EFFECTS OF CRAB SHELL AND CHARCOAL REINFORCEMENTS ON THE MECHANICAL PROPERTIES OF POLYESTER MATRIX COMPOSITES

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ABSTRACT

Composites are produced when two or more materials are used to give combination of properties that cannot be attained otherwise. This study aims to use crab shell and charcoal reinforcements to enhance the mechanical properties of polyester composites and decrease the environmental pollution caused by the agro waste. In this study, 5 – 25 wt. % of 100 g of grounded charcoal and crab shell with an average particles size of 150 µm were used for polyester matrix composites. Flexural strength, impact resistance, hardness and elastic modulus tests were carried out on the developed samples. The microstructure of the samples revealed a uniform distribution of the reinforcements within the polymer matrix with different morphology of the biocomposites. The results showed that the greatest flexural strength value of 361.37 MPa was obtained at 25 wt. % and the highest Brinell hardness number (BHN) was 118.27 at 20 wt. %. However, the highest modulus of elasticity was 335.63 MPa at 15 wt. % reinforcement with crab shell reinforced and was 308.64 MPa with charcoal reinforcements at 20 wt. %. Furthermore, the highest impact energy was 5.49 J for crab shell and 5.31 J for charcoal reinforced polyester composite. The development of the biocomposites of these materials will decrease the environmental pollution and improve the properties of the polyester matrix composites for engineering applications.

KEYWORDS: Polyester composites, Charcoal, Crab shell, Casting, Flexural strength
1. INTRODUCTION

Polymer matrix composites (PMCs) are produced from polyester, epoxy, and vinyl ester which can be reinforced by fibers or particles. Polyester, epoxy, and vinyl ester transfer the applied load to the fibers or particles which enhance the physical and mechanical properties of the resin. Recently, engineering applications of polymer matrix composites have significantly increased as a result of the improvement recorded in the properties of the composites. It has been established that PMCs exhibit appreciable strength, stiffness and resistance to corrosion (Tapkire et al., 2014; Jassim, 2017).

Despite the suitable properties exhibited by PMCs, it has a negative effect on the environment such as pollution due to the non-biodegradability of carbon/glass fiber reinforced polymer composites (Grover et al., 2015). Polymer reinforcement with natural fillers is essential for the development of PMCs which has a great attention these days. They have significant advantages over synthetic fillers such as low cost and density, comparable tensile strength, ability to reduce abrasion of machinery, non-toxicity, reduced energy consumption, recyclability and biodegradability (Malkapuram et al., 2009). Fibers and particles are used as fillers because they are economical, effective, and are suitable to enhance the properties of polymers. The mechanical properties of polymer matrix composites are usually enhanced as a result of the uniform dispersion of volume or weight fraction of particles in the polymer matrix (Hassan et al., 2012; Bello et al., 2015). The reinforcement of polymers with particulates plays an important role to improve the mechanical properties of polymer matrix composites (Singla and Chawla 2010; Hemanth et al., 2014).

Many researches have been carried out using polyester and agro wastes as matrix and reinforcements respectively. Laly et al (1997) studied the effect of fibre length and content on the flexural strength, impact resistance and aging behaviour of short banana fiber reinforced polyester composites. The results showed that the tensile strength increased by 28 % and 13 % for flexural strength. Raghad et al (2015) also studied the effect of Arko shell (AS) particulates on the tensile strength, modulus of elasticity, hardness and impact energy of polyester composites. The results showed a considerable increase in tensile strength, modulus of elasticity, hardness and impact energy of the composites as Arko shell (AS) particulates increased.

Durowaye et al (2014) also studied the effect of coconut shell and palm fruit particulates on the tensile strength, impact energy and hardness of polyester composites. Particles of coconut shell and palm fruit of varied weight fractions (5 – 30 wt. %)of 100 g were separately added to 70 – 95 g corresponding weight of polyester resin. The results indicated that the ultimate tensile
strength of coconut shell particulates polyester composite was 70 MPa, while it was 62.5 MPa for palm fruit particulates polyester composite. The highest impact energy value of coconut shell particulates polyester composite was 4.76 J while that of palm fruit particulates polyester composite was 4.60 J. The highest hardness value of coconut shell particulates polyester composite was 208 BHN while that of palm fruit particulates polyester composite was 182.30 BHN. It was noted that coconut shell reinforced polyester exhibited relatively higher mechanical properties when compared to the palm fruit reinforced polyester due to stronger bonding between the coconut shell particles and the polyester resin.

