Journal
of Science
Research

Production and characterization of *Nypa fruitican* reinforced low density polyethylene composites

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Abstract

The use of *Nypa fruitican* in reinforcing Low Density polyethylene (LDPE) is reported in the current-study. The fibers were chemically modified using soda pulping process, phosphorylation and maleic anhydride treatment. The composite materials were produced with a single-screw extruder using both treated and untreated fibers. The extruded compound was processed into samples using compression/injection moulding. The weight percent of cellulose in the polymer composites was 2.5% and 5.0%. The effects of the fibre-loading and surface chemical treatment on the mechanical and physical properties of the composites were comparatively examined. The result of FTIR spectra showed that modification of the fibre took place due to substitution of hydroxyl functional group in the untreated fibre. The surface modification of the *Nypa* fiber resulted in the improvement of the mechanical properties of the composites. The highest Young's modulus and tensile strength values were observed in the composite with 5% maleic anhydride treated fibre loading. Composite containing 2.5% untreated fibre-loading gave the highest value of elongation at break indicating that elongation at break is inversely proportional to fibre loading. Water absorption and thickness swelling increases with fiber-loading but varied with the surface chemical treatments employed. The results showed that modified *Nypa fruitican* can successfully be utilized in the production of composites with improved mechanical properties.

Keywords: *Nypa fruitican,* Low Density Polyethylene (LDPE); fiber reinforcement; modification; interfacial adhesion; composites.

Introduction

An amalgamation of two materials of different structure and composition to form another distinct material with improved physical and mechanical properties is generally referred to as a composite. Progress in material research and exploitation has led to the tremendous development of various composite products that is applicable in aeronautics, automobiles, industrial and medical facilities [1, 2]. More importantly, there is a renewed interest in the development of polymer composites reinforced with natural fibre. Natural fibers especially non-wood fibers such as banana [3], hemp [4, 5], bamboo [6], rice and wheat husk [7], flax [8], kenaf and sisal [9] and palm fiber [10] are being used extensively in reinforcing composite derived from polyethene, polypropene, polystyrene and other polymers. The growing interest in the use of natural fiber sterns from the fact that it is relatively abundant, renewable, recyclable and biodegrable. Apart from this, natural fibers have high specific strength, high toughness yet light weight, low density, low cost and good thermal properties [11-13]. When compared with synthetic fibers, natural fibers have reduced dermal and respiratory irritation. They are non-corrosive as well as less abrasive to processing equipment.

The major challenge in the use of natural fibers in reinforcing polymer is the compatibility of the hydrophilic fiber with the hydrophobic polymer. Poor adhesion between the fiber and polymer matrix would result in poor mechanical property of the composite. In solving the problem, two methods are generally adopted. The first approach is the application of a compatibilizer. As the name implied, a compartibilizer achieves good dispersion of the polymer in the fiber. Depending on the nature of the fiber and/or polymer, the compatibilizer either removes the fiber/polymer weak boundary layers, develops a highly cross linked inter-phase region, improves the wettability between the two materials or form covalent bond with both materials. The second approach involves fiber modification or pre-treatment which can be physical or chemical. Fiber can be modified physically by steam explosion or irradiation with UV or gamma ray. Chemical modification of fibers which is the most effective involves fiber functionalization which can be mercerization, benzoylation, esterification, silanisation, pulping, phosphorylation, maleic anhydride or other treatments [14-16].

Nypa fruitican is a monoecious plant that is under-utilized but very common in southern part of Nigeria. It is majorly used in the locality for making broom, chewing sticks and roofing material.The plant is highly invading, spreading rapidly across the Niger Delta mangrove ecosystem, thereby constituting adverse environmental effects such as the blockage of the water ways and endangering of aquatic animals [17].A careful search in the literature revealed recently that *Nypa fruitican was*chemically modified with methyl methacrylate and silane to form a composites with polylactic acid / recycled low density polyethylene [18]. In the present study, *Nypa fruitican* was used toreinforce virginlow density polyethyleneafter chemical modification with caustic soda, phosphoric acid, and maleic anhydride. The effect of modification was examined on the properties of the resulting composites.

