Original Research Article

Effect of Surface Treatment on the Mechanical Properties of Epoxy filled with Dates Palm *(Phoenix dactylifera)* Particulates Composite.

Abstract

Treatments of lignocellulosics material have been found to be useful in preparation of polymer composites since such treatment help to improve their properties. Epoxy filled with untreated and 5% NaOH treated date particulates of particle size 150 μm composites were prepared with filler loadings ranging from 10 % to 50 % using hand layup techniques. Mechanical properties of the composite samples were determined in accordance with ASTM standards. Tensile and flexural tests were measured with the aid of universal testing machine in accordance with ASTM D3039 and ASTM D790 standard tests for tensile and flexural respectively for polymer composite. SEM morphology, water absorption, was equally studied. Results showed that the introduction of 10 % filler loading of the untreated and treated date filler reduced the tensile strength of the unfilled epoxy resin by 20.2 % and 11.1 % respectively. The date pits (DTP) composites gave maximum and minimum tensile strength values of 29.35 MPa at 10 % of date pits/epoxy (DTP/EP). Composites produced from the treated filler showed appreciable properties that is better than the untreated filler and can be used to produce particle board, interior parts of automobile, ceiling and tiles in building application.

Keywords: Lignocellulosics, composites, particulates, tensile strength, flexural strength.

Introduction

Quest for a better life makes man to always research and think of the best way life of comfort could be achieved. As a result, most research and development are focusing on the development of new composite materials. The use of polymer matrix composite has found wide application in our modern day world. This is as a result of the combination of properties which these materials possess. Some of the properties of polymer matrix composites include specific strength, high modulus, good fracture and fatigue properties as well as corrosion resistance (Agunsoye and Edokpia, 2013). The need for polymer composite with better result increases the quests of researcher to employ several ways in which properties of such composite could be enhanced. One of such way is chemical treatment such as sodium hydroxide treatment. The interfacial adhesion between the filler and polymer has a determining influence in the mechanical properties of composites, however to improve mechanical properties through the use of fillers is by treating it with coupling agents besides by changing its particular size. i.e improvement of interfacial bonding can be achieved by addition of coupling agent, that is compactibilizer and by changing

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the particles size. The ability to convert date palm pits filler into useful engineering materials with a better quality sharpened the focus of this present research work.

Date palm is a monocot plant in the Arecaceae family, cultivated in dry tropical regions worldwide for its edible sweet fruit. It contains a single seed (kernel) about 2–2.5 cm long and 6–8 mm thick. The kernel is a major by-product of the date palm-processing industry. They contained 7.1–10.3 % moisture, 5.0–6.3 % protein; 9.9–13.5 % fat; 46–51 % acid detergent fibre; 65–69 % neutral detergent fibre; and 1.0–1.8 % ash. Date pit is mainly used as animal feed (Hamada *et al*., 2002)

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Plate 1a: Date palm raw fruits Plate 1b: Date palm pits

Epoxies are thermosetting resin materials characterised by two or more oxirane rings or epoxy groups within their molecular structure. The commonest epoxy resin is the diglycidyl ether of bisphenol A (DGEBA), which is prepared by the reaction of epichlorohydrin (ECD) and bisphenol A (BPA). ECD is prepared from polypropylene (PP) by reacting chlorine with sodium hydroxide (Hodd, 1990).

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Thus epoxy resins are available in various consistencies from low viscous liquid to a tack-free solid (Bauer, 1979).

