Synthesis and characterization of hybrid polypropylene matrix composites reinforced with carbonized *Terminalia catappa* shell particles and *Turritela communis* shell particles

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**ABSTRACT**

The use of natural fillers in plastics to substitute conventional synthetic fibres is effective and economical. Eco-friendly bio-composites polypropylene matrix composites reinforced with blended carbonized *Terminalia catappa* (almond) shell particles and *Turritela communis* (periwinkle) shell particles were synthesized by mould casting. Five to twenty-five weight percent of reinforcement was used and the microstructure, water absorption and mechanical properties of developed hybrid composites were evaluated. The microstructure showed a fairly uniform distribution of reinforcement particles in the matrix. The hybrid composite exhibited the best mechanical properties in terms of ultimate tensile strength (8.26 MPa), hardness (134.22 BHN), impact energy (21.81 J), and flexural strength (6.89 MPa) at 15 wt. % filler concentration. These indicate the efficacy of hybridization and the synergy between tropical almond shell ash and periwinkle shell particulates.

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Bio-composites; natural fillers; polymer matrix; mechanical properties

1. Introduction

It has been established that polymers have some limitations such as low stiffness and low resistance to impact on loading. Hence, polymers do not usually have the requisite mechanical strength for application in various fields. The reinforcement of polymers substantially enhances their mechanical properties and makes them more suitable for a large number of diverse applications. Polymeric materials reinforced with synthetic fibres such as glass, carbon and aramid provide advantages of high stiffness and strength to weight ratio as compared to conventional construction materials, i.e. wood, concrete and steel. Despite these advantages, the widespread use of synthetic fibre-reinforced polymer composites has the tendency to decline because of their high costs, their use in non-efficient structural forms, and most importantly, their adverse environmental impact [1].

Polymers are ideal materials because of resistance to corrosion, low coefficients of friction as glazing materials, low density and high toughness along with high transparency properties. The practical choice of polymeric materials is, however, not only determined by the mechanical and tribological properties but also by the price, simplicity of production, processing and the practical limitations in the real application [2,3].

Particulate fillers are used to modify the physical and mechanical properties of polymers in many ways. Polymeric materials are noted for their versatility, high resistance to chemicals, outstanding adhesion to a variety of substrates, toughness, high electrical resistance, durability at high and low temperatures, low shrinkage upon cure, flexibility, and the ease with which they can be poured or cast without forming bubbles [4]. The addition of such particulate fillers into polymers is primarily aimed at cost reduction and stiffness improvement for commercial applications [5]. Addition of fillers is favoured because it is a cheap, effective and a fast method to modify the properties of the base material. The degree of improvement often depends on the type of filler (synthetic or natural), particle size and shape, filler content, and surface treatment which promotes interaction between the filler and the polymer matrix [6]. Various kinds of polymers and polymer-matrix composites reinforced with filler particles have a wide range of industrial applications such as electrical industries, commercial and military aircrafts, heaters, electrodes [7], floor covering, composites with thermal durability at high temperature [8]. Polypropylene (PP) is one of the most important commodity polymers and is used in many areas, such as home appliances, automotive parts, construction and other important industrial applications [9].

The need for non-toxic and environmentally friendly materials favours the use of natural fillers, over inorganic and synthetic fillers, as fillers in polymeric materials. Other researchers have used lignocellulosic fillers as reinforcing material in different polymer
matrices [10,11]. Sisal leaves particles were used in reinforcing PP matrix by compression moulding to assess the possibility of using it as a new material for engineering applications. The results revealed that sisal particles were uniformly dispersed in the matrix with strong interfacial bonding which enhanced the mechanical properties of the composites [12]. Several lignocellulosic materials are used as fillers or reinforcement in thermoplastic composites, including fibres of sugarcane, banana, jute, ramie, flax, pineapple, curaua, sisal, cotton, coir, luffa cylindrical [13] and palm leaf waste [14]. Lignocellulosic materials have become important as fillers or reinforcements in polymer or ceramic matrices due to their advantages in relation to other inorganic or synthetic materials [15]. Some of the advantages of these materials are: they are fully and easily recyclable, meeting minimum recycling content requirements; they are non-abrasive to machinery; they have the same performance for lower weight and are stronger (25–30%) for the same weight; they result in non-brittle fracture on impact and are more shatter resistant; they have lower processing energy requirements and a low thermal expansion coefficient; they have a natural appearance, are easily coloured and are low cost, costing less than the base resin [13].