Materials and methods

Low Density Polyethylene (LDPE) was supplied in pellet form by Sasol Polymers, Johannesburg, South Africa. It has a Melt Flow Index MFI of 7.0 g/10min (ASTM D-1238), a melting point of 106^{o}C, an average molar mass (MW) of 96000 g mol^{-1}, and a density of 0.918 g cm^{-3}. *Nypa* palm (fond, leaves and petioles) were obtained from the riverside area of Oron Local Government, Akwa Ibom State, Nigeria. Phosphoric acid, maleic anhydride and other reagents used in the study were of analytical grade. A single screw extruder was fabricated and housed at the Department of Chemistry, University of Ibadan.

Pretreatment of sample

The *Nypa* plant was first washed thoroughly with water in order to remove silica (sand) from the plant. It was then dried in the sunlight for 24 hours. The fibre was sorted out so as to remove other solid impurities. The sample was later oven dried prior to shredding at 105^{o}C. Blending and sieving were carried out so as to ensure uniformity and proper mixing with the LDPE. This also helps to increase the surface area of the fiber. The dried, shredded and grounded fiber was designated as Untreated Fiber (UF).

Modification of Nypa fruitican fibre

The *Nypa fruitican* fibers were subjected to the following surface chemical modification: soda pulping, phosphorylation and maleic anhydride treatment.

Soda pulping

About 400g of the *Nypa* fibres were soaked in the inner jacket of an autoclave digester containing 10% NaOH. The jacket was then placed into the outer jacket which was filled with some water to serve as water bath. The set up was well tightened so as to build enough pressure. It was then heated for 2 hours at a constant temperature of 120^{o}C after which the inner jacket was removed and the content filtered. The residue (pulp) was washed with water to neutrality, sundried and later oven dried to a constant weight. The chemically pulped sample was tagged pulped fiber (PF).

Treatment with maleic anhydride

201 g of maleic anhydride was dissolved in 2 dm^{3}of acetone and about 250 g of fiber was soaked in it. The content was heated in a water bath for 2 hours at 55^{o}C. The fiber was rinsed with water until a pH of 7.0 was obtained from the filtrate and then dried at a constant temperature of about 80^{o}C. The fiber so treated was termed Maleated Fiber (MF). Figure 1 shows the possible reaction between maleic anhydride and cellulose:

Phosphorylation

This was carried out in line with the procedure reported by Irene *et al* [19]. About 300 g of untreated *Nypa fruitican* fibers were soaked in 3 dm^{3} of 5% phosphoric acid solution for 2 hours at a constant temperature of 150^{o}C. The content was then filtered and the residue washed several times with distilled

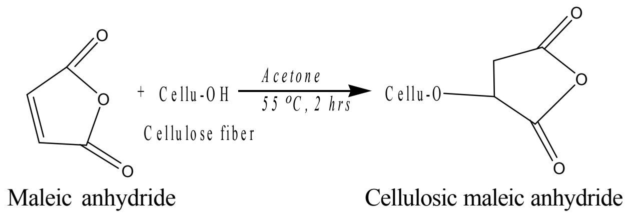


Figure 1. Equation showing possible reaction between cellulose and maleic anhydride.

water until the pH of the filterate was 7. The residue was dried to a constant weight in an oven and termed Phosphorylated Fiber (PhF). The possible reaction between cellulose and phosphoric acid is shown in Figure 2.

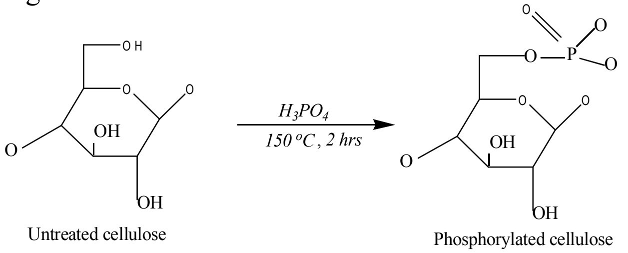


Figure 2. Equation showing possible reaction between cellulose and phosphoric acid [20].