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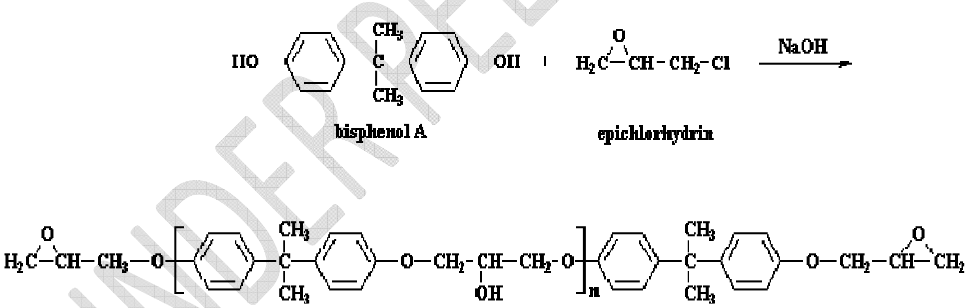

Scheme 1: Reaction for the synthesis of DGEBA-type epoxy resin

Epoxies are among the most important classes of thermosetting polymer which are widely used as matrices for fibre-reinforced composite materials and as structural adhesive. Epoxies are amorphous, highly cross-linked polymer and this structure result in the materials possessing various desirable properties such as high tensile strength and modulus, uncomplicated processing, good thermal, chemical and corrosion resistance, and dimensional stability (Imoisili *et al.,* 2012). The resins equally possess outstanding adhesion properties, low shrinkage upon cure and good electrical properties (Joel, 2003).

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Chemical treatments have been done to improve adhesion or interfacial bonding between natural fibres and synthetic polymers (Li *et al*., 2007). These will inevitably enhance the basic properties of natural fibres reinforced polymer composites (Arif *et al*., 2010; Aranjo *et al*., 2008). Alkaline treatment, bleaching, acetylation and steaming are such various processes applied to improve fibre matrix interaction (Das *et al*., 2000; Shukla and Pai, 2005; Corrandini *et al*., 2006). The primary drawback of the use of natural fibre is the lower processing temperature due to the possibility of lignocellulosic degradation, lack of good interfacial adhesion, poor resistance to moisture absorption. Studies have shown the effect of moisture absorption on mechanical properties of composites can be improved modifying reinforcing fibres by chemical treatment. The coupling agent contains chemical groups, which can react with the fibre and the polymer. The bonds formed are covalent and hydrogen bonds which improve the interfacial adhesion. The use of compatibilizers; surface modification techniques such as treatments, acetylation, graft co-polymerisation or the use of maleic-anhydride–polypropylene copolymer has been reported to overcome the incompatible surface polarities between the natural fibre and polymer matrix. The influence of surface treatments of natural fibres on the interfacial characteristics was also studied (Timothy *et al.,* 2008). Works that have been carried out on the use of natural fibres/fillers with polymeric materials are endless, and several others researches have shown the various properties such as physical, mechanical, thermal, water absorption e.t.c obtained from the natural fiber/ filler composites. Thus, the use and enhancement of these date pit fillers will add more information to those provided in the literature.

Expreimental

Materials: Epoxy Resin (commercially available epoxy resin (3554A) of density 1.17 g/cm^3) and Polyamine amine (Hardener3554B) of density 1.03 g/cm^3 were procured from a local supplier in Ojota- Lagos, Nigeria. The date palm fruits were obtained from Gwagwalada market in Gwagwalada, Area Council, F.C.T; Nigeria.

Methods: The date pits (DTP) were separated from their fruits manually, thereafter; they were washed, cleaned, dried and grounded with hammer mill to obtain filler powder. The fillers were made to pass through wire mesh screen to obtain particle size of 150 µm. The particulate fillers were thereafter modified by alkali treatment. The treated fillers were obtained by soaking in 5 % NaOH for 4 hours and thereafter washed with water, followed by neutralising the basic solution with few drops of acetic acid and carefully monitored using litmus paper.

The fillers were then oven dried for 24 hrs at temperature of about 70 °C before use so as to reduce the moisture content. Samples were thereafter stored in a sealed container prior to compounding.

Compounding: The composites with varying degrees of filler percentage (i.e. 10, 20, 30, 40, & 50 wt %) were prepared. This was achieved by mixing the various filler ratios with the epoxy to form homogenous blends. The mixing was achieved via manual stirring method for 10 minutes. The volume ratio of resin to hardener was 2:1, and after thorough mixing with the filler, the resin was poured onto the cavity of glass mould of dimensions 160 mm x 70 mm x 4.5 mm overlaid with

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aluminium foil so as to serve as releasing agent. The mixture was allowed to cure at room temperature for 24 hours before removal from the mould. Neat resins without filler were equally prepared to serve as control. The prepared block composites were thereafter machined into shapes ((140 x20x 4.5mm) for analyses.

