performance carbon fibre epoxy systems used in military aircraft and spacecraft [2]. One sector where the use of composite materials is still evolving is the automotive industry. Composite materials offer great potential in reducing vehicle weight, thus, increasing fuel efficiency and reducing CO\textsubscript{2} emissions. In addition to weight reduction, a number of individual parts can be produced making the high-volume composite car concept cost effective [2-3].

In its most basic form, a composite material is one which is composed of at least two elements working together to produce material properties that are different to the properties of those elements alone. In practice, most composites consist of bulk material (the ‘matrix’) and reinforcement of some kind, added, primarily to increase the strength and stiffness of the matrix [4].

In recent years, there has been a perceived shortage of wood fibre for composite products due to competition for fibre by pulp mills, reduced harvesting and manufacturing, and diminished log quality. Also, there is pressure from environmentalists to reduce forest use and regulatory legislation pending on the disposal of agri-fibres [4-8]. For example, any potential to reduce field burning is an environmental benefit and helps address the issue of restricted open burning. There are
tremendous quantities of agricultural biomass available for non-agricultural use, such as paper and composite products.

Some previous studies on the potential of using agro-waste on the production of polymer composites are as follows: Patricio Toro et al. [9] studied Egg Shell (ES) as a new bio-filler for polypropylene composites. The work proved that ES composites showed lower modulus of elasticity (E) values than talc composites. Talc filler could be replaced up to 75% with eggshell, while maintaining a similar stiffness and E compared to talc composites.

Hornsby et al. [10] studied the microstructure, thermal and mechanical properties of flax and wheat straw as reinforcing additives in thermoplastics. In their study, the addition of flax and wheat straw caused a significant increase in tensile modulus, particularly in the case of flax fibres, which gave higher tensile yield strength and Charpy toughness.

Abdullah et al. [11] studied the water absorption and mechanical properties of high density polyethylene/egg shell composite. It was found that the addition of egg shell powder to the polymer led to a decrease in tensile strength, modulus of elasticity and shore-D hardness. On the other hand, it increases the exposure time, the water absorption of polyethylene/egg shell composite increases by increasing the wt% of egg shell.

Ahmad et al. [12] studied the use of rice husk and rice husk ash as reinforcement in polypropylene composites and the influence of coupling agents on their mechanical properties. They found that the flexural modulus and tensile modulus increased with reinforcement content, while elongation at break and Izod impact strength showed a minimal decrease.

Recently, Hassan et al. [13] studied the morphological and mechanical properties of carbonized waste maize stalk as reinforcement for eco-composites. They found that the tensile strength, tensile modulus and compressive strength values increased as the carbonized maize stalk ash content increased, but there was a gradual decrease in impact strength. These results show that the carbonized maize stalk ash can be used to improve the strength of polymer matrix composites for use in automobile and building applications.

Aigbodion et al. [14] studied the tribological behaviour of recycled low density polyethylene (RLDPE) polymer composites with bagasse ash particles as reinforcement using a pin-on-disc wear rig under dry sliding conditions. The influence of wear parameters, such as applied load, sliding speed, sliding distance and percentage of bagasse ash fillers, on wear rate was investigated. The results show that the addition of bagasse ash as the filler material in RLDPE composites increases the wear resistance of the composite greatly.

Atuanya et al. [15] investigated the suitability of using recycled low density polyethylene (RLDPE) in wood composite board manufacture. The composite board was produced by compressive moulding by increasing the percentage of RLDPE from 30 to 50 wt%, with an interval of 10 wt%, at temperatures of 140 and 180°C, pressure of 30 to 40 kg/cm² and pressing time of 7 to 13 min. The results show that the Modulus Of Elasticity (MOE) and Modulus Of Rupture (MOR) meet the minimum requirements of the European standards, for general purposes. The boards produced had a tensile strength within the requirements, and, thus, RLDPE can be used in board production for general purpose applications.