Composite preparation

The pretreated *Nypa fruitican* fibre was shredded, grinded and sieved with a screen of mesh size 0.20 mm in order to obtain homogenous fractions. The fibre was oven dried at 70°C for 1 hour to eliminate any free moisture before mixing it with the polymer matrix. The LDPE pellet was compounded with the fibre at 2.5 and 5.0 % of the total mass fractions of the composite (Table 1). The mixture was first mixed manually before being fed into a single-screw extruder at a controlled feed rate. The extruder was operated at three different temperature zones: 130-140°C near the feeder, 150-160°C in the middle zones, and 170-180°C at the die section. The screw speed was maintained at 102 rpm. The molten strands of the composites from the extruder were chopped into pellets as they came out of the die section into a water-filled plastic bowl. Re-compounding of the pellets was carried out to ensure homogenous mixing of the fibre with the polymer matrix and to obtain samples for rheological measurements.

Dumb-bell shaped-test specimens (height = 1.06 mm, diameter = 26 mm and length = 160 mm) for determina-tion of the mechanical properties of the composites were formed by injection molding at 160°C to 170°C. Samples of the test specimens produced are as shown in Figure 3.

Table 1. Composition of nypa reinforced LDPE eomposites.

S/N	*Nypa fruitican**		LDPE	
	(%)	(g)	(%)	(g)
1	2.5	12.5	97.5	487.5
2	5	25	95	475

*Treated and untreated *Nypa fruitican.*

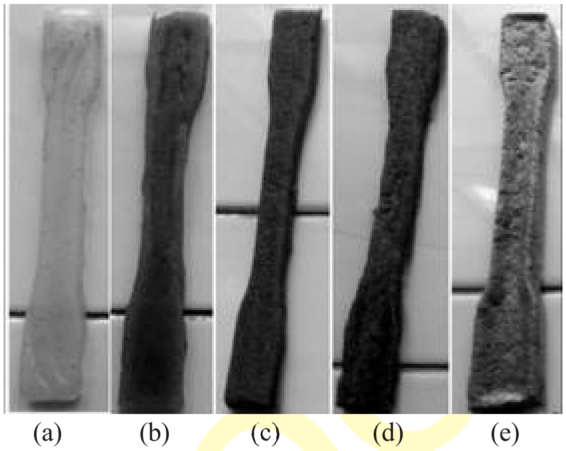

(a) (b) (c) (d) (e)

Figure 3. Dumb-bell shaped-test specimens of (a) LDPE and 2.5 % *Nypa* fiber/LDPE composites: (b) UF/LDPE, (c) MF/LDPE, (d) PhF/LDPE and (e) PF/LDPE.

Physical properties of the composites

The water absorption property of the composites was carried out in accordance with the method reported by Sgriccia *et al* [21] and Sandeep *et al* [22]. It was based on the difference between the weight of test specimen soaked for 24 hours and the oven dry weight test specimen. The thickness swelling was measured based on the difference in their thickness before and after soaking in water for 24 hours using a venier caliper.

Mechanical properties of the composites

Tensile testing was determined with the dumb-bell shaped-test specimens in accordance to the standard procedure of GB 1447-1983 at a cross head speed of 0.16667 mm/sec. Three replicate specimens were tested for each set. This test was carried out using the Instron Testing Machine. The following parameters were obtained from the stress-strain curve: maximum load (*N*), tensile stress at maximum load (Mpa), tensile strain at maximum load (%), load at break (standard) (*N*), tensile stress at break (standard) (Mpa), tensile extension at break (mm), and extension at maximum load (mm).

Morphology and FTIR analysis

The Scanning Electron Microscope (SEM) was employed to examine the fracture surface of the fibers and the composites formed. The sample was sputter coated with gold palladium and observed under the SEM model JEOL JSM-7600F operated at 15 kV. Fourier-transform infrared spectroscopy (FTIR) Perkin Elmer Version model 10.03.07) was used to obtain some qualitative information about the functional groups and chemical characteristics of modified and untreated *Nypa* fiber. Each spectrum was obtained within the range of 500 to 4000 cm^{-1}.