Tropical almond fruits (Terminalia catappa) are among the most significant lignocellulosic materials. Almond fruits are very important crops grown in the world’s temperate regions and the shells account for about 35–75% of the total fruit weight. Consequently, about 0.8–1.7 million tons of almond shell is left annually. Almond shell is the lingo-cellulosic material forming thick endocarp or the husk of the almond tree fruit. Almond shells are separated from the edible seeds since they have no important industrial use and are normally incinerated or dumped. Burning agricultural residues causes environmental problems such as air pollution, soil erosion and decreases soil biological activity.

Periwinkles (Turritella communis) are a large family of gastropod molluscs found on the shore. Periwinkles are harvested from the seabed and are such a veritable source of income. The shell contains calcium carbonate as one of the major chemical constituents. It is a domestic waste and found littering many dustbins in cities, farm yards and markets in many coastal communities. Periwinkle shells are crushed and sometimes burned and used as supplement in livestock feed because they contain important mineral elements. They are also said to be liming materials for acidic soils.

The use of polymer-based materials as a replacement for metals and their alloys in automotive parts is essentially for weight reduction and subsequent cost efficiency. There is an increased interest in the use of natural fillers as reinforcement in plastics to substitute conventional synthetic fibres in some applications and this has become one of the main concerns to study the potential of using natural fillers as reinforcement for polymers. Hence, this study is aimed at using natural fillers as reinforcement for polymers by investigating the effects of weight per cent addition of blended carbonized almond shell particles and periwinkle particles on the physical and mechanical properties, and morphology of PP matrix composites.

2. Methodology

2.1. Materials and equipment

The reinforcement materials used in this study are tropical almond shell particles obtained from the shell of the fruits and periwinkle particle got from the periwinkle shell while the matrix is PP. They were all sourced...
locally in Lagos, Nigeria. Pictures of these materials and structure (PP) are presented in Figures 1 and 2 while the mineral and proximate composition of tropical almond shell is presented in Tables 1 and 2. The equipment used for the characterization of the composites are Instron universal testing machine, impact and micro-hardness tester, and ASPEX 3020 model variable pressure scanning electron microscope (SEM).

2.2. Materials preparation

Both almond and periwinkle shells were separately washed in clean water to remove the dirt and sun dried for one day after which they were milled using a milling machine and sieved to fine powder (150 μm) using standardized sieve (100 BSS).

2.3. Carbonization of almond shell particulates

The 150 μm almond shell particles were packed into a graphite crucible and fired in a controlled atmosphere using a muffle electric furnace at a temperature of 600°C for 5 h. The carbonized particles (Figure 1) were kept in a sealed envelope to avoid water absorption prior to the time for compounding the composite.

Table 1. Mineral composition of tropical almond shell [17].

| Minerals | Amount (μg/g dry weight) |
|----------|--------------------------|
| Na       | 13.61                    |
| Ca       | 320                      |
| Mg       | 400                      |
| P        | 22,000                   |
| Zn       | 0.5                      |
| Mn       | 9.5                      |
| Fe       | 49.0                     |

Table 2. Proximate composition of tropical almond shell [17].

| Minerals      | Amount (wt. %) |
|---------------|----------------|
| Carbohydrate  | 78.140         |
| Crude fat     | 16.350         |
| Moisture      | 2.840          |
| Crude fibre   | 1.980          |
| Crude protein | 0.650          |
| Ash           | 0.039          |

2.4. Production of the composites

In synthesizing the reinforced PP composites, the mass of the PP was varied with that of the reinforcement to give a total of 80 g per sample. The required materials were weighed using an electronic weighing balance. Hence, the proportion of the materials mixture presented in Table 3 is the weight fraction (wt. %) of 80 g for each of the samples. Weighed amount of matrix (PP pellets) was placed in a crucible, charged into a furnace and heated to 200°C until molten form was achieved. Measured proportions (5–25 wt. %) of the reinforcement were added to the molten matrix and stirred thoroughly for 10 min using a long stainless steel rod to avoid clustering and to achieve faster distribution of the reinforcement in the matrix. The composite slurry was steadily poured into the wooden mould and allowed to cure for 1 h after which they were removed from the moulds. Three batches of reinforced composites were produced with varied weight fractions (wt. %) of (a) periwinkle shell particles, (b) carbonized almond shell particles and (c) hybrid (equal mixture of periwinkle and almond shell particles). Batch A are the PP matrix composites of varied wt. % reinforcement of periwinkle shell particles. Batch B