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Results and Discussion

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Table 1: The tensile strength and modulus of date pits (150 µm) / epoxy composites

%Filler Content	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (mm)	% Elongation at break	Break Load (KN)
0	33.00	0.668	5.17	4.93	2.90
10	26.34	0.722	3.47	3.33	2.11
20	25.75	0.843	2.75	3.24	1.95
30	22.32	1.003	2.00	2.86	1.69
40	14.7	1.362	1.09	2.13	1.26
50	13.44	1.382	1.00	1.81	1.08

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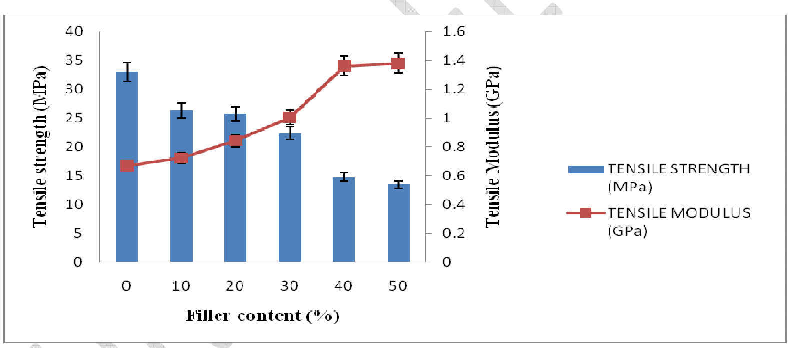

Figure 1: Effect of filler loading on the tensile strength and modulus of date pits/ epoxy composites.

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Table 2: Effect of filler loading on the tensile strength and modulus of NaOH treated date pits/ epoxy composites.

%Filler Content	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (mm)	% Elongation at break	Break Load (KN)
0	33.00	0.668	5.17	4.93	2.90
10	29.35	0.722	3.49	3.68	2.58
20	26.22	0.808	3.40	3.57	2.31
30	19.25	0.82	3.00	3.05	1.69
40	17.33	0.814	2.23	2.19	1.53
50	15.44	0.851	1.90	1.99	1.36

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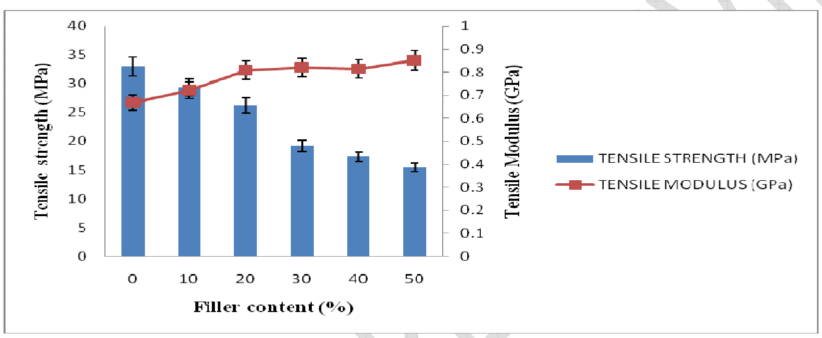

Figure. 2: Effect of filler loading on the tensile strength and modulus of NaOH treated date pits/ epoxy composites.

