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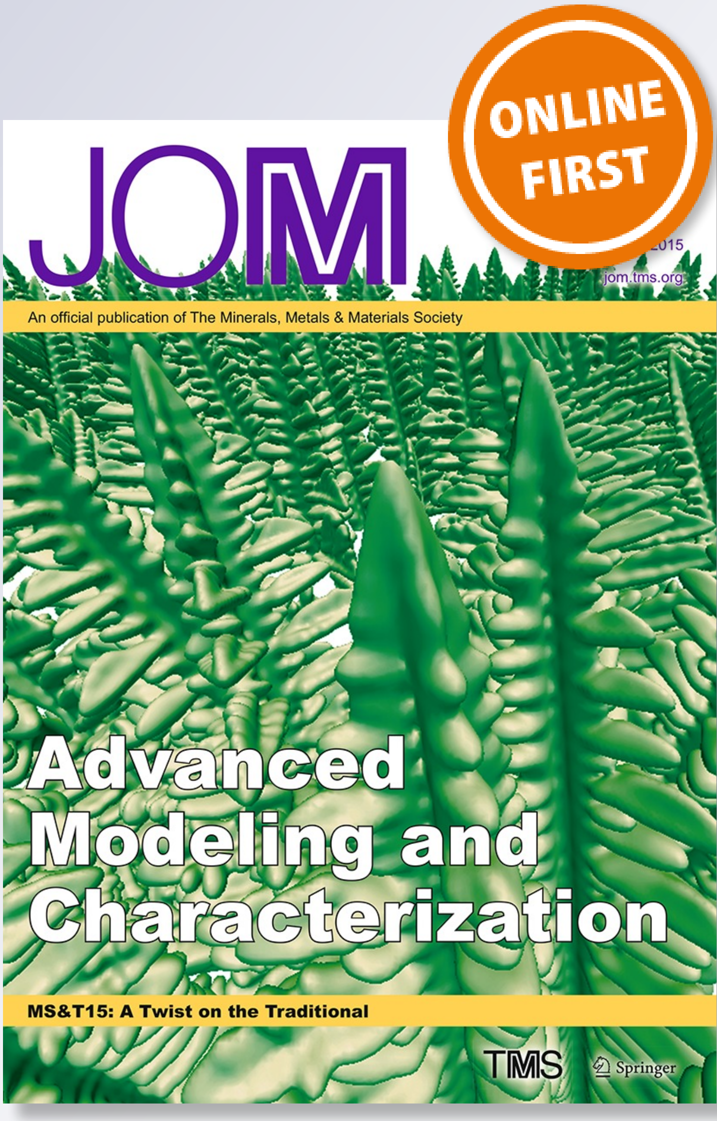

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Mechanical Behavior of Electrospun Palmfruit Bunch Reinforced Polylactide Composite Fibers

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In this study, the mechanical characteristics of electrospun palm fruit bunch reinforced poly lactic acid (PLA) nanofiber composites using treated and untreated filler was examined. Poly lactic acid–palm fruit bunch–dichloromethane blends were electrospun by varying the concentration of the palm fruit bunch between 0 wt.% and 8 wt.%. A constant voltage of 26 kV was applied, the tip-to-collector distance was maintained at 27.5 cm and PLA-palm fruit bunch-dichloromethane (DCM) concentration of 12.5% (w/v) was used. The results revealed that the presence of untreated palm fruit bunch fillers in the electrospun PLA matrix significantly reduces the average diameters of the fibers, causing the formation of beads. As a result there are reductions in tensile strengths of the fibers. The presence of treated palm fruit bunch fillers in the electrospun PLA matrix increases the average diameters of the fibers with improvements in the mechanical properties. The optimal mechanical responses were obtained at 3 wt.% of the treated palm fruit bunch fillers in the PLA matrix. However, increase in the palm fruit fillers (treated and untreated) in the PLA matrix promoted the formation of beads in the nanofiber composites.