Results and discussion

Moisture absorption and thickness swelling

The result of the water-absorption and thickness-swelling of the composite after immersion in water for 24 hours is shown in Figures 4 and 5 respectively. Generally, the amount of water absorbed by the composite at 2.5 % fiber content was very low and negligible especially for the MF and PF reinforced composite. However, at 5.0% fiber content, the phosphorylated fibre composite showed the highest thickness swelling and moisture absorption. This was probably due to the effect of the phosphoric group introduced into the fibre. In all, the pulped fiber composite had the lowest water absorption value. The soda-pulping treatment removes significant amount of lignin and hemicelluloses from the fiber [23], which makes it to collapse and glue more tightly together, thus reducing the water absorption capacity of the composite. Thus, in terms of low moisture absorption, pulped fiber will be preferred to maleated and phosphorylated fiber in re-inforcing polymer matrix for composites production especially at relatively high humidity conditions.

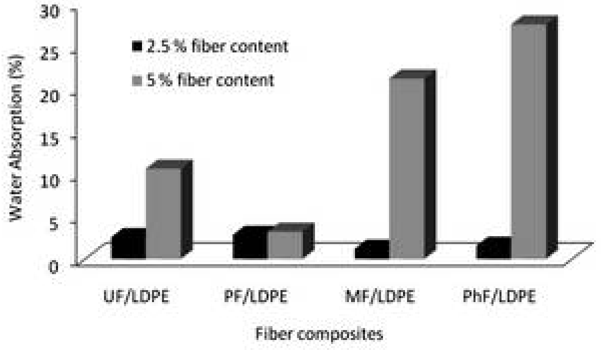


Figure 4. Water absorption properties of the composites with respect to the fiber content.

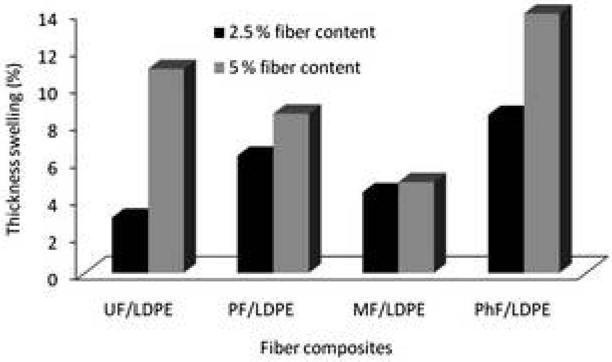


Figure 5. Variation in thickness properties of the composites with fiber content/treatment.

Mechanical properties of the composites

The effects of surface modification on tensile properties of the biocomposites produced are presented in Figures 6 and 7. All the composites, (except 2.5% pulped fibre loading) gave high values of tensile stress. In all, both the 2.5 % and 5.0 % maleated fibre loaded composites gave the highest value of tensile stress (10.62MPa and 23.27MPa) and the highest Young's Modulus (246.06 MPa and 115.01 MPa), respectively. Composites containing phosphorylated fibre showed higher value for tensile stress and Young's Modulus compared to the pulped and untreated fibre composites. The increase in tensile strength or modulus is primarily attributed to the presence of *Nypa* fibre, which allowed a uniform stress distribution from LDPE matrix to dispersed fibre phase [23, 24]. Generally, composites containing modified fibre showed higher values for Young's modulus compared to the untreated fibre composites and this occurred as the percentage composition of the fibre increases. This enhancement obviously revealed the effectiveness, good dispersion and improved interfacial bonding of the modified *Nypa* fibre in the LDPE matrix [18, 22].

As expected, elongation at break decreases with increasing fibre loading. Composite with 2.5% untreated fibre content showed the highest mean value for elongation at break (20.50 mm) while 5.0% maleated fibre gave the lowest value (8.99 mm) (Figure 8). This has been attributed to the decrease in the deformation on the stiffness matrix surface between the filler and the matrix [18]. As the fiber content increases, the elongation or deformation decreases.