Aigbodion et al. [16] studied high density polyethylene (HDPE) composite reinforced with 20 wt% Orange Peel Ash particles (OPAp). Thermogravimetric analysis (DTA/TGA) (space) was conducted on the HDPE/orange peel ash particle composite to clarify the effect of OPAp on the thermal decomposition behavior of the resultant composite. The values of the activation energy for thermal decomposition reflected the improvement of the thermal stability of the HDPE/OPAp composite. The study has established that orange peel ash particles are beneficial as being thermal decomposition resistant and reinforcing particles in the HDPE matrix composite.

Agunsoye et al. [17] studied the effect of palm kernel shell on the microstructure and mechanical properties of recycled polyethylene (RLDPE) reinforced with palm kernel shell particulate composite as a new material for engineering applications. The composites were produced by a compounding and compressive moulding technique, varying the palm kernel shell particles from 5-25 vol%, with particle sizes of 150, 300 and 400 µm. The results show that composites produced with 150 µm particle size had the best properties of the entire grade and that the grade can be used for interior applications such as car seats, dash boards and car interiors for decorative purposes or for other interior parts of an automobile where high strength is not considered a critical requirement.

This foregoing research motivated our investigation into the possibility of using breadfruit seed hull waste material and recycled low density polyethylene, which are abundantly available in Nigeria, for the manufacture of breadfruit seed hull ash polymer matrix composite. The present investigation has focused on the utilization of abundantly available breadfruit seed hull ash in a useful a manner by dispersing it into a polymer matrix to produce composites.

A recent publication by the author and his co-workers [18] shows the characterization of breadfruit seed hull ash for potential utilization in metal matrix composites for automotive applications. They found that the African breadfruit tree (Treculia africana) is native to many tropical countries, like the West Indies, Ghana, Sierra, Nigeria and Jamaica, and that one
breadfruit pod may contain up to 100-200 seeds. The breadfruit is about the size of a football or more, is greenish in color and the seed hull is brown or black. The edible seed is whitish yellow. The seeds can be de-hulled to remove the seed hull (shell), which is discarded as waste. Results of the characterization of breadfruit seed hulls as reinforcer material are very promising and have properties similar to other agro-waste that has been used.

2. Materials and methods

2.1. Materials/equipment

The raw materials used for this research are African breadfruit seed hull, obtained as waste from breadfruit processing units market at Awka, Anambra State, Nigeria (Figure 1), and recycled low density polyethylene.

The breadfruit seed hull was dried for 48 hrs in the sun and ground to powder. The powder was placed in a graphite crucible and fired in an electric resistance furnace at a temperature of 1300°C to form breadfruit hull ash. The ash was ball milled at a speed of 200 rpm for 6 hours to obtain a fine powder of 2 μm (Figure 2). Recycled low density polyethylene (RLDPE) was collected from the refuse dump site in Awka, Anambra state, Nigeria (Figure 3), and was washed, dried and pulverized into particles.

The equipment used in this research includes: a metal mould, hydraulic press, Avery Dennison impact tester, rockwell hardness, Instron machine, grinding and polishing machine, Scanning Electron Microscope (SEM), and a two roll mill.

2.2. Method

The fabrication of the various composites was carried out using a compression mould technique. The formulations comprise 5-25 wt% of BFSHAp. After drying in an oven at 105°C, the breadfruit seed hull ash and the RLDPE were compounded in a two roll mill at a temperature of 130°C into a homogenous mixture. The mixture was placed in a 350 mm by 350 mm rectangular mould and pressed to a thickness of 4 mm. At the end of the press cycle, the composites were removed from the press for cooling.

The Scanning Electron Microscope (SEM) JEOL JSM-6480LV was used to examine the surface morphology of the breadfruit seed hull ash particles and composite samples. The surfaces of the specimens were examined directly by scanning electron microscope JEOL JSM-6480LV. The samples were washed, cleaned thoroughly, air-dried and coated with 100 Å thick platinum in a JEOL sputter ion coater and observed SEM at 20 kV. The digitized images were recorded.

Test samples were cut from the composites for the mechanical test according to the recommended standard for each test. Prior to the test, all the samples were conditioned at a temperature of 23 ± 2°C and relative humidity of 65% according to ATM D618-08 [19].