| Matrix | Reinforcement |
|--------|---------------|
| PP (wt. %) | 150 μm periwinkle shell particles (wt. %) | 150 μm almond shell particles (wt. %) | 150 μm hybrid (periwinkle + almond) shell particles (wt. %) | Total (wt. %) |
| 100 (control) | – | – | – | 100 |
| 95 | 5 | – | – | 100 |
| 90 | 10 | – | – | 100 |
| 85 | 15 | – | – | 100 |
| 80 | 20 | – | – | 100 |
| 75 | 25 | – | – | 100 |
| BATCH TWO |
| 95 | – | 5 | – | 100 |
| 90 | – | 10 | – | 100 |
| 85 | – | 15 | – | 100 |
| 80 | – | 20 | – | 100 |
| 75 | – | 25 | – | 100 |
| BATCH THREE |
| 95 | – | – | 2.5 PE + 2.5 AL | 100 |
| 90 | – | – | 5 PE + 5 AL | 100 |
| 85 | – | – | 7.5 PE + 7.5 AL | 100 |
| 80 | – | – | 10 PE + 10 AL | 100 |
| 75 | – | – | 12.5 PE + 12.5 AL | 100 |

Note: PE: periwinkle shell particles (wt. %); AL: almond shell particles (wt. %).
are the PP matrix composites of varied wt. % reinforcement of carbonized almond shell particles. Batch C are the PP matrix composites of varied wt. % reinforcement of equal mixture of periwinkle shell and carbonized almond shell particles (hybrid). For 5 wt. % of hybrid, 2.5 wt. % periwinkle shell particles + 2.5 wt. % almond shell particles were mixed with 95 wt. % PP matrix. For 15 wt. % of hybrid, 7.5 wt. % periwinkle shell particles + 7.5 wt. % carbonized almond shell particles were mixed with 85 wt. % PP matrix. Control samples containing only PP matrix were produced without the addition of reinforcement.

2.5. Properties evaluation tests

The samples were etched with a solution of HF and HNO$_3$ in volume ratio 1:12 at room temperature (for 10 s) and then examined using an ASPEX 3020 model variable pressure SEM equipped with Noran Voyager energy dispersive X-ray spectroscopy (EDS). The samples to be observed under the SEM were mounted on a conductive carbon imprint left by the adhesive tape prepared by placing the samples on the circular holder and coated for 5 min to enable it conduct electricity. The samples were analysed at an accelerating voltage of 15 kV for the EDS.

Universal Instron Machine, model 3369 was used to carry out this test. The tensile test specimen preparation and testing procedures were conducted in accordance with the ASTM D412 1983 using dumbbell test piece. The tests were performed at a fixed cross-head speed of 10 mm/min at 25°C. Each tensile specimen is positioned in the Instron universal tester and then subjected to tensile load, as the specimen stretches the computer generates a graph as well as all the desired parameters until the specimen fractures.

Hardness test was conducted on the samples of dimension 25 mm × 25 mm × 10 mm in accordance with ASTM E10 standard using a Brinell hardness measuring machine. As the sample was mounted on the machine, a load of 5 kN was applied on it for about 10 s and the diameter of indentation left in the sample was measured with a low powered microscope. The Brinell harness number is calculated by dividing the load applied by the surface area of the indentation.

Impact energy test was carried out in accordance with ASTM D790 standard using an Izod impact tester. The samples were prepared to a size of 55 mm × 10 mm × 10 mm with a 2 mm deep V-notch at the centre of the samples. Each sample was clamped vertically with the notch facing the striker. The striking pendulum was allowed to swing downwards from a height of 1.3 m at a velocity of 5 ms$^{-1}$ impacting the sample. The energy absorbed to fracture each specimen was read off from the instrument’s dynamometer.
The flexural test measures the behaviour of materials subjected to a simple beam loading. Three points flexural testing were conducted at room temperature using the testometric testing machine. The flexural test was carried according to ASTM D790-03 standard procedure at a cross-head speed of 20 mm/min, maintaining a span of 65 mm.

The porosity level of the samples was determined based on ISO 175 standard. The samples were first dried and weighed before soaking in ordinary tap water at room temperature for 24 h and weighed again. The percentage of water absorption in the composite was then calculated by weight difference between the samples before and after immersion in water as shown in Equation (1) [18]:

\[
\text{Water absorption} = \frac{\text{Final weight} - \text{Initial weight}}{\text{Initial weight}} \times 100\%.
\]  

3. Results and discussion

3.1. Microstructure

In the SEM micrograph of Figure 3(a), the whitish portions show the PP (matrix) phase while the grey portions are the blend of the phases of the periwinkle shell particles reinforcement and the matrix. The periwinkle shell particles are well distributed in the matrix coupled with the strong interfacial bonding of the particles with the matrix [19]. This must have been responsible for the improvement in the high tensile and impact strengths exhibited by the composite. In Figure 3(b), the whitish portions show the presence of PP matrix while the dark portions are the almond particles reinforcement phase. The dark portions reveal little cluster of the reinforcement particles which are areas of stress concentration resulting to reduced tensile strength. However, this composite exhibits very good impact energy and can find application where impact strength is more important such as in the bumper and dash board of some cars. In Figure 3(c), there is uniform dispersion of hybrid
reinforcement particles and very good bonding between the reinforcements and the PP matrix. The high impact strength exhibited by this composite is as a result of good compatibility between the tropical almond and periwinkle shell particles.

