Preparation and Water Absorption Properties of *Parinari polyandra*
Fruit Shell Reinforced Epoxy Composites

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Abstract- The need to protect the environment has led to renewed research interest in sustainable bio-based materials such as natural fibre-reinforced polymer composites. *Parinari polyandra* (Benth) fruit shell (PPFS) is a woody biomass residue that is scarcely explored. This work reports the use of *parinari* as the fiber reinforcement in epoxy resin matrix biocomposites. The biocomposites were prepared from 2mm sized particles using hand layup method and by varying fibre contents from 0 to 40 wt %. The biocomposites affinities for water were determined by short and the long-term water absorption tests according to ASTM standards. Water absorption capabilities of the biocomposites increased with increasing fibre contents while 10 wt% fibre content gave excellent moisture resistance property. The lowest water absorption of 0.01 and 0.2% for short term and long-term tests respectively occurred in the 10 wt % filler content which compared very well with the control at short term test. PPFS is hereby suggested as a suitable natural filler material for bio-epoxy composite with desirable water absorption resistance properties.

Keywords- Agricultural waste, Biocomposites, Parinari, Water absorption, West Africa

1 INTRODUCTION

Owing to the global environmental concerns (Odetoye et al., 2019), more recent research has been targeted towards green technology and development of eco-friendly materials such as bio-composites (Bansal et al., 2016; Adekomaya & Adama, 2018; Rahman et al, 2019). More so, disposal of agricultural waste into running water leads to the breeding of mosquitoes and environmental pollution, uncontrolled surface run off leading to gully erosion which made some places inhabitable (Ferronato & Torretta, 2019). Afforestation for subsequent utilization of fruits, seeds and other plant parts for bio-composites production is a sustainable drive towards the replacement of wood in furniture, building and vehicle construction materials (Suhaily et al., 2012).

Bio-composites can be regarded as eco-composites or green composites. They are materials composed wholly or in part of constituents obtained from a renewable resource as matrix or fillers (Jamaludin et al., 2015, Prithivirajan et al., 2015). For polymer bio-composites, the matrix most commonly comprises of either a thermoplastic or thermostet polymer. Lignocellulosic agricultural residues are potential alternative waste materials to substitute plastic and glass composite fillers due to their abundance, renewability and biodegradability when compared to thermoplastic polymer composites reinforced by inorganic fillers. The use of plant for matrix reinforcement include fibres such as cotton, flax, hemp (Rahman et al., 2019), fibres from recycled wood (Fowler et al., 2006) and agricultural residues (rice husks, coconut fibres, corn straw, soy stalk, wheat straw). Woody reinforcement has found application in automotive industry for non-structural components as interior glove box, door panels and indoor construction materials and to produce consumer items such as radio and speaker cases (Hughes., 2016). Wood-ash polymer composite has also found application as a body armour material (Sanusi et al, 2016).

Water absorption is an important property considered for the suitability of the bio-composite materials in applications (Paturel & Dhakal, 2020). Lignocellulosic plants consisting mainly of cellulose, hemicellulose and lignin, have natural affinity for water. The lignin accounts for the rigidity of plants (Abdulkhalil et al., 2013) and is expected to have the least affinity to water among the three constituents, being a three-dimensional polymer with an amorphous structure. Parinari fruit shell is a woody endocarp which consists mainly of lignin (30 wt %) and cellulose (45 wt%) on dry basis (Odetoye et al, 2013a). The lignin content is comparable to that of wood from tree stem which have lignin contents ranging from 15 - 40 % (Novaes et al., 2010).

The *Parinari polyandra* (Benth) is locally known as *abo idofin* (Yoruba) and *Gwanja kusa* (Hausa) in Nigeria. Though, it exists naturally in the forests, it is also found dotting the built-up areas. The fruits are usually found wasting on the ground since they are not edible. Parinari seed oil has been recommended as suitable for alkyd resin production (Odetoye et al., 2013b). However, the woody fruit shell residue obtained during the oil extraction procedure is enormous compared to the oil obtained (Afolabi et al., 2015). The disposal of the fruit shell residue may constitute a nuisance to the environment if not utilized. This study reports a preliminary investigation on the preparation of parinari-epoxy biocomposite, with focus on the water absorption properties.

2 MATERIALS AND METHODS

2.1 MATERIALS

Parinari fruits were gathered around the trees available at the premises of the University of Ilorin, Ilorin, Nigeria. Epoxy resin K230B, a polymeric chain of Bisphenol A, was selected as the matrix while Araldite HY951 triethylenetetraamine hardener was the curing agent. Epoxy resin was selected as the matrix due to easy handling and curing at room temperature, toughness, strong adhesion, chemical resistance and other specialized properties and compatibility. Epoxy resin...
belongs to the family of thermoset plastics which do not give off reaction products when cured and has low shrinkage (Bansal et al., 2016).

The *Parinari polyandra* Benth seeds were removed before drying the shell. The *Parinari* shells were air-dried for five days and further dried in the oven at 100 °C for 3 hours (to ensure that the shells are dry enough prior to grinding). The dried shells were then reduced in size using the grinding mill machine. The particles were then sieved using a sieve size of 2 mm which were then separated from the oversized and the under sized particles as shown Figure 1.'