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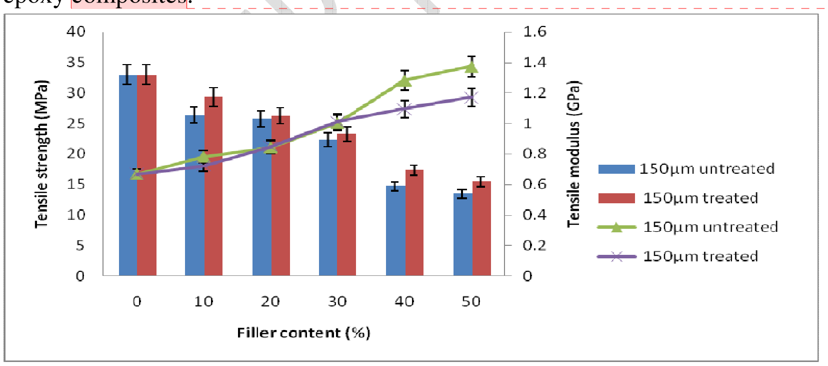

Figure 3: Effect of filler loading on the tensile strength and modulus of NaOH treated and untreated date pits/ epoxy composites.

Elongation at break: The results of the effect of filler loading on the elongation at break of epoxy filled with untreated and treated date pits particulate composites are shown in Tables 1 -2 and depicted in Figure 4

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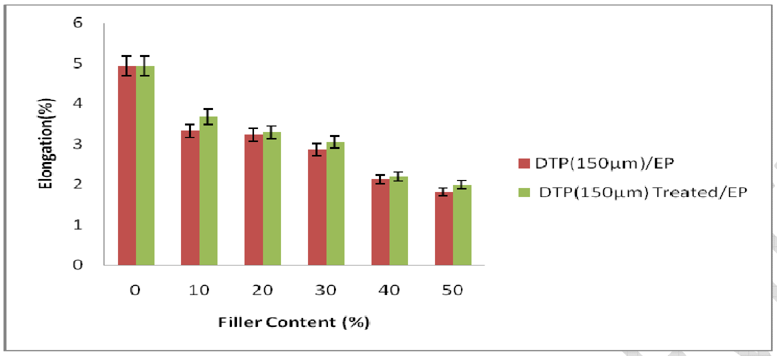

Figure 4: Effect of filler loading on the percentage elongation at break of NaOH untreated and treated date pit/ epoxy (DTP/ EP) composites.

Flexural Test: The results of the effect of filler loading on the flexural strength and modulus of epoxy filled with untreated and treated date pits particulate composites are shown in Tables 3 - 4 and depicted in Figures 5 to 7

Table 3: The flexural strength and modulus of date pits / epoxy composites

%Filler Content	Flexural Strength (MPa)	Flexural Modulus (GPa)	Elongation (mm)	% Elongation
0	45.31	2.116	0.026	2.6
10	42.92	2.149	0.018	1.80
20	41.71	2.446	0.017	1.75
30	40.15	2.521	0.016	1.64
40	39.12	2.716	0.015	1.46
50	30.5	2.733	0.012	1.19

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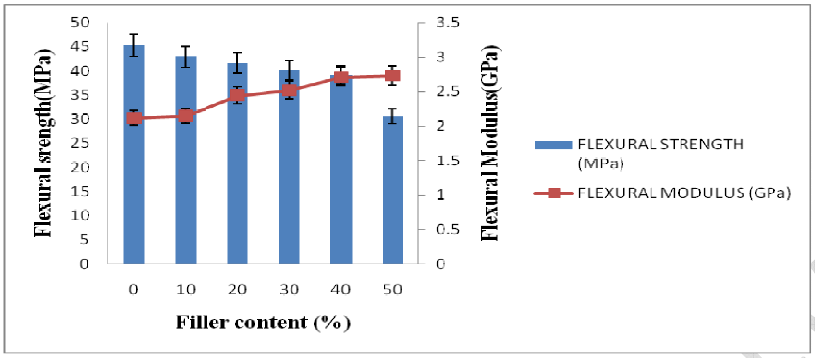

Figure 5: Effect of filler loading on the flexural strength and modulus of untreated date pits/ epoxy composites.