INTRODUCTION

Electrospinning is a versatile and cost effective technique for the production of multi-functional sub-microfibers and nanofibers from electrically charged polymer solutions, polymer-composite solutions or melts.[1–3] Polymer nanofibers have a diameter in the order of a few nanometers to over 1 micrometer and possess unique characteristics namely an extraordinarily high surface area per unit mass with significant porosity, excellent structural properties, high axial strength with extreme flexibility, low basic weight and low cost.[4,5] Electrospun nonwoven mats have found applications in areas like filters, sensor devices, electrical conductors, protective cloths, wound dressing, tissue engineering, vascular grafts, and drug delivery systems among others.[6,7] A drug-containing electrospun fiber mat is a promising controlled release formulation for future biomedical applications. The resulting mat from nano fibers containing drugs can be applied topically for skin and wound healing, or post processed for other kinds of drug release.[5,8]

Biodegradable polymer solutions such as, polylactide (PLA), polyglycolide (PGA), polylactide-co-glycolide (PLGA) and polycaprolactone (PCL) have been successfully electrospun and used for tissue scaffold applications. This has been applied in biomedical and bioengineering as their biocompatibility and degradation properties are known.[9,10] Studies carried out experimentally and theoretically have shown that the mechanical properties of these electrospun biodegradable polymers can be improved through electrospinning of the blends of these polymers. Incorporation of other materials into the polymer solutions prior to electrospinning has proved to enhance its mechanical properties. Materials like nanoscale clay particles and carbon nanotubes (CNT) have been successfully incorporated into or reinforced electrospun PLA.[11,12]

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Nanoscale clay particles have been incorporated in electrospun PLA fibers to control modulus and biodegradation rate for potential biodegradable packaging applications.[13] Carbon nanotubes have been incorporated in electrospun PLA fibers for potential use as bone graft materials.[14,15] However, researches on the use of natural fibers as fillers in electrospun PLA fibers are limited.

In this study, treated and untreated palm fruit bunch particulates are incorporated to reinforce PLA. Both the polymer matrix and the fillers are biodegradable. The mechanical properties of this low mass fraction of palmfruit bunch fillers reinforced PLA nano fiber composite are presented.

EXPERIMENTAL METHODOLOGY

Materials

Empty palm fruit bunches were obtained from a farm located in Badagry, Lagos State, Nigeria. PLA pellets are obtained from Nature Works LLC supplier in China. Analar grade dichloromethane (DCM) with a purity of 96% (v/v) was obtained from Fanor Agencies Limited, Ojota Lagos, Nigeria. The electrospinning machine used for the study was designed and manufactured by the authors using local materials. The machine was tested and calibrated before use.

Methods

Preparation of Palm Fruit Bunch Fibers

Palm fruit bunches were collected, washed, sun dried for 2 weeks and then cut into small pieces. The cut bunches were ground to pass 10 mm screen in a mechanical crusher. These were de-waxed using benzene–ethanol treatment in a Soxhlet extractor, washed to neutrality and oven dried at 45°C. The resulting fiber particulates were fed into an autoclave. Saturated steam is admitted into its chamber, the valve is closed and the temperature rose to 175°C at 1 bar. When the material attained the reaction temperature the valve is released onto cause rapid pressure reduction giving rise to explosive decomposition of the fiber particulates and the resulting fiber particulates were oven dried. Fiber particles were then treated with crude cellulase (enzyme for the hydrolysis process) by suspending in 50 mL of 50 mM sodium (Na) acetate buffer pH 4.8 in a conical flask. The hydrolysis was performed at 50°C in a shaking bath at 15 rpm for 2 h. The hydrolyzed fiber particulates were soaked in 2% solution of NaOH overnight to remove some cementing ingredients like hemicellulose and pectin through beta elimination. These alkaline treated fiber particles were neutralized by washing in distilled water and bleached by soaking in 8% solution of hydrogen peroxide overnight. The bleached pulp is rinsed in distilled water. The bleached fiber particles were further treated with equal amount of 10% (w/w) nitric acid and 10% (w/w) chromic acid by dipping in equal amount of solution and raising the temperature to 60°C for 15 min to initiate the reaction and then allowed to stay for 24 h. The treated fiber particles were then washed in distilled water, centrifuged in ethanol, sun dried in still air, sieved to 150 μm particles and stored in a dried sealed bottle.