The basic method of determining the density of composite samples by measuring the mass and volume of the sample was used. A clean sample was weighed accurately in air using a laboratory balance and then suspended in water. The weight of the sample
when suspended in water was determined, and the volume of the sample was determined from the effect of displacement by water (Archimedian principle). The density of the sample was estimated from the following equation [19]:

\[
\text{Density} = \frac{\text{Mass}}{\text{Volume}}
\]

Test specimens with dimensions of 50 mm x 50 mm were prepared for the evaluation of the water absorption test, in accordance with the ASTM D4762-11a Standard Guide for Testing Polymer Matrix Composite Materials. The thickness of each specimen at three locations was measured and each specimen weighed with a digital balance. Then, the test specimens were placed in water and soaked for 24 h. Further measurement of the weight of the soaked samples was undertaken.

The tensile test of the composite samples was conducted on an Instron testing machine with a strain rate of \(2 \times 10^{-3} \text{s}^{-1}\), as specified by the American Society for Testing and Materials [19].

A static bending test (dry) was conducted, according to the ASTM D1037 standard, on size 150 x 50 x 4 mm, and bending speed of 10 mm/min [19].

The impact test of the composite samples was conducted in accordance with ASTM D256-93 [19], using a fully instrumented Avery Denison test machine. A Charpy impact test was conducted on notched samples.

The hardness of the composites was determined by a rockwel hardness machine (BS903 part B 26) [19], using a 1.56 mm steel ball indenter, a minor load of 10 kg, and a major load of 100 kg. Before the test, the mating surfaces of the indenter, plunger rod and test samples were thoroughly cleaned.

3. Results and discussion

A photograph of the composites (Figure 4) shows visually uniform distribution of breadfruit seed hull ash particles and RLDPE. The distribution of particles is influenced by compounding the breadfruit seed hull ash particles and RLDPE in a two roll mill, which resulted in good mixing.

The surface morphology of the breadfruit seed hull ash is seen in the Back Scattered Electron (BSE), as shown in Figure 5. Breadfruit seed hull ash particles were observed to be solid in nature, but irregular in size. Some spherical shaped particles can also be seen in Figure 5. The EDS analysis of breadfruit seed hull ash morphology consists mainly of Fe, Cr, Si, C, O, Mg and Al as shown in the scan (Figure 5).

The microstructure of the RLDPE matrix revealed chains of an amorphous structure with linear boundaries between adjacent spherulites (Figure 6). From the EDS spectrum, it can be clearly seen that the functional group of the RLDPE was revealed.

The surface morphologies of the composites by SEM are show in Figures 7-11. Morphological analysis using SEM clearly shows a difference in the morphology of the RLDPE (Figure 6) and the composites (Figures 7-11). The microstructure clearly shows that when the breadfruit hull ash particle is added to the RLDPE, morphological changes in the structure occur.

The microstructure reveals that there is a reasonably uniform distribution of BFSHAp particles and the RLDPE. The breadfruit seed hull ash particles are embedded within the amorphous matrix and randomly distributed in the matrix planar boundaries. The surface of the breadfruit seed hull ash particles is smooth, indicating that the compatibility between particles and the RLDPE is fairly good. It can be seen that the breadfruit seed hull ash particles are not well detached from the RLDPE surface, as the weight fraction of breadfruit seed hull particles increased in the RLDPE. This is due to fairly good interfacial bonding between the polymer and the particles. Similar observation was obtained from the work of Hornsby et al. and Abdullah et al. [10-11].

The unreinforced RLDPE reveals the presence of Hand C, as evident from the EDS spectra (Figure 6). The EDS analysis of the composite materials (Figures 7-11), reveals the presence of H, Si, Fe, Mg, O, Cr and K in the composites, since the EDS of breadfruit seed hull ash particles consists of C, Si, Mg, Na, Cr, O, K, Al (Figure 5). Figures 7-11 clearly show that there is proper intimate mixing of breadfruit husk particles with the RLDPE. The particle-matrix interface plays an important role in composite properties, and a strong particle-matrix interface bond is critical for their high mechanical properties [8-12]. Delamination between the particles and the polymer matrix was not observed in this study.