Table 4: The flexural strength and modulus of treated date pits/ epoxy composites

%Filler Content	Flexural Strength (MPa)	Flexural Modulus (GPa)	Elongation (mm)	% Elongation
0	45.31	2.116	0.026	2.6
10	44.30	3.049	0.015	1.50
20	44.00	3.353	0.013	1.26
30	43.12	3.502	0.012	1.20
40	42.61	3.621	0.011	1.10
50	40.23	3.702	0.010	1.00

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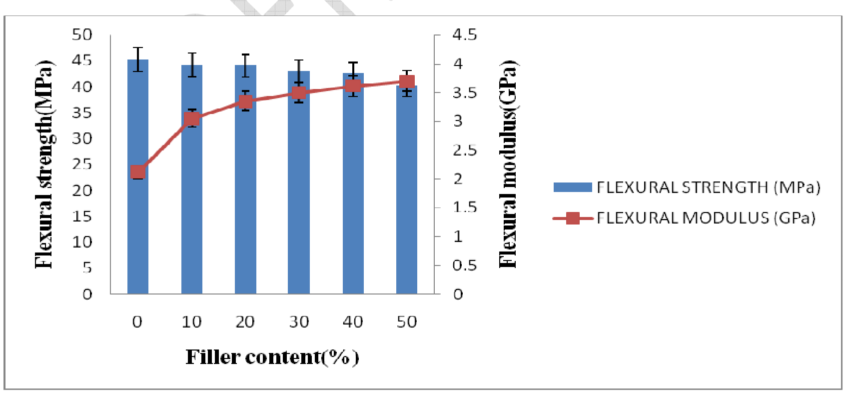

Figure 6: Effect of filler loading on the flexural strength and modulus of treated date pits/ epoxy composites.

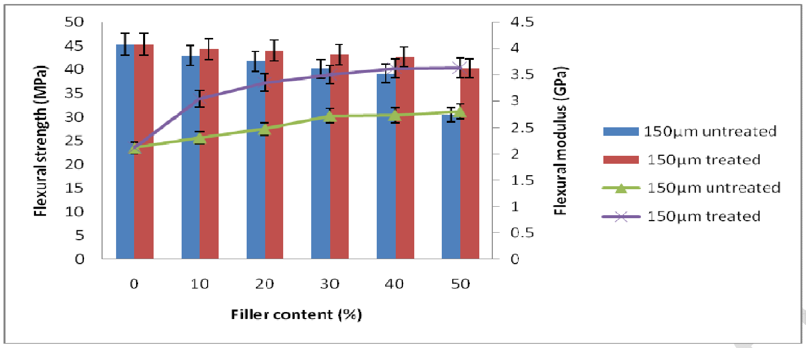

Figure 7: Effect of filler loading and particle size on the flexural strength and modulus of treated and untreated date pits/ epoxy composites.

Water Absorption: The effect of time on hydration capacity of epoxy/untreated and treated date pits particulate composite are illustrated in Figures 8 and 9 respectively.

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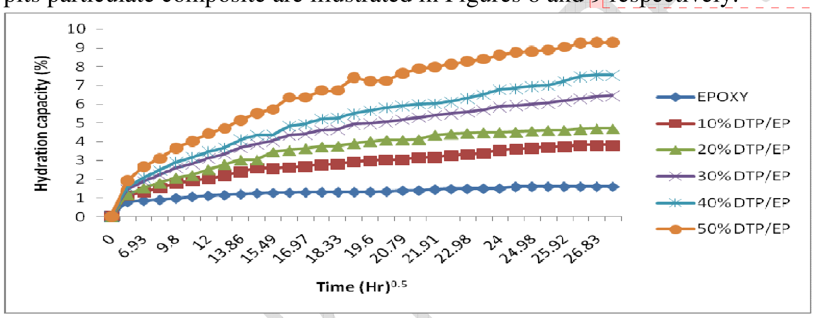

Figure 8: Water absorption curves of untreated date pits/ epoxy composite.