Electrospinning Solution Preparation

Mixtures of PLA and palm fruit bunch (treated and untreated) were dissolved in DCM at a constant composition of 12.50% (w/v). The solutions were left in the sealed bottles for 24 h in order to dissolve the PLA and palm fruit bunch.

Process Setup and Electrospinning

An experimental setup was constructed to produce nanofibers by the electrospinning process. The process takes place in a sealed acrylic enclosure. The polymer/fiber solution is fed into the syringe. The syringe was inclined at 30° to the horizontal with the polymer solution and mounted on a retort stand with the aid of a clamp. The diameter of syringe needle was 1.5 mm. A high voltage supply source with 26 kV, 5 mA, 125 W was used. A stationary rectangular stainless steel collector of 30 by 28 mm was placed at 27.5 cm from the tip of the syringe. The process is initiated by connecting the syringe to the voltage source which initializes the electrospinning phenomenon when switched on. The electrospinning process was repeated by varying the weight fraction of the fibers in the mixture between 0 wt.% and 8 wt.%.

Characterization of Eletrospun Nanofibers

Mechanical Measurements

Tensile testing of electrospun fibers was performed on 3×2 cm tensile specimens using an Instron Model 313 having Bluehill TM Version 1.00 analysis software at Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria. The hardness of the samples were measured using Tensometer indenter hardness machine type W serial number 1005, which is located at the Department of Materials Science and Engineering Obafemi Awolowo University, Ile-Ife Osun State, Nigeria.

Water Absorption Test

The water absorption test was done at two different temperatures (14°C and 50°C). In both cases electrospun fiber samples were immersed in the water for 2 h. Adventurer RS232 weighing scale was used to weigh the samples before and after immersion. The volume of water used for the test at 14°C was 50 cl per sample. After immersion, the samples were allowed to drain naturally for about 10 min on a white towel before their masses were re-weighed. The hot water test was done using laboratory mercury in-glass thermometer with temperature range between −10°C and 110°C and an electric water heater. The samples were placed on a plastic container and put on the electric heater with the thermometer inserted. The temperature was regulated between 55°C and 50°C during the experiment for a period of 2 h after which measurement was taken.

Scanning Electron Microscopy (SEM)

A scanning electron microscope (Model: ASPEX 3020) located at the Materials Science and Engineering Laboratory of Kwara State University, Nigeria was used to study the morphological features of the composite fibers. It was operated at 15 kV to determine the fiber morphology of the electrospun samples. The electrospun samples were coated with conducting carbon tape. The Digital SEM images of the samples were captured at 100× and 250× magnifications. The average diameters of fibers and beads were determined by using an ImageJ software.

RESULTS AND DISCUSSION

Fiber Diameter

Selected samples were subjected to SEM analysis and the imageJ software used to analyse the average fiber diameter. Table I shows the average fiber diameter of the samples while Fig. 1 shows the SEM images of the selected samples. The electrospun sample reinforced with 3 wt.% treated palm fruit bunch fillers has the largest average diameter of 12.06 μm (see Fig. 1b) with no beads. However, the presence of untreated palm fruit bunch fillers in the electrospun PLA matrix significantly reduced the diameters of the fibers as undesirable beads were found sparsely on the fiber surface (see Fig. 1d, e). The smallest diameter of fibers was recorded for composites with 8 wt.% of untreated fillers (3.38 μm) followed by the composites with 3 wt.% of untreated filler (5.22 μm). Electrospun composite fibers with treated palm fruit fillers of 8 wt.% showed fiber diameter of 10.14 μm. The decrease in fiber diameter has been attributed to increase in filler loading or viscosity of solution arising from the domination of electrical conductivity.[16]