The results reveal that the presence of breadfruit seed ash particulates slightly increase the density of the PMCs. The density of the reinforced PMCs particle composites increased from 0.75 g/cm³ at 0 wt% BFSHAp, in addition to 1.15 g/cm³ at 25 wt%
Figure 5. SEM/EDS microstructure of breadfruit seed hull ash at 2 micrometer.

Figure 6. SEM/EDS of the microstructure of the RLDPE.

Figure 7. SEM of the microstructure of the composite with 5 wt% BFSHAp.
Figure 8. SEM of the microstructure of the composite with 10 wt% BFS HAp.

Figure 9. SEM of the microstructure of the composite with 15 wt% BFS HAp.

Figure 10. SEM/EDS of the microstructure of the composite with 20 wt% BFS HAp.
BFSHAP (Figure 12). Hence, not much change in the PMCs density was observed. This work is in line with earlier work carried out by Abdullah [11]. The Water Absorption (WA) of the composites is shown in Figure 13, and it is not too high.

The low level of water absorption recorded may be due to the compounding of the BFSHAP and RLDPE; this increased the interfacial bonding between the RLDPE and the breadfruit seed hull ash, which led to a decrease in the porosity level, and, hence, the low water absorption level of the composites.

The swelling that occurs during water absorption is the sum of two components, namely, swelling by hygroscopic particles and the release of compression stresses imparted to the composites during the pressing of samples in the hot press [1-3]. The result obtained is in par with the work of Abdullah et al. [11] who also found that the water absorption of the high density polyethylene/egg shell composites increased by increasing exposure time for the same filler content.

The hardness values of the composite samples increased as the percentage of breadfruit seed hull particles was increased in the RLDPE matrix (Figure 14), which is 60% increment in the hardness values over that of the unreinforced sample at 25 wt% of BFSHAP. This is due to an increase in the percentage of the hard and brittle phase of the ceramics body in the polymer matrix. In comparison with the unreinforced RLDPE matrix, a substantial improvement in hardness values was obtained in the reinforced polymer matrix. This is in line with the earlier work of Patricio et al. and Hassan et al. [9,13].

The increase in modulus of elasticity with increasing breadfruit seed hull ash particle addition is expected, since the addition of breadfruit seed hull ash
particles to the RLDPE increases the stiffness of the composites (Figure 15).

The tensile strength increased from 6.3 MPa at 0 wt% of BFSFAp to a maximum of 12.40 MPa at 20 wt% BFSAFap (Figure 16), which is 90.76% increment in tensile strength over that of the un-reinforced sample. The high values of tensile modulus and tensile strength observed in this work may be due to the fairly good distribution and dispersion of the BFSFAp in the RLDPE matrix, resulting in strong-particle-RLDPE matrix interaction. This good particle dispersion improved particle-RLDPE matrix interaction and, consequently, increased the ability of the BFSFAp to restrain gross deformation of the RLDPE matrix. The tensile strength obtained in this study remained within acceptable levels [14,20].

From the bending strength of the RLDPE/BFSFAp particulate composites obtained experimentally from the three point bend tests, it is interesting to note that bending strength increases with an increase in BFSFAp in the RLDPE matrix. For example, the bending strength of 60.50 N/mm² was recorded for the RLDPE matrix and 105.70 N/mm² at 25 wt% BFSFAp (Figure 17), which is a 74.71% increment in the bending strength over that of the unreinforced sample. There is an improvement in the bending strength of the composite as the particle weight fraction increases. The platy nature and random-in-plane arrangement of the particles likely lead to rigidity and better absorption of compressive forces, leading to increases in overall bending strength (Figures 6-11).

The results of the impact strength shows that the impact strength of the composites slightly increased with an increase in breadfruit seed hull ash particle addition (Figure 18).

