Effect of Agro Waste Particles on the Mechanical Properties of Hybrid Unsaturated Polyester Resin Matrix Composites

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Received: Feb 12, 2019 Revised: April 28, 2019 Accepted: May 2, 2019

Abstract: The efficacy of reinforcement of polyester resin matrix composites with agro waste particles to effect improvement on the disadvantage of low mechanical properties for optimal performance was studied. 5-25 wt. % of coconut shell, periwinkle shell, and cow bone particles were applied in reinforcing unsaturated polyester resin matrix by mould casting and the microstructural and mechanical characteristics of the composites were evaluated. There was uniform distribution of the agro waste particles in the polymer composites matrix from the scanning electron microscopy (SEM) result. The hybrid composite at 15 wt. % reinforcement demonstrated the highest mechanical properties in terms of ultimate tensile strength (66.73 MPa), flexural strength (76.76 MPa), hardness (87.76 BHN), and impact energy (23.16 J). This shows the efficacy of hybridisation and the high potential of the composite for wider applications.

Keywords: Polyester resin, agro waste, hybridisation, mechanical properties

1. Introduction
Polymeric materials are choice materials due to their resistance to corrosive media, appreciable toughness, low density, shrinkage, cost, flexibility, and ease of casting. They are also preferred because of their ease of processing and production. For example, there has been an increase in the use of unsaturated polyester resin. This has resulted into an annual usage of more than two million tons of unsaturated polyester resin being used worldwide for the production of a wide range of products which include sanitary-ware, pipes, tanks, gratings, components for marine and automotive industries. Generally, there is an increasing potential for the application of unsaturated polyester resin in many areas. The low cost, ease of usage, and weight advantage have made polyester resin to be the choice material for structural and decorative applications. Unsaturated polyester resin has also been used for making thermoset composites especially with glass fibres. Despite these advantages, polymers generally do not possess high impact energy and other mechanical properties thereby limiting their application in some areas. In order to overcome these shortcomings, polymer matrix composites (PMCs) have been developed using synthetic fillers. For example, using high strength fibres to reinforce polymers has greatly improved the mechanical properties of PMCs thereby making them to be suitable for wider application. However, there are some draw backs due to the high cost of synthetic fibres, difficulties in their processing, and their adverse environmental impact. This has increased the interest of replacing these synthetic
fibres reinforced PMCs with readily available alternatives which can serve the same purpose of reinforcement.

The degree of improvement of properties is often predicated on the type of reinforcement (either synthetic or natural). The use of natural fillers for reinforcement of composites is receiving much attention. They have significant advantages over synthetic fillers (fibres) such as low cost and density, comparable specific tensile properties, ability to reduce abrasion of machinery, non-toxicity, reduced energy consumption, renewability, recyclability and biodegradability [6]. The use of particles as fillers is being encouraged because they are economical, effective, and are good for modifying the properties of polymers. PMCs are usually strengthened and hardened as a result of the uniform dispersion of volume or weight fraction of fine particles in the polymer matrix. Many natural fillers have been investigated for use in industries such as flax, hemp, wood, rice husk, snail shell, wheat, barley, and oats [2]. Rahman et al. [8] have proven that addition of wood dust to recycled polyethylene terephthalate (PET) enhanced the mechanical properties of the PET polymer matrix. Chen et al. [3] have also proven that reinforcement of recycled high density polyethylene (HDPE) and PET polymer matrix by rice husk (RH) particles led to an improvement in the mechanical properties. Agunsoye et al. [1] showed that the addition of cow bone particles to recycled low density polyethylene (LDPE) enhanced the mechanical properties of the LDPE polymer matrix. Also, Isiaka and Adewole [5] proved that reinforcing polyester resin matrix with cow bone particles resulted in improvement of the mechanical properties of the PMCs. Natural fillers are now fast evolving as potential alternatives to inorganic or synthetic materials in various applications as building materials and automotive components [9].