FIBER MORPHOLOGY

The morphology of the electrospun fibers were characterized by SEM (see Fig. 1). It is observed that the electrospun PLA has fibers with very smooth surface near uniform diameters. This means the PLA solution developed a minimum polymeric chain network and entanglement concentration leading to beadless fibers. The fiber average diameter is given in Table I. The electrospun sample reinforced with 3 wt.% treated palm fruit bunch fillers has fibers with relatively smooth surfaces and near uniform diameters. The surfaces of the fibers look toughen as the fillers are dispersed on the fiber surface with no beads. The electrospun sample reinforced with 8 wt.% treated palm fruit bunch fillers showed similar results to 3 wt.% treated palm fruit bunch fillers with beads on the surface. These surfaces were rough compared to that of unreinforced PLA and PLA + 3 wt.% filler. Thus, increase in the weight fraction of the filler leads to a decrease in the surface quality of the fiber and the formation of beads. The electrospun sample reinforced with 3 wt.% untreated palm fruit bunch fillers has smaller diameter fibers with limited number of beads. However, samples' fibers reinforced with 6 wt.% untreated palm fruit bunch fillers have smaller diameters and large number of beads. The presence of beads can be attributed to the aggregation of filler particles. This idea is supported by the work of Chien and Wang[17] who found that addition of 1 wt.% of carbon nanotubes to PLA led to relatively uniform fiber shape and fewer beads while addition of up to 5 wt.% increased the beads. In that study, agglomeration of the filler particles was observed using TEM. Beads are undesirable in electrospun fibers as these act as defects and may lead to inferior mechanical properties of electrospun fibers.[18–20] The untreated fillers were found to lead to excess formation of beads on the surface of the electrospun fibers showing that the treatment earlier carried out on the filler had a marked effect on the adhesion between the filler and the PLA during electrospinning and consequently eliminate filler particles agglomeration.

Mechanical Responses

Figure 2 showed the tensile strength of electrospun fibers in relation to increase in weight fraction of the reinforcements. It was noted that composite fibers with treated reinforcements exhibits superior tensile strength to those of untreated reinforcements. Composite fibers with treated reinforcement showed initial increase in tensile strength with weight fraction of the reinforcement to maximum value (0.9 MPa) at 3 wt.% of the reinforcement but decreased steadily on further addition. However,

Table I. Average fiber diameter of the samples

Sample	PLA	PLA + 3 wt.% treated fiber	PLA + 8 wt.% treated fiber	PLA + 3 wt.% untreated fiber	PLA + 8 wt.% untreated fiber
Average fiber diameter ($\times 10^3$ nm)	10.11	12.06	10.14	5.22	3.38