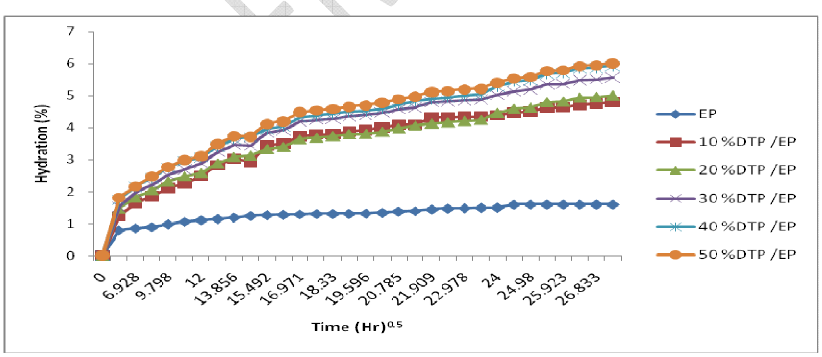

Figure 9: Water absorption curves of treated date pits/ epoxy composite

Study of the morphology of the composites was carried out and the results are as shown in plates 2 to 5. The scanning was done on the fracture surface of the composites.

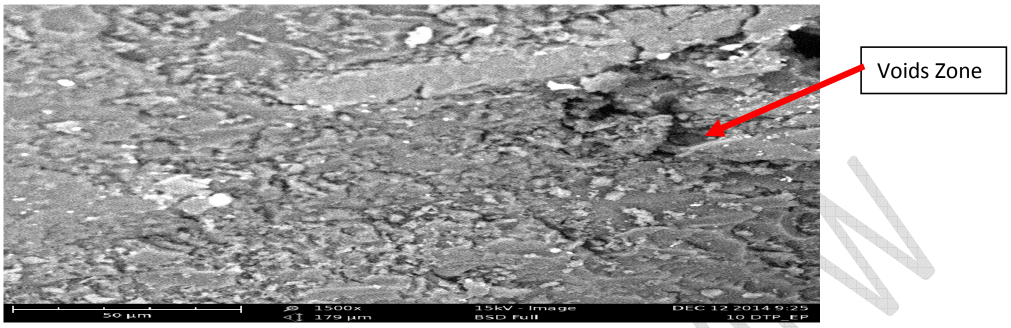

Plate 2: SEM micrograph of the fracture surface of 10% date pits filler /epoxy composite at 1500x Magnification.

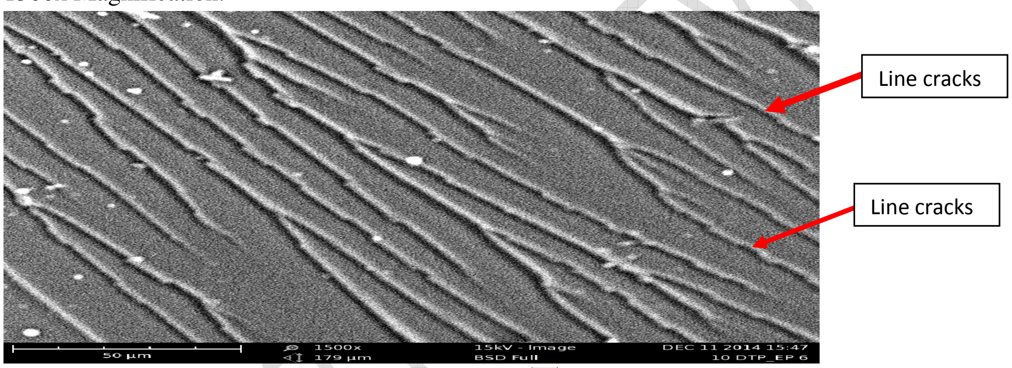

Plate 3: SEM micrograph of the fracture surface of 10 % treated date pits filler /epoxy composite at 1500x Magnification

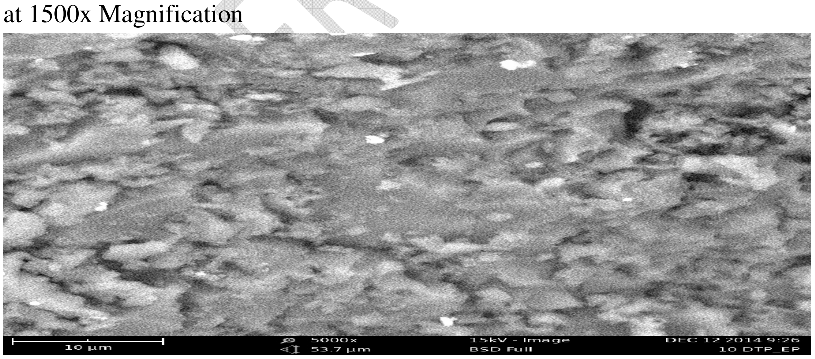

Plate 4: SEM micrograph of the fracture surface of 10% date pits filler/epoxy composite at 5000x Magnification