As societies begin to realize the importance of using renewable bio-products, there has been a shift to agricultural materials. Agro waste (plants and animals) have recently been researched into in great extent to reduce the problem of waste disposal, and produce much more inexpensive materials at low production cost. The use of this agricultural waste in the development of composite materials for various domestic and industrial applications has proven the suitability and viability of these materials. Hence, the need for the development of polyester resin matrix composites reinforced with agro waste (coconut shell, periwinkle shell, and cow bone) particles and the hybrid of these materials. This could further enhance the mechanical properties of the PMCs thereby expanding the areas of application.

2. Materials and Methods

2.1 Materials

Coconut shell, periwinkle shell, cow bone, unsaturated polyester resin, unsaturated polyester resin, mould release agent, Cobalt Naphthanate (accelerator), and methyl ethyl ketone peroxide (catalyst) are the materials used. Some of these materials are shown in Fig. 1 while the structure and composition of the unsaturated polyester resin are shown in Fig. 2 and Table 1 respectively.
Fig 1: Photographs of the raw materials (a) Sun dried cow bones (b) 150 μm cow bone particles (c) As-received coconut shells (d) 150 μm coconut shell particles (e) As-received periwinkle shells (f) 150 μm periwinkle shell particles

Table 1: Composition of unsaturated polyester resin

| Materials     | Propylene glycol | Phthalic anhydride | Maleic anhydride | Styrene monomer | Additive/Pigment paste |
|---------------|------------------|--------------------|------------------|----------------|------------------------|
| Weight (%)    | 23               | 21                 | 16               | 38             | 2                      |

Fig. 2: Chemical structure of a typical unsaturated polyester resin linkage [4]
2.2 Composite Samples Production

Each of the samples was prepared and weighed using an electronic weighing balance to give a total of 80 g. The proportion of the materials mixture presented in Table 2 is the weight fraction of 80 g for each of the samples. Desirable reinforcement quantities were added to the matrix (polyester resin) and stirred with a glass rod until a proper blend was obtained. 1 g of catalyst and 0.5 g of accelerator were added to each blend and was thoroughly stirred for proper blending. 80 g of each mixture was poured inside a paper tape coated wooden mould and allowed to solidify after which the samples were removed from the mould. The same process was adopted for all samples produced with changes in the weight fraction as shown in Table 2. 1st batch is polyester resin reinforced with varied wt. % of coconut shell particles. 2nd batch is polyester resin reinforced with varied wt. % of periwinkle shell particles. 3rd batch is polyester resin reinforced with varied wt. % of cow bone particles. 4th batch is the hybrid sample which is polyester resin reinforced with equal mixture of coconut shell, periwinkle shell, and cow bone. 5 wt. % hybrid implies that 1.7 wt. % coconut shell + 1.7 wt. % periwinkle shell + 1.6 wt. % cow bone particles were blended with 95 wt. % polyester resin matrix. 25 wt. % hybrid implies that 8.3 wt. % coconut shell + 8.3 wt. % periwinkle shell + 8.4 wt. % cow bone particles were blended with 75 wt. % polyester resin as illustrated in Table 2.

Table 2: Quantity of materials

| Matrix (wt. %) | Reinforcement (wt. %) | Total (wt. %) |
|---------------|-----------------------|---------------|
| Polyester resin | CSP | PSP | CBP | Hybrid (CSP + PSP + CBP) | |
| 100 (control) | - | - | - | - | 100 |
| 95 | 5 | - | - | - | 100 |
| 90 | 10 | - | - | - | 100 |
| 85 | 15 | - | - | - | 100 |
| 80 | 20 | - | - | - | 100 |
| 75 | 25 | - | - | - | 100 |
| 1st Batch | | | | | |
| 95 | - | 5 | - | - | 100 |
| 90 | - | 10 | - | - | 100 |
| 85 | - | 15 | - | - | 100 |
| 80 | - | 20 | - | - | 100 |
| 75 | - | 25 | - | - | 100 |
| 2nd Batch | | | | | |
| 95 | - | - | 5 | - | 100 |
| 90 | - | - | 10 | - | 100 |
| 85 | - | - | 15 | - | 100 |
| 80 | - | - | 20 | - | 100 |
| 75 | - | - | 25 | - | 100 |
| 3rd Batch | | | | | |
| 95 | - | - | - | 1.7 CSP + 1.7 PSP + 1.6 CBP | 100 |
| 90 | - | - | - | 3.3 CSP + 3.3 PSP + 3.4 CBP | 100 |
| 85 | - | - | - | 5 CSP + 5 PSP + 5 CBP | 100 |
| 80 | - | - | - | 6.7 CSP + 6.7 PSP + 6.6 CBP | 100 |
| 75 | - | - | - | 8.3 CSP + 8.3 PSP + 8.4 CBP | 100 |
| 4th Batch | | | | | |
CSP = Coconut Shell Particles
PSP = Periwinkle Shell Particles
CBP = Cow Bone Particles