### 3.2. Tensile strength

From Figure 4, there is a steady increase in the ultimate tensile strength (UTS) of the composites with increasing reinforcement. All the composites exhibit maximum tensile strength at 20 wt. % reinforcement. However, the hybrid composite exhibits the maximum tensile strength value of 8.26 MPa when compared with others. This is due to the compatibility of the almond and periwinkle shell particles and strong interfacial bonding between the fillers and matrix [19]. Beyond 20 wt. % reinforcement, there is a decrease in the tensile strength of the composites which could be due to poor adhesion which negatively affected stress transfer between the particles–matrix interface [1,20].

### 3.3. Hardness

From Figure 5, it is noticed that the hardness of the unreinforced PP matrix (control) is very low when compared with the reinforced composites. The hardness of almond and periwinkle shell particles reinforced composites increased up till 10 wt. % reinforcement but decreased beyond 10 wt. % while that of the hybrid increased up till 15 wt. % reinforcement. The hybrid composite exhibits the maximum hardness of 134.22 BHN at 15 wt. % filler concentration which is due to the strong interfacial bonding [19] and the presence of hard material like calcium in periwinkle shell particles. The decrease in hardness beyond 15 wt. % reinforcement may be due to poor interfacial bonding or surface adhesion of the fillers and propylene matrix [21].

### 3.4. Impact energy

From Figure 6, all the reinforced composites exhibit higher impact energy than the unreinforced PP matrix (control). This indicates the positive effect of reinforcement in enhancing the impact energy of the composites before fracture. The hybrid and almond shells particles reinforced composites exhibit maximum impact energy of 21.81 and 18.09 J, respectively, at 15 wt. % reinforcement due to the strong interfacial bonding between the particles of reinforcement and matrix. The decrease in impact energy beyond...
15 wt. % reinforcement may be due to agglomeration of reinforcement particles leading to ease of crack propagations [22,23] and improper bonding between the matrix and the reinforcements [21].

### 3.5. Flexural strength

From Figure 7, the flexural strength of PP is 0.96 MPa. All the reinforced composites exhibit higher flexural strength than the unreinforced (control). This also indicates the positive effect of reinforcement in enhancing the flexural strength of the composites. Addition of periwinkle and almond shells particles increases the flexural strength of the composites to a maximum value of 5.07 and 6.38 MPa, respectively, at 15 wt. % filler concentration. It is observed that the highest flexural strength of 6.89 MPa is exhibited by the hybrid composites at 15 wt. % filler concentrations. Reduction in flexural strength beyond 15 wt. % filler concentration may be attributed to controlled mobility of matrix by filler particles [24]. As amount of reinforcement increases, there is reduction in total surface area available for matrix–filler interaction. The total area for deformation stress also affects the behavioural pattern of this result. The decrease observed in the periwinkle and tropical almond reinforced composites may also be due to porosity.

### 3.6. Water absorption

In all the composites as shown in Figure 8, the water absorptivity increases with time but the hybrid and carbonized almond shell particles reinforced composites exhibit low water absorption. The lowest water absorption value of 0.0094 is exhibited by the 25 wt. % reinforced hybrid composite. The low water absorption may be attributed to the strong interfacial bonding of the reinforcement with the matrix [19] and also due to the fact that carbonized tropical almond shell is a hydrophobic material and as such decreases the water absorptivity of the composites. The periwinkle shell particles reinforced composites exhibit high water absorption due to the presence of some pores which reduces their mechanical properties.

### 4. Conclusions

Hybrid PP matrix composites reinforced with periwinkle shell particles and carbonized almond shell particles have been successfully synthesized and characterized. The hybrid composite exhibited the best physical and mechanical properties in terms of porosity, UTS, hardness, impact and flexural strength compared to others. Fifteen weight per cent concentration is the optimal level of reinforcement which yielded the maximum mechanical properties beyond which there was a decline in the mechanical properties. Enhancement of the mechanical properties in the hybrid composite is due to the compatibility of the almond and periwinkle shell particles and strong interfacial bonding between the fillers and matrix. Poor interfacial bonding or surface adhesion of the fillers and PP matrix, agglomeration of reinforcement particles and poor stress transfer between the particles–matrix interface are factors responsible for the decrease in the mechanical properties.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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