Bai and Rao (2014) also investigated the chemical resistance and flexural strength of bamboo/glass reinforced polyester hybrid composites. The chemical resistance of the composites was studied as per ASTM D543-87 standard. For chemical resistance, concentrated hydrochloric acid (10 %), concentrated nitric acid (40 %) and glacial acetic acid (8 %), the alkalis namely aqueous solutions of sodium hydroxide (10 %), ammonium hydroxide (10 %) and sodium carbonate (20 %) and the solvents – benzene, carbon tetra chloride, toluene and water were selected. In each case, ten pre-weighed samples were dipped in the respective chemicals under study for 24 hours, removed and immediately washed thoroughly with distilled water and dried by pressing them on both sides with filter papers. The final weight of the samples and % weight loss/gain was determined. The resistance test was repeated for ten samples in each case and the average values reported. The results showed that the hybrid reinforced fiber composites showed better resistance to the acids. It was also observed that the flexural strength of the hybrid composites increased with increased glass fiber content. These properties were found to be higher when alkali treated bamboo fibers were used in hybrid composites. The elimination of amorphous hemi-cellulose with alkali treatment led to higher crystallinity of the bamboo fibers with alkali treatment may be responsible for these observations.

The current study aims to enhance the mechanical properties of polyester composites by using the crab shell and charcoal as reinforcement.

2. MATERIALS AND METHODS

2.1. Materials
The charcoals and crab shells are used as reinforcement and were obtained from a local market in Mushin, Lagos, Nigeria. The polyester resin (unsaturated), catalyst and accelerator were obtained from Ojota chemical market, Lagos. Wooden moulds, masking tape, plastic containers, stirring rod, balance and standard sieves were used in this study as shown in Fig. 1.
Firstly, crab shells and charcoals were washed in water and dried in the sun for two days. They were ground by using a pulverizer and manually sieved to 150 μm with the aid of a British standard sieve (BSS) of 100. The polyester resin was weighed using an electronic weighing balance. The polyester resin was poured into a beaker and also weighed. The crab shell and charcoal particulates were poured into a petri dish and weighed. This process was repeated for the five weight formulations used for this research. The formulation used for the polyester resin was:

$$\frac{x}{100} \times 100 \text{ g}$$

Where: x is the percentage of resin.

The formulation used for the reinforcement was:

$$\frac{y}{100} \times 100 \text{ g}$$

Where: y is the percentage of reinforcement.

The casting method was used for the production of the samples. Five composite mixtures (A – E) with particulate compositions of 5 wt. %, 10 wt. %, 15 wt. %, 20 wt. %, and 25 wt. % were prepared.
obtained. The fillers were added in the right proportions to the polyester matrix and drops of catalyst and accelerator were also added. The mixture was then stirred vigorously using a stainless steel rod so as to achieve uniform distribution of the reinforcements and avoid air bubbles. Each of the mixtures was then poured into a wooden mould lined with paper tape and polyvinyl alcohol (PVA) to serve as a releasing agent. The dimensions and shapes of the cavities were tailored to the size and shape of the sample as per ASTM standard D638-03 with clearance for shrinkage. Thereafter, the samples were left to cure at room temperature for 24 hours. The proportions of the materials used are shown in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reinforcement (wt. %)</th>
<th>Polyester resin matrix (wt. %)</th>
<th>Reinforcement (g)</th>
<th>Polyester resin matrix (g)</th>
<th>Total (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5</td>
<td>95</td>
<td>5</td>
<td>95</td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>90</td>
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<td>100</td>
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<td>C</td>
<td>15</td>
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<td>E</td>
<td>25</td>
<td>75</td>
<td>25</td>
<td>75</td>
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2.3. Test Methods
Samples were excavated according to ASTM –E 407-99 by using Keller's reagent (95 ml water, 2.5 ml HNO3, 1.5 ml HCl, 1.0 ml HF) by swabbing manually for 15 secs at room temperature. Thereafter, the microstructural features were then examined using an optical metallurgical microscope. Beam with dimensions of 5 x 50 x 120 mm was used to measure three-point flexural strength according to ASTM D7264M – 15. Impact energy testing was carried out using an Izod impact tester according to ASTM D256 standard. The hardness of the samples was carried out by using Brinell hardness machine according to ASTM D785 standard while the modulus of elasticity of the composite samples was determined according to ASTM E111-97 standard.

3. RESULTS AND DISCUSSION
3.1. Microstructure
As presented in Fig. 2a, some traces of impurities appeared as dark particles in the unreinforced composite sample. In Figs. 2b – 2k, these impurities and dark particles are more pronounced. These dark particles can be attributed to be charcoal and crab shell reinforcements. The micrographs of Figs. 2b – 2k also revealed that there was inhomogeneity in the microstructure of the samples as particles appeared in dendritic and oval shapes and agglomeration of the particles in the polyester matrix. The inhomogeneity and agglomeration which could be as a
result of poor interfacial bonding impaired the impact energy, hardness and modulus of elasticity of the composite samples resulting in reduction in properties exhibited. This agrees with the submission/report of Mechtali et al (2015), Rufai et al (2015) and Durowaye et al (2019).