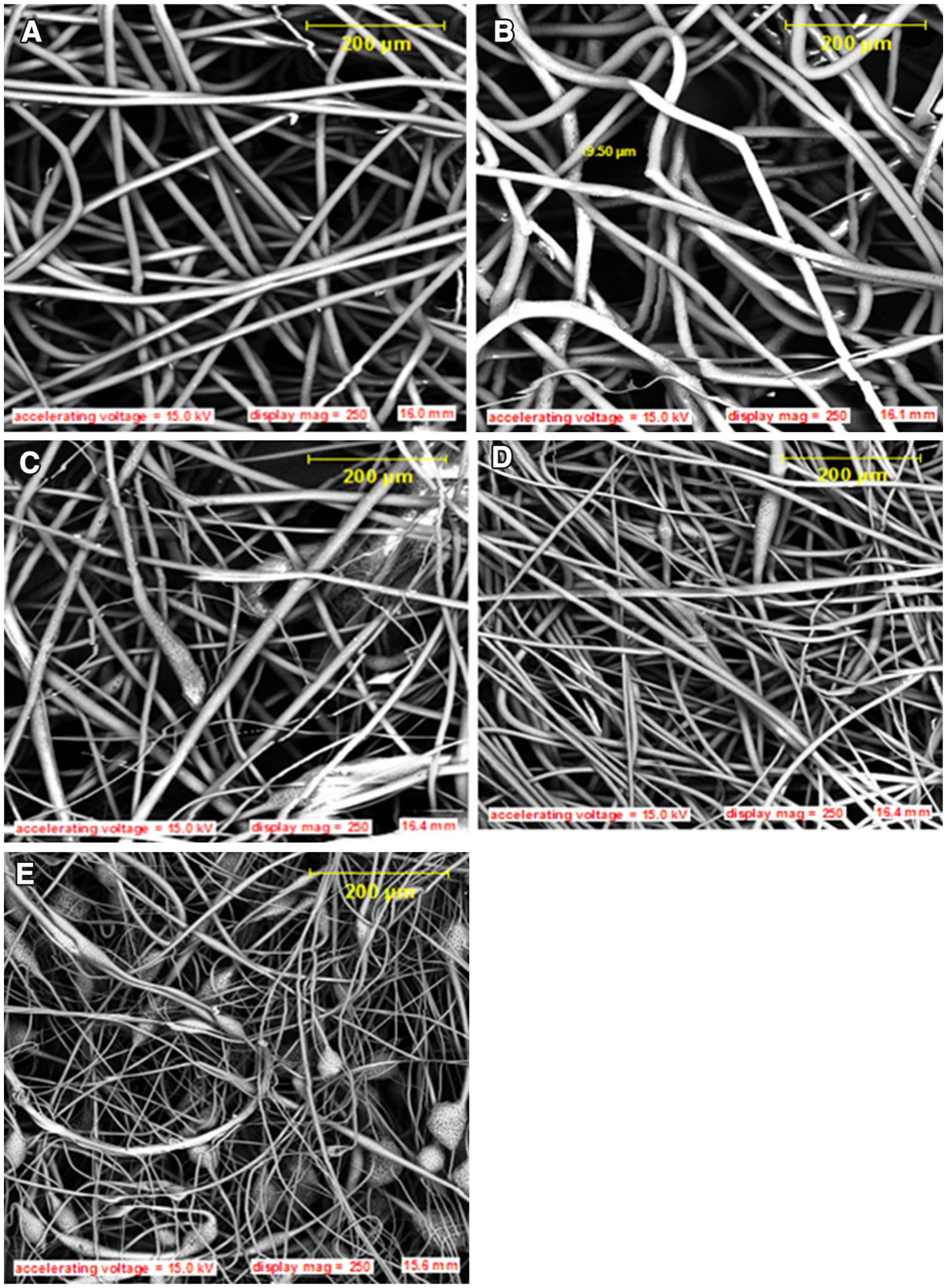

Fig. 1. Morphologies of fibers of; (a) PLA, (b) PLA + 3 wt.% treated palm fruit bunch, (c) PLA + 8 wt.% treated palm fruit bunch, (d) PLA + 3 wt.% untreated palm fruit bunch and (e) PLA + 8 wt.% untreated palm fruit bunch.

composite fibers with untreated reinforcement continuously decreased in tensile strength with reinforcement addition. Arshad et al.[21] and Hammajam et al.[22] have shown that chemically treated empty palm fruit bunch fillers in thermoplastic polymer matrix significantly improved the mechanical properties. Chemical treatment of palm fruit bunch fillers improves the tensile strength of the fibers due to expulsion of the hemicellulose, pectin, lignin and waxy contents.[23] The presence of untreated palm fruit bunch fillers in the electrospun PLA matrix significantly reduced the fibers' diameters, causing the formation of beads. This results into decline in tensile strengths of the reinforced fibers as in samples with 3 wt.% and 6 wt.% fillers where average diameters of 5.22×10^3 nm and 3.38×10^3 nm respectively were obtained. However, electrospun fibers with 8 wt.% treated filler have large fiber diameter of 10.14×10^3 nm but with poor tensile strength attributed to the presence of beads in the fibers. It was noted earlier, that the presence of beads were caused by agglomeration of filler

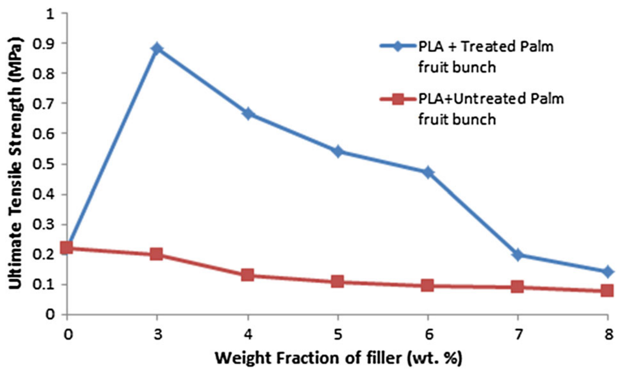

Fig. 2. UTS characteristics of PLA composite fibers with concentration of reinforcement.

