### ISSN 0511-5728

The West Indian Journal of Engineering Vol.39, No.1, July 2016, pp.63-71

# Mechanical and Microstructural Characteristics of Rice Husk Reinforced Polylactide Nano Composite

Samson O. Adeosun a, Abraham K. Aworinde, Ihuoma V. Diwe, and Samuel A. Olaleye

a.c Department of Metallurgical and Materials Engineering, University of Lagos, Nigeria; E-mails: samsonoluropo@yahoo.com; favour111@yahoo.com

<sup>b</sup>Department of Mechanical Engineering, Covenant University Ota, Ogun State, Nigeria; E-mail: abraham.aworinde@covenantuniversity.edu.ng

<sup>d</sup> Department of Mechanical Engineering, University of Lagos, Nigeria; E-mail: solaleye@unilag.edu.ng

<sup>Ψ</sup> Corresponding Author

(Received 4 September 2015; Revised 26 April 2016; Accepted 23 May 2016)

**Abstract:** The application of polylactides in tissue engineering is attracting significant interest. Using renewable; low cost; health and environmental friendly agro waste as reinforcement in electrospun polylactide nano composite fibres reduces the need for petroleum based fillers and enhances the strength of polylactides. In this paper, the morphological, mechanical and water permeability properties of electrospun treated and untreated rice- husk reinforced polylactide- nano- composite fibres are presented. The treated rice- husk particulates were ground, subjected to steam explosion and chemical treatment to remove its lignin and hemi-cellulose contents so as to increase the crystallinity of the filler. The addition of 4wt. and 6 wt. % untreated rice- husk filler increased the tensile strength by 95% and 43% respectively. Young's modulus, fracture stress, water permeability and other properties are also enhanced. This work shows that; the mechanical properties and biodegradability of scaffolds for tissue engineering can be improved by reinforcing polylactide with rice-husk instead of petroleum-based polymeric- nano- fiber composites.

Keywords: Nano-composite, fibre, polylactide, rice- husk, mechanical properties, morphology

#### 1. Introduction

There is a growing awareness that the world's petrochemical resources are not only finite (