Fig. 2. Optical micrographs of the samples (a) Unreinforced polyester resin (b) 5 wt. % charcoal reinforced (c) 5 wt. % crab shell particles reinforced (d) 10 wt. % charcoal particles reinforced (e) 10 wt. % crab shell particles reinforced (f) 15 wt. % charcoal particles reinforced (g) 15 wt. % crab shell particles reinforced (h) 20 wt. % charcoal particles reinforced (i) 20 wt. % crab shell particles reinforced (j) 25 wt. % charcoal particles reinforced (k) 25 wt. % crab shell particles reinforced.
3.2. Flexural Strength

As illustrated in Fig. 3, five samples reinforced with varied weight percentage (5 – 25 wt. %) of crab shell particles were produced. Likewise, five samples reinforced with varied weight percentage (5 – 25 wt. %) of charcoal particles were produced. The results showed that the flexural strength of polyester matrix composites decreased with increasing the crab and charcoal content up to 10 wt. % due to poor dispersion of the particulates in the matrix resulting to weak adhesion/bonding. An increase in the flexural strength was observed from 10 to 20 wt. % for charcoal reinforced and 10 to 25 wt. % for crab shell reinforced samples. The uniform dispersion of the particulates as observed in the microstructure and strong adhesion of the particulates and polyester matrix must have contributed to the enhancement of the flexural strength of the composites which is similar to the earlier report/postulation of Hassan et al (2012) and Bello et al (2015). This is predicated on the fact that composites properties depend critically on the level and nature of the adhesion/bonding between the reinforcement and the bulk polymer matrix because it is through this medium that stresses are transmitted to the reinforcements (Renner et al., 2005). The crab shell particles reinforced polyester composite exhibited the highest flexural strength of 361.37 MPa at 25 wt. % reinforcement while the charcoal reinforced sample exhibited 303.14 MPa at 20 wt. % reinforcement.

In the earlier work of Durowaye et al (2017), unreinforced polyester resin sample exhibited flexural strength of 35.42 MPa which is low when compared with that of crab shell and charcoal reinforced samples. This clearly shows the effect of reinforcement on the flexural strength of the samples. The decrease observed in the flexural strength could be due to poor interfacial bonding between the particles and the polyester matrix as a result of inhomogeneity and agglomeration of the particles. This agrees with the submission/report of Mechtali et al (2015), Rufai et al (2015) and Durowaye et al (2019).
Impact Energy

As illustrated in Fig. 4, five samples reinforced with varied weight percentage (5 – 25 wt. %) of crab shell particles were produced. Likewise, five samples reinforced with varied weight percentage (5 – 25 wt. %) of charcoal particles were produced. The results showed that the impact energy of polyester matrix composites increased with increasing the crab and charcoal content up to 20 wt. % due to the strong adhesion/bonding between the reinforcement and the polyester matrix (Renner et al., 2005).

The impact energy of both crab shell particles and charcoal particles reinforced composites decreased when reinforcement was beyond 20 wt. %. This could be due to the formation and propagation of cracks and micro-voids that occurred during impact loading (Manikandan and Rajkumar, 2016). The crab shell and charcoal particulates reinforced polyester composite exhibited highest impact energy of 5.49 J and 5.31 J respectively at 20 wt. % reinforcement. In the earlier work of Durowaye et al (2017), unreinforced polyester resin sample exhibited impact energy 19.6 J. This is higher than that of the reinforced samples. The reduction in the impact energy could be due to agglomeration of the particulates in the resin matrix which agrees with the report of Mechtali et al (2015), Rufai et al (2015) and Durowaye et al (2019).
3.4. Hardness

As illustrated in Fig. 5, five samples reinforced with varied weight percentage (5 – 25 wt. %) of crab shell particles were produced. Likewise, five samples reinforced with varied weight percentage (5 – 25 wt. %) of charcoal particles were produced. The results showed that the hardness of both crab shell particles and charcoal particles reinforced composites decreased with increasing reinforcement from 5 to 10 wt. % and increased up to 20 wt. %. The decrease could be due to agglomeration of the particulates in the resin matrix which agrees with the report of Mechtali et al. (2015), Rufai et al. (2015) and Durowaye et al. (2019) while the increase could be due to strong adhesion/bonding between the reinforcement and the polyester matrix which agrees with the report of Renner et al. (2005).