FTIR characterisation of the fiber

The FTIR spectra of treated and untreated fibers are shown in Figures 9 (a-c). Common to the spectra are

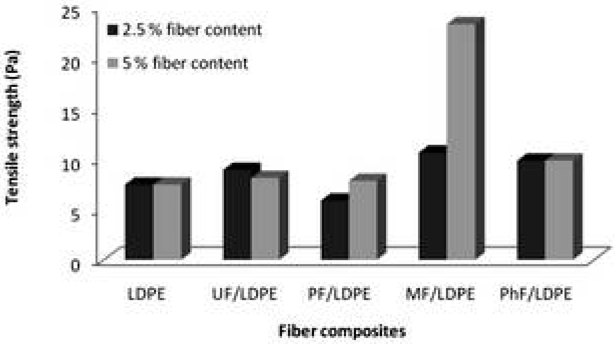


Figure 6. Variation in tensile strength of the composites with fiber treatment and content.

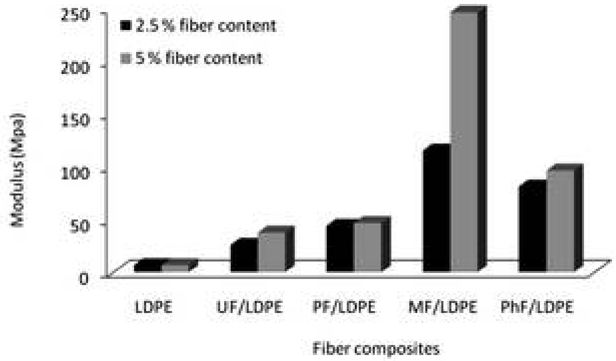


Figure 7. Variation in tensile modulus of the composites with fiber treatment and content.

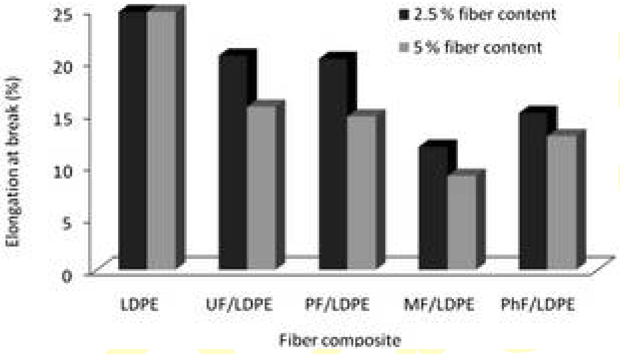
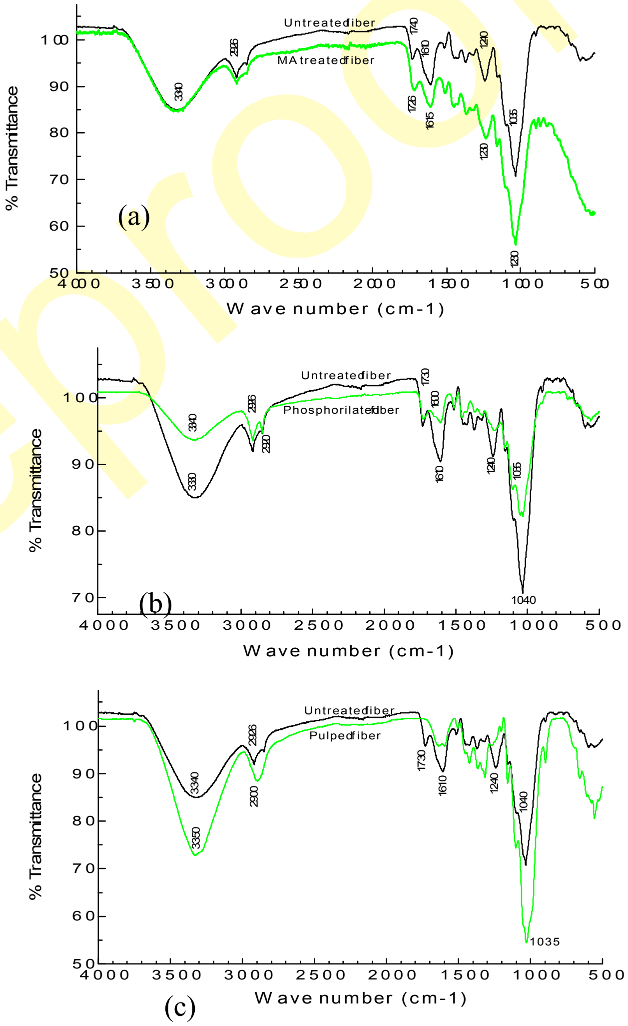