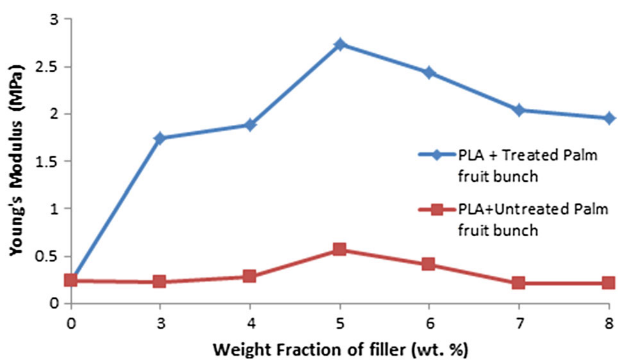

Fig. 3. Young's modulus characteristics of PLA composite fibers with concentration of reinforcement.

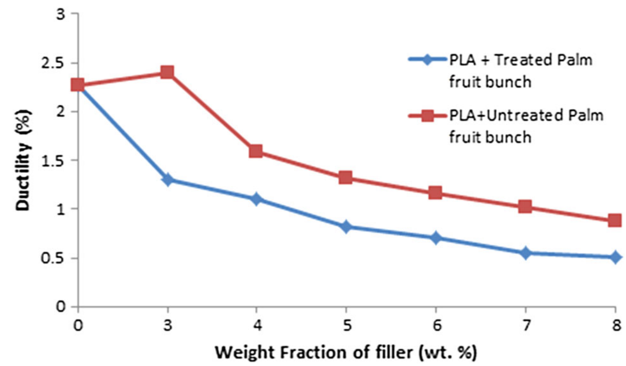

Fig. 4. Ductility characteristics of PLA composite fibers with concentration of reinforcement.

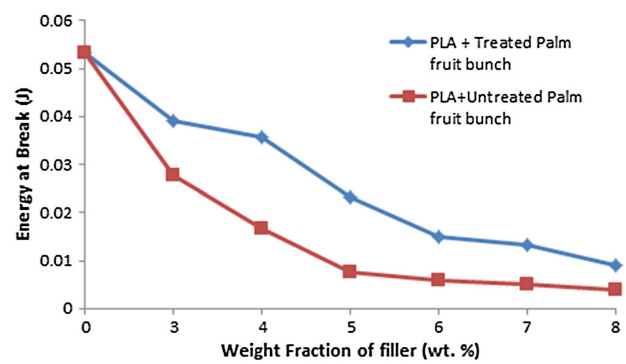

Fig. 5. Energy at break of PLA composite fibers with concentration of reinforcement.

particles and this case may be caused by increasing volume fraction. On the other hand increased viscosity is also known to cause increase in fiber diameter and consequently poor tensile response. The electrospun sample reinforced with 3 wt.% treated palm fruit bunch fillers has the largest average diameter of 12.06×10^3 nm with no beads. This results in improved tensile strength of 0.88 MPa.

Effect of addition of palm fruit bunch on the Young's modulus of the electrospun PLA fibers is shown in Fig. 3. The elastic modulus of composite fibers with treated fillers increased with increase in filler content to a maximum at 5 wt.% of the filler but decreased with further filler addition. A similar trend was shown by composite fibers with untreated fillers but with a marginal increase. The Elastic modulus increased gradually to a maximum at 5 wt.% filler but decreased continuously to a minimum with further filler additions. The Figure showed superior Elastic Modulus for composite fibers with treated fillers compared to composites with untreated fillers. This superiority may be attributed to a strong adhesion between the fillers and the PLA in the electrospun fibers. This could be seen in Fig. 1d and e where fibers with untreated fillers possessed beads with rough surface morphology.