2.3 Microstructural Examination

The samples were etched using Keller’s reagent (95 ml water, 2.5 ml HNO₃, 1.5 ml HCl, 1.0 ml HF) by swabbing for 15 secs at room temperature. Thereafter, an ASPEX 3020 model variable pressure scanning electron microscope was used to examine their microstructure.

2.4 Tensile Strength Determination

The tensile test samples of dimension 120 mm x 80 mm x 50 mm were prepared using QualiLathe-210–CNC lathe machine and an Instron universal testing machine was used in accordance with the American Standard testing and measurement method D412 (ASTM D412 1983). The machine was operated at a cross head speed of 10 mm/min. Each sample was positioned in the Instron universal tester and then subjected to tensile load. As the sample stretched, the computer generated graph as well as all the desired parameters until it fractured. A graph of load versus extension was plotted automatically by the tester and various properties of the specimen determined are: tensile strength, tensile strain, modulus, and tensile strain at break.

2.5 Flexural Strength Determination

A three-point flexural test was conducted on the samples of dimension 120 x 50 x 10 mm in accordance with ASTM D7264 using a testometric machine with serial number 25257 and capacity 25 KN with a cross-head speed of 20 mm/min while maintaining a span of 100 mm.

2.6 Hardness Determination

The hardness of the samples of dimension 25 mm x 25 mm x 10 mm was determined in accordance with ASTM D 785 standard using a Brinell hardness machine with ball indenter of diameter 20 mm and maximum load of 4000 N. Each sample was mounted on the machine and a load of 10 kg was applied for about 15 seconds and the diameter of indentation left on the sample was measured with a low powered microscope. The hardness number was calculated by dividing the load applied by the surface area of the indentation using the expression below. Three hardness readings were taken for each sample at different locations and the average was determined using equation (1).

\[
\text{Hardness (HBN)} = \frac{2P}{\pi D (D - d)}
\]

where: P is load (kg), D is diameter of indenter (mm), d is the diameter of indentation (mm), \( \pi = 3.142 \)

2.7 Impact Energy Determination

Test samples of dimension 75 mm x 10 mm x 10 mm with a 2 mm deep V-notch at their centers were subjected to impact test using an Izod impact tester in accordance with ASTM D 256 standard. Each sample was clamped vertically with the notch facing the striker and the striking pendulum was allowed to swing downward from a height of about 1.5 m with a velocity of 5 ms⁻¹ impacting the sample. The energy absorbed to break each sample was read from the dynamometer.
3. Results and Discussion

3.1 Microstructure

As illustrated in Figs. 3a to 3e, the gray portions in the microstructure of the samples indicate the presence of polyester resin matrix phase. Formation of pores is more pronounced in Fig. 3a which had adverse effect on the mechanical properties of the unreinforced sample. Fig. 3b shows a fairly uniform dispersion of the coconut shell particles in the unsaturated resin matrix. Fig. 3c also shows a fairly uniform dispersion of cow bone particles in the unsaturated resin matrix. The micrograph in Fig. 3d also shows a fairly uniform dispersion of periwinkle shell particles in the matrix. This must have been responsible for the improvement in the mechanical properties of the composites when compared with that of the unreinforced resin matrix. In Fig. 3e, uniform dispersion of the hybrid reinforcing particles is observed in the microstructure. There is also strong adhesion of particles – polyester resin interphase thereby preventing particles pulling out. These are the two major factors that led to improvement in mechanical properties of the hybrid samples compared to others.
3.2 Ultimate Tensile Strength