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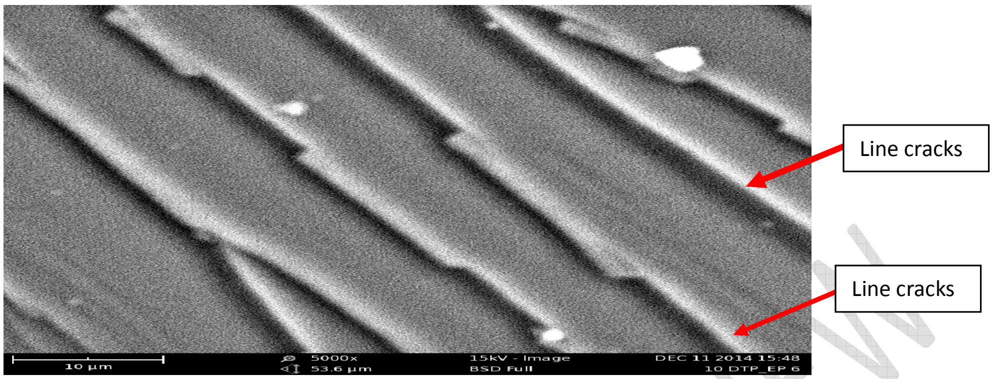

Plate 5: SEM micrograph of the fracture surface of 10 % treated date pits filler /epoxy composite at 5000x Magnification

Discussion: Figure 1 & 2 shows the effect of filler loading on the tensile strength and modulus of untreated and treated date pits/ epoxy composites. It can be seen generally that the tensile strength decreases with increase in filler loading. The minimum and maximum value was observed for treated sample at 50 % and 10 % filler ratio with 15.44 MPa and 29.35 MPa respectively. The NaOH treatment improved the tensile strength of date pits/ epoxy (DTP/EP) composite by 11 % and 15 % at 10 % and 50 % filler loading respectively. The higher mechanical properties of the samples due to chemical modification were an indication of improved interaction and stress transfer between the particles.

The modulus of the treated sample also showed a corresponding increase as the filler loading increases. The modulus of treated date pits/epoxy was at maximum and minimum value at 50 % and 10 % with 0.85 GPa and 0.72 GPa respectively as against the neat resin value of 0.67 GPa.

Figure 3 compares the effects of filler loading on the tensile strength and modulus of the treated and untreated filler of date pits/ epoxy (DTP/EP) composites. The result revealed that the treatment had positive impacts on the strength of the composite. The maximum tensile strength of untreated date pits/ epoxy (DTP/EP) composite increased from 26.34 MPa to highest value of 29.35 MPa; while the minimum value increased from 13.44 MPa to 15.44 MPa when the filler was treated with 5 % NaOH at the same filler loading. The addition of 10 %wt and 50 %wt ratio of untreated date pits filler into epoxy resin reduces the tensile strength by 20 % and 59 % respectively, while the flexural strength was reduced by 5.2 % and 32.7 %. Incorporation of the filler into the resin reduces the ductility of the resin. However, treatment of the filler with 5 % NaOH helps to improve such mechanical properties. The treatment improved the tensile strength of untreated DTP/EP at 10 % filler loading by 11.4 %. Also, the treatment equally improved the ductility of the composites. For example, elongation at break of DTP/EP at 10 %, 20 % and 50 % improved by 10.5 %, 10.2 % and 9.9 % respectively.