2.2 METHODS

2.2.1 Preparation of Composite

The particles with 2 mm uniform screen sizes were then blended together with the epoxy resin and hardener matrix, which had been pre-constituted at a ratio of 2:1. The fibre content was varied for 0 wt%, 10 wt %, 20wt %, 30wt % and 40wt % fillings in the matrix. Using the hand layup method, the mixture was poured into the mould after being properly mixed until homogeneity was achieved with a stirrer. The mould with a dimension of 110mm by 30mm by 3mm (as shown in Figure 2) was then covered with its lid and left to cure at room temperature (25°C) for 24 h. Hand layup method offers better mechanical properties compared to other methods like compression moulding vacuum bagging and vacuum assisted resin infusion methods (Raajeshkrishna & Chandramohan, 2020). The bio-composite samples were then removed from the mould and tested for water absorption properties.

![Fig. 1: Parinari shell particles](image1)

![Fig. 2: (a) Rectangular mould 110mm x 30mm x 3mm (b) bio-composite filled mould (c) covered mould during composite curing (d) cured samples (0, 10, 20, 30, 40 wt% filler contents)](image2)

2.3 DETERMINATION OF PARINARI SHELL PARTICLE DENSITY

An empty density flask of known volume was weighed when empty and filled with parinari shell particles and reweighed. The density of the particles was calculated:

$$\rho_{\text{particle}} (g/cm^3) = \frac{W_p - W_x}{V_0}$$  \hspace{1cm} (1)

where, $W_p$ = weight of filled density flask (g)
$W_x$ = weight of empty density flask (g)
$V_0$ = volume of the flask (cm$^3$)
2.4 WATER ABSORPTION TEST
Water absorption test was done according to ASTM D570 standard. The samples were initially dried in the oven at 60 °C for 24 h and placed in desiccator to cool. Then the samples were immersed in distilled water at room temperature (25 °C) for the prescribed periods of time. Then the samples were then removed, dabbed with clean dry cloth and weighed. Water absorption was expressed as increase in weight per cent. These weights were recorded on both short term and long-term bases.

\[
\% \text{ water absorbed} = \frac{(\text{Wet weight } - \text{Dry weight})}{\text{Dry weight}} \times 100
\]

\(\text{(2)}\)

3 RESULTS AND DISCUSSIONS
3.1 DENSITY
Table 1 and Figure 3 show the variation of density with filler concentration. Considering the effect of varying the filler loading on the density of the composite, it was observed that the 30 wt % loading of fibre has the highest density of 1.76g/cm³. The density of the binder in terms of epoxy and hardener was less than that of the fibre. As the fibre content increased, the density increases up to the point of 30 wt% fibre where the density reached a climax and started dropping. This trend is similar to the results obtained for date palm wood composite (Alshammar et al, 2019). This observation is indicative of optimal filler loading occurring at 30wt% for good binding and compactness as shown by density value for epoxy-parinari fibre composite. Additional increase in fibre loading composition gave a less compact composite.

Table 1. The variation of density with filler concentration in the composite

| S/N | Percentage filler loading (wt %) | Density (g/cm³) |
|-----|---------------------------------|----------------|
| 1   | 10                              | 1.19           |
| 2   | 20                              | 1.55           |
| 3   | 30                              | 1.76           |
| 4   | 40                              | 1.73           |

4.2 WATER ABSORPTION TEST
The water absorption results of the short term and long-term tests are as shown in Figures 4 and 5, respectively. The short-term and the long-term water absorption results indicated that highest water absorption occurred in the 40 wt % filler content while the lowest water absorption occurred in the 10 wt % filler content which compared very well with the control (sample without filler content). Water absorption in 10 wt % filler content sample was highly negligible as no weight increase was observed, indicating an outstanding high resistance to water absorption. This can be attributed to better interfacial bonding achieved with lesser contents of fillers in the matrix. The increased contents of fillers posed more micro-cracks and openings for water absorption (Jamaludin et al., 2015).

The trend observed indicates that the percentage weight of water absorbed increased with increasing fibre contents which agrees with earlier works on lignocellulosic materials (Abral & Hartono, 2017). Similar trend was reported for flax straw bio-composite (Zykova et al. 2017). The water absorption increased with increasing filler content due to the hydrophilic nature of the parinari shell component which contained hydroxyl groups of the cellulosic matter (Odetoye et al., 2013a) facilitating hydrogen bonding between water and the parinari shell particle.

Table 2. Short-term weight absorption variation with filler loading

| S/N | Dry Weight | Wet Weight | Filler %Wt Loading | Percentage water absorbed |
|-----|------------|------------|--------------------|--------------------------|
| 1   | 13.77      | 13.77      | 10                 | 0                        |
| 2   | 17.93      | 17.95      | 20                 | 0.11                     |
| 3   | 20.37      | 20.28      | 30                 | 0.44                     |
| 4   | 19.96      | 20.30      | 40                 | 1.70                     |

Fig. 3: Variation of density with filler content

Fig. 4: Short-term variation of water absorption with filler loading (2hrs)
This trend is characteristic to natural fibre-reinforced composites (Alshammar et al., 2019). The phenomenon can be attributed to the polar lignocellulosic component of natural fibres and the existence of gaps, pores, micro-cracks usually found in the interface between natural fibres and epoxy matrix (Muñoz & García-Manrique, 2015).

5 CONCLUSION

The production of parinari-epoxy bio-composite from Parinari polypandra (Benth) fruit shell was reported for the first time using a thermosetting resin namely epoxy and its hardener through hand layup method at room temperature. The product samples exhibited desirable water absorption properties while excellent water resistance was obtained with the 10 % fibre content sample. The epoxy composite of Parinari polypandra (Benth) fruit shell is recommended as a potential substitute for wood materials in bio-composites as a means of reducing deforestation. Further work is ongoing on the use of cheaper polymer matrices and determination of the mechanical and morphological properties of parinari shell bio-composites.

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