The variation in ductility of composite fibers with weight fraction of fillers is shown in Fig. 4. The Figure showed a continuous decrease in both composites with filler addition, while composite containing untreated fillers showed better ductility. The unreinforced PLA (~2.25%) has comparable elongation to 3 wt.% untreated filler reinforced PLA (~2.4%).

The effect of fillers' addition on the tensile energy to break (TEB) of composite fibers are shown in Fig. 5. All composites show sharp decrease in the ability to withstand sudden load with increase in filler addition to a minimum value at 8 wt.% filler. Composites with treated filler showed better tensile energy at break to the untreated filler composites. The TEB indicates the total energy absorbed per unit volume of the electrospun fibers up to the point of rupture. It is an indication of the toughness of the material. The result showed that the electrospun PLA fiber experienced decline in resistance to rupture as content of palm bunch filler particles increased. However, treated filler composites showed improved TEB compared to untreated filler samples.

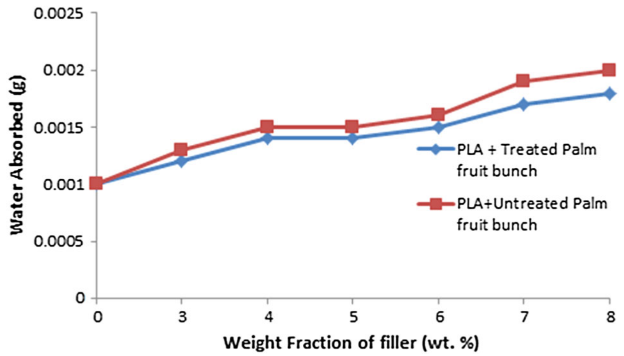

Fig. 6. Water absorption trends in palm fruit bunch reinforced PLA fibers at 14°C.

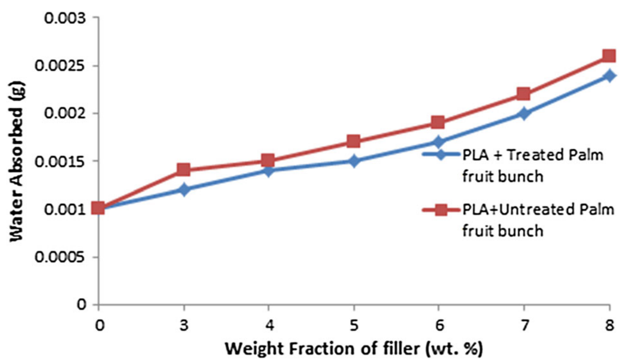

Fig. 7. Water absorption propensity in palm fruit bunch reinforced PLA fibers at 50°C.

Water Absorption

The electrospun PLA (control) sample absorbed the least water at both temperatures of 14°C and 50°C while the electrospun PLA + treated palm fruit bunch fillers absorbed some water but not as much as electrospun PLA + untreated palm fruit bunch fillers at both temperatures (see Figs. 6, 7). It is believed that the electrospun PLA (control) sample absorbs the least water because it contains no palm fruit bunch which is hydrophilic and has the capacity to absorb water. It is widely believed that natural fibers are polar in nature, and hence have poor moisture resistance because of the presence of organic matters in its matrix. However, the moisture resistance is improved by chemical treatment of the fibers.[21] This could be seen in Figs. 6 and 7 where electrospun fibers with treated fillers had low water adsorption rate than those with untreated fillers in both cases.

CONCLUSION

From the this study the following deductions are made;

1. The electrospun PLA reinforced with treated palm fruit bunch samples have better moisture resistance than the electrospun PLA reinforced with untreated palm fruit bunch.
2. The moisture resistance of the electrospun fibers is improved by chemical treatment of the reinforcement.
3. The higher the weight fraction of filler (treated and untreated) in the PLA matrix, the higher the formation of beads resulting in diminishing tensile strengths.
4. The optimal mechanical responses are obtainable at 3 wt.% treated palm fruit bunch.

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