Figure 8. Variation in elongation at break of the composites with fiber treatment and content.

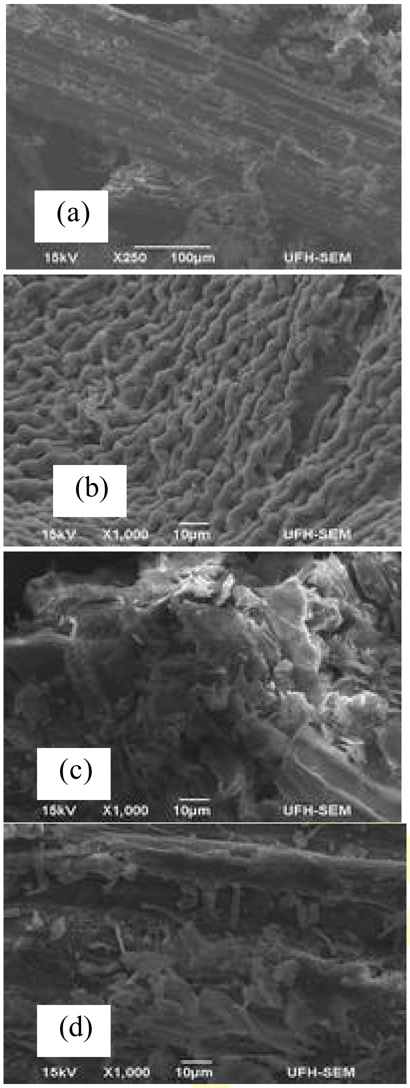
the absorption peaks around 3,340 cm^{-1}, 2,900cm^{-1} and 1040cm^{-1}, corresponding to the O–H stretching, asymmetric C–H stretch and C–O stretching respectively. In addition, the Untreated fiber gave absorption peak at 1,740 cm^{-1} for C=O, 1,610 cm^{-1} for C=C of aromatic ring, 1,240 cm^{-1} and 1,040 cm^{-1} for C–O stretching of aryl group in lignin. The maleic anhydride treated fiber showed similar peaks but at slightly shifted wave number (Figure 9a). Similar observation was reported by Zhou *et al* (2013) when powder bamboo was treated with maleic anhydride [25]. The hydroxyl group of the fiber was not affected by the maleic anhydride treatment. On the other hand, the phosphoric acid treated fiber showed a reduction in the hydroxyl content of the fiber as evidence in the intensity of the broad band of O-H absorption peak (Figure 9b). Most of the acid probably reacted with the O-H group in the fiber. However, the hydroxyl group of the fiber was enhanced by the pulping process which gave the highest intensity for the O-H absorption peak (Figure 9c). This was expected as the caustic soda in the pulping process increases the O-H group in the fibers. It was observed that the C=O peak in the untreated fiber disappeared in the pulped fiber which may be due to the removal of lignin and some hemicelluose from fiber during the pulping process [26].



Figures 9. FTIR spectra of the untreated fibre with **(a)** Maleic anhydride **(b)** Phosphorylated and **(c)** Pulped treated fibre.