High strain rates or impact loads may be expected in many engineering applications of polymer composite materials. The suitability of a polymer composite for such applications should, therefore, be determined not only by usual design parameters, but by the impact or energy absorbed [1-4]. For all the composite samples, notched impact energy increased with increasing BFSFAp content (Figure 18). This was not expected, but the result is in agreement with the work of other researchers [3,20,21]. The notch acts as a crack initiator, therefore, the notched impact test is a measure of crack propagation, while the
Figure 18. Variation of impact energy with different wt% breadfruit seed hull ash/RLDPE composites.

Figure 19. SEM of the fracture tensile sample of RLDPE.

unnotched impact test includes crack initiation and propagation [21].

The SEM of the fracture surface of the RLDPE and its composite at 20 wt% BFSHAp are shown in Figures 19-20. Morphological results obtained from the SEM micrograph in Figures 19-20 clearly show that there is proper intimate mixing of breadfruit seed hull ash particles with the RLDPE in the bio-composites synthesized. There are no voids in the composites: individual particles are covered with the RLDPE matrix. These factors are responsible for increases in the results of the tensile strength and impact energy obtained in this present study.

The results obtained in this research were compared with a typical bumper beam material called LFRT. The analysis revealed that the results obtained at 20 wt% BFSHAp indicate that some mechanical properties, such as hardness values, density, Young’s modulus, flexural strength and impact energy, are similar to LFRT by Cheon et al. [2]. The new material also must improve the ability to absorb more impact load and increase the protection of the front car component.

4. Conclusions

In the present research, different experimental techniques have been used to characterize the microstructure and properties of RLDPE and its composites containing different weight fractions of breadfruit seed hull ash particles. From the results of the investigation and discussion, the following conclusions can be made:

1) This work shows the successful fabrication of RLDPE and the breadfruit seed hull ash particle composite by compounding and compression moulding.

2) Uniform distribution of the breadfruit seed hull ash particles in the microstructure of the polymer composites is a major factor responsible for the improvement in the mechanical properties.

3) The good and better interfacial bonding between the RLDPE and the breadfruit seed hull ash particles resulted in the appreciable values of water absorption obtained.

4) There is not much difference between the density of unreinforced RLDPE and that reinforced with breadfruit seed hull ash particles. This means that a low weight component can be produced.

5) The hardness values obtained from RLDPE reinforced with breadfruit seed hull ash particles increased with an increase in the weight fraction of breadfruit seed hull ash particles.

6) The developed composites have better properties at the ranges of 20 wt% BFSHAp addition. For optimum service conditions, breadfruit seed hull ash particles addition should not exceed 20 wt%.
References


Biographies

Clement Uche Atuanya obtained MS and PhD degrees, respectively, from the Moscow Institute of Steel and Alloys, Moscow, Russia, and the University of Benin, Nigeria. He is currently senior lecturer in the Department of Metallurgical and Materials Engineering at Nnamdi Azikiwe University, Awka, Nigeria, and his research interests include composites (polymer and metal). Atuanya is a registered engineer, member of the Material Society of Nigeria and the Nigerian Metallurgical Society. He has over 30 scientific articles and two books to his credit.

Solomon Nwigbo obtained a BS degree (Mechanical), in 1997, from the Federal University of Technology, Owerri, Nigeria, an MS degree (Industrial/Production Engineering), in 2001, from the University of Ibadan, and a PhD degree (Manufacturing Engi-
neering), in 2009, from Nnamdi Azikiwe University, Awka, Nigeria, where he is currently senior lecturer in the Department of Mechanical Engineering. His current research interests cover natural fiber reinforced composites, flame and fire engineering and joining processes. Dr. Solomon is a member of IAENG and the Nigerian Institute of Engineering Management. He has published more than 20 journal papers.

**Philo K. Igbokwe** is Professor of Chemical Engineering in Nnamdi Azikiwe University, Awka, Nigeria, and is currently the Dean of the Faculty of Engineering. She has supervised over five PhD degree dissertations, more than twenty MS degree theses, and has also headed research teams in her particular fields of interest, including clay composites, adsorption, flocculation and separation techniques.