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The higher tensile strength of the samples due to chemical modification was an indication of improved interaction and stress transfer between the particles. The treatment on the filler helps to reduce the effect of impurities such as oil and fat on the interaction between matrix (resin) component and filler thereby improving the stress transfer process that will ultimately culminate into higher strength as seen in Figure 3. The improved strength of the composite as a result of sodium hydroxide treatment can also be linked with reduction in lignin content of the filler as lignocellulosic material are originally composed of cellulose in lignin matrix, reduction of the natural matrix (lignin) in the filler will help the resin to bind better with the cellulose in the filler, thereby giving an improved strength. On the other hand, the modulus increased as the filler loading increases. However, it can be seen from the Figure 3 that the modulus of the untreated sample composite improved greatly at 40 % filler loading more than that of the treated composite sample. Modulus of untreated date pits/ epoxy composites at 40 % was 1.28 GPa while that of treated date pits/ epoxy composite at the same filler weight percent was 1.09 GPa.

Water absorption capacity: The percentage hydration of untreated date particulate / epoxy at room temperature of about 25 ^{o}C has the following values after 24 hours (a day) of absorption as depicted in Figure 8: 1.13 %, 1.16 %, 1.44 %, 1.58 %, and 1.91 % at 10 %, 20 %, 30 %, 40 %, 50 % filler loading respectively while the unfilled epoxy resin gives 0.789 %. The test shows that the absorption continues to increase daily and after 768 hours (32 days), the following values were obtained: 3.82 %, 4.71 %, 6.48 %, 7.56 %, and 9.82 % for the corresponding 10 %, 20 %, 30 %, 40 %, and 50 % filler weight content. The daily absorption is primarily due to the hydrophilic nature of the lignocellulosic filler. The unfilled epoxy reached maximum absorption value of 1.61 % after 648 hours (27days). However, the rate of absorption for all the composites was at maximum after the first 24 hrs of absorption. In comparison to the result shown in Figure 8, one can deduced that treated DTP/EP composite is stronger as depicted in Figure 9 which gives 1.13 %, 0.97 %, 1.21 %, 1.28 %, and 1.51 % at 10 %, 20 %, 30 %, 40 %, 50 % filler loading respectively.

Morphology: Plate 2 and 3 reveals the state of dispersion of 10 % of untreated and treated date pits particulate in epoxy composites (DTP/EP) at 1500x and magnification respectively. It can be observed in the SEM micrograph in plate 3 that the filler dispersed uniformly in the matrix and a strong interfacial bonding exits between the filler and the resin except the line cracks seen. Thus, the line cracks can be as result of manual mixing employed during fabrication. Also, plates 4 and 5 further shows the interaction of 10 % of the untreated and treated filler with the epoxy resin at higher magnification. From the results, it can be seen that the interfacial bonding between the filler and matrix was higher in plate 5 which might be due interaction between filler and the resin as a result of the filler treatment (Sarojini, 2013). Plate 4 equally showed the presence of pulled out traces, voids which is an indicative of weak interfacial adhesion at the interface which further confirmed the reduced tensile and flexural strength observed in the untreated filler composite.

Conclusion: Date pits pits particulates have been used successfully as fillers in the preparation of epoxy composites. The addition of the filler increased the bulk of the composite. Properties

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such as tensile and flexural modulus, hardness were improved while properties such as tensile strength and flexural strength were affected negatively. Incorporation of 10 % untreated filler into epoxy resin improved the tensile and flexural modulus of DTP/EP composites by 8 % and 1.6 %.

The addition of 10 %wt and 50 %wt ratio of untreated date pits filler into epoxy resin reduces the tensile strength by 20 % and 59 % respectively, while the flexural strength was reduced by 5.2 % and 32.7 %. Incorporation of the filler into the resin reduces the ductility of the resin. However, treatment of the filler with 5 % NaOH helps to improve such mechanical properties. The treatment improved the tensile strength of untreated DTP/EP at 10 % filler loading by 11.4 % , Also, the treatment equally improved the ductility of the composites thereby increasing the impact strength. For example, elongation at break of DTP/EP at 10 %, 20 % and 50 % improved by 10.5 %, 10.2 % and 9.9 % respectively.

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