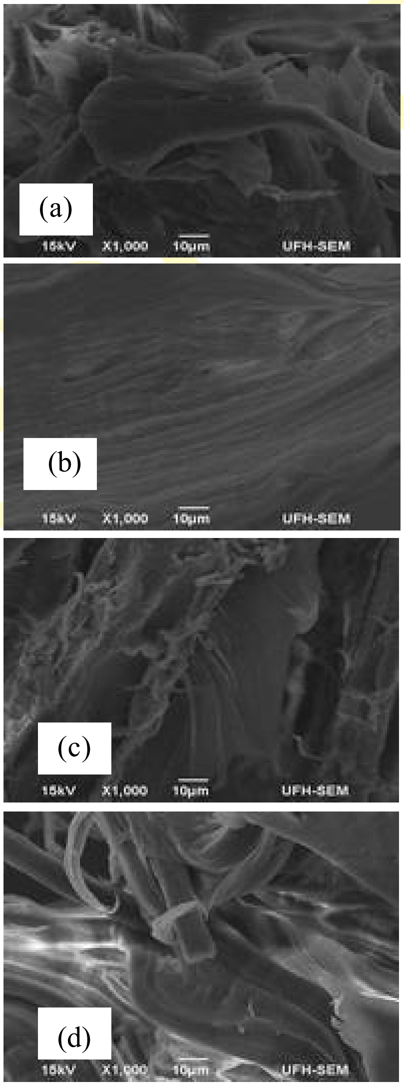
SEM

The SEM results of the treated and untreated fibers are shown in Figures 10(a-d). The micrograph revealed that there were changes in the morphology of the fiber surface as a result of the chemical treatment. The maleic anhydride and phosphoric acid treated fibers (Figures10b and c) became more fibrillated compared to the untreated fiber (Figure 10a) while the surface of the pulped fibers became rough. Thus, the chemical treatment increases the effective surface area of the fiber for good contact with the matrix.



Figures 10. SEM images of **(a)** Untreated **(b)** Pulped, **(c)** Maleic anhydride and **(d)** Phosphorylated fibres.

The morphology of the fractured surface of the fiber – reinforced LDPE composites are shown in Figures 11. The MF-LDPE composites exhibited better dispersion of the fibers in the polymer matrix than the untreated, phosphorylated and pulped fiber – LDPE composites which is an evidence of good interfacial interaction and bonding of the fiber within the matrix. There was no evidence of fiber pull outs in the matrix, suggesting that the maleated fibers were strongly embedded in the matrix more than the other chemically treated fibers. This may possibly be the reason the mechanical properties of MF-LDPE composites were higher than others. Next is the phosphorylated fiber which showed improved interfacial bonding in the LDPE matrix compared to the pulped and untreated samples. While one expect a good interfacial bonding of the rough pulped fiber within the LDPE matrix, the poor interaction may be traced to the efficiency of mixing. It was observed that most of the pulped fibers, because of their lighter weight after pulping, stayed on top of the polymer matrix in the extruding maching leading to poor dispersion of the fiber in the matrix.



Figures 11. SEM Image of **(a)** UF-LDPE **(b)** MF-LDPE **(c)** PhF-LDPE **(d)** PF-LDPE.

Conclusion

Low Density Polyethylene had successfully been reinforced with *Nypa fruitican* fibre. The result obtained showed that the fibre responded positively to chemical treatments. The surface chemical modifications of the fibers resulted in the improvement of the modulus and tensile strength of the *Nypa* fiber/ LDPE composites. The maleated fiber /LDPE composites gave the highest modulus and tensile strength with improved fibermatrix interaction and no evidence of fiber pullouts in the SEM images of the tensile fractured surfaces. This was closely followed by the composites reinforced with phosphorilated, soda pulped and untreated fibers. The composite containing 2.5% untreated fibre loading gave the highest value for elongation at break indicating that the higher the percentage fibre composition, the lower the elongation at break. Water sorption properties of the composites increases with fiber contents but varied with the surface treatment methods.

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Journal of Science Research
Volume 15, 2016, ISSN 1119 7333
Citation: Ogunsile, B. O. and Mafolasire, A. A.
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