As shown in Fig. 4, the ultimate tensile strength (UTS) of the reinforced samples are greater than the control sample which was not reinforced. At 15 wt. %, the hybrid sample demonstrated the greatest ultimate tensile strength value of 66.73 MPa. This shows the ability of the blend of particles of coconut shell, periwinkle shell, and the cow bone in enhancing the UTS. The uniform dispersion of the hybrid reinforcing particles as observed in the microstructure and strong adhesion of particles – polyester resin interphase must have contributed to the improvement of the UTS. The greatest tensile strength value of the hybrid composite sample falls within the range of values stated by Patel and Gohil [7]. A reduction in UTS is observed beyond 15 wt. % which could be weak adhesion which adversely affected load distribution.

3.3 Flexural Strength

As illustrated in Fig. 5, there is a progressive increase in flexural strength of reinforced samples with increasing reinforcement up to 15 wt. %. It is an indication of improving characteristics.
of the reinforced samples to resist deformation under bending stress. At 15 wt.% the hybrid sample exhibited the greatest flexural strength value of 76.76 MPa. Uniform dispersion of the hybrid reinforcing particles in the microstructure and strong adhesion of particles – polyester resin interphase must have contributed to the improvement of the flexural strength. A reduction in the flexural strength of the reinforced samples is observed above 15 wt.% reinforcement which may be due to the controlled mobility of polyester matrix by particles as amount of reinforcement increased. Hence, a decrease in the total surface area available for particles-matrix interaction in the samples.

![Graph of flexural strength against wt. % reinforcement of the composites](image1)

**3.4 Hardness**

The hardness value of the unreinforced sample is 80.16 BHN. The reinforced samples exhibited higher hardness than the unreinforced as shown in Fig. 6. The hybrid composite exhibited the highest hardness of value of 87.76 BHN at 15 wt.% reinforcement. This indicates the ability of the blend of particles of coconut shell, periwinkle shell, and cow bone in enhancing the hardness of the sample. The uniform dispersion of the hybrid reinforcing particles as observed in the microstructure and strong adhesion of particles – polyester resin interphase must have also contributed to the improvement of the hardness. The reduction observed in hardness above 15 wt.% reinforcement may be due to weak adhesion of particles and polyester resin.

![Graph of hardness against wt. % reinforcement of the composites](image2)
3.5 Impact Energy

As illustrated in Fig. 7, there is a progressive increase in impact energy of the reinforced samples up to 15 wt. % reinforcement. Generally, the reinforced samples exhibited greater impact energy than the unreinforced with the hybrid sample exhibiting the greatest impact energy value as of 23.16 J at 15 wt. % reinforcement. Uniform dispersion of the hybrid reinforcing particles as observed in the microstructure and strong adhesion of particles – polyester resin interphase must have also contributed to the improvement of the impact energy. Reduction observed in impact energy above 15 wt. % reinforcement may be due to weak adhesion of particles and polyester. This may also be due to agglomeration of particles which enhanced pores formation resulting into formation and propagation of cracks.

![Graph of impact energy against wt. % reinforcement of the composites](image)

**Fig. 7: Graph of impact energy against wt. % reinforcement of the composites**

4. Conclusion

In this study, polyester resin matrix composites reinforced with particles of agro waste (plant and animal) have been successfully synthesized and characterised.

- Hybrid sample demonstrated the highest mechanical characteristics with respect to ultimate tensile strength (66.73 MPa), flexural strength (76.76 MPa), hardness (87.76 BHN), and impact energy (23.16 J) at 15 wt. % particles addition.
- The positive effects of particles reinforcement on the mechanical properties of the PMCs have been demonstrated.
- The hybrid composite at 15 wt. % reinforcement meets the structural and surface conditions necessary for biomedical application.

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