The crab shell and charcoal particles reinforced samples exhibited highest hardness values of 118.27 BHN and 109.02 BHN respectively at 20 wt. % reinforcement. In the earlier work of Durowaye et al. (2017), unreinforced polyester resin sample exhibited hardness of 129.08 BHN. This is higher than that of the reinforced samples. The reduction in the hardness could be due to agglomeration of the particulates in the resin matrix as earlier reported.
3.5. Modulus of Elasticity

As illustrated in Fig. 6, five samples reinforced with varied weight percentage (5 – 25 wt. %) of crab shell particles were produced. Likewise, five samples reinforced with varied weight percentage (5 – 25 wt. %) of charcoal particles were produced. The results showed that the modulus of elasticity of both crab shell particles and charcoal particles reinforced composites increased with increasing reinforcement up to 15 wt. % and decreased up to 20 wt. %. The decrease could be due to agglomeration of the particulates in the resin matrix which agrees with the report of Mechtali et al (2015), Rufai et al (2015) and Durowaye et al (2019) while the increase could be due to strong adhesion/bonding between the reinforcement and the polyester matrix which agrees with the report of Renner et al (2005).

The crab shell particles reinforced polyester composite exhibited the highest modulus of elasticity value of 335.63 MPa at 15 wt. % reinforcement. The high modulus of elasticity of the crab and charcoal reinforced polyester composites at 15 wt. % and 20 wt. % respectively could be as a result of strong interfacial bonding and the absence of voids or porosity in the samples which is similar to the earlier postulation of Rafah, (2015) and Renner et al (2005).

The decrease in the modulus of elasticity could be due to agglomeration of the particulates as earlier reported. In the earlier work of Durowaye et al., (2017), unreinforced polyester resin sample exhibited modulus of elasticity of 1000 MPa. This is higher than that of the reinforced samples. The reduction in the modulus of elasticity of the reinforced samples could be due to agglomeration of the particulates as earlier reported.
Fig. 6. Modulus of elasticity of polyester matrix composites with different crab shell and charcoal content.

From the DMTA thermograph of the charcoal reinforced polyester composite samples shown in Fig. 7a, the storage modulus decreased with temperature reaching a turning point at about 97\(^0\)C whereas the loss modulus increased up till about 97\(^0\)C before decreasing. The loss tangent (tan \(\delta\)) showed a noticeable peak that occurred at 123\(^0\)C. For the crab shell reinforced composite in Fig. 7b, the storage modulus decreased with temperature reaching a maximum at about 125\(^0\)C whereas the loss modulus increased up till about 130\(^0\)C before decreasing. The loss tangent (tan \(\delta\)) showed a noticeable peak that also occurred at 144.7\(^0\)C.

When compared to the tan \(\delta\), the loss modulus and storage modulus occurred at a lower peak for all the samples. This could be attributed to molecular motions taking place in the samples. These molecular motions are most efficiently indicated by the loss tangent (tan \(\delta\)). The tan \(\delta\) peak is linked with the transition at which the material changes from glass to rubber and the temperature at the maximum of this tan \(\delta\) peak is usually the glass transition temperature (Tg) of the composite. It can be seen from the figures above that only one peak in the tan \(\delta\) curve was observed. This can be interpreted to mean that there was no occurrence of a secondary reaction. It was also observed that the area under the loss modulus (tan \(\delta\)) region of the charcoal reinforced samples was similar to that of the crab shell reinforced samples. This might be an indication of that both polymer composite samples exhibited similar molecular weight distribution. From Figs. 7a and 7b, it can be seen that the crab shell reinforced composites have higher glass transition temperature.
4. CONCLUSIONS

Using crab shell and charcoal particles to reinforce polyester composite contribute to enhance the mechanical properties of polyester composite and the main conclusions are stated below.

1. Microstructure revealed a fairly uniform distribution with agglomeration of the reinforcements within the polymer matrix and the differences in morphology of the biocomposites.

2. The crab shell particles reinforced polyester composite exhibited the highest flexural strength of 361.37 MPa at 25 wt. % reinforcement and highest hardness value of 118.27 BHN at 20 wt. % reinforcement. Hence, 20 – 25 wt. % reinforcement is recommended for application where flexural strength and hardness are required.

3. The crab shell particles reinforced polyester composite exhibited the highest modulus of elasticity value of 335.63 MPa at 15 wt. % reinforcement. The high elastic modulus of the polyester with 15 wt. % of crab shell and 20 wt. % of charcoal reinforcements could be as a result of strong interfacial bonding and the absence of voids or porosity in the samples.

4. The crab shell particulates reinforced polyester composite exhibited the highest impact energy of 5.49 J at 20 wt. % reinforcement. Hence, 20 wt. % reinforcement is recommended for application where impact energy is required. The formation and propagation of cracks and micro-voids within the composites led to a reduction in the impact energy.

5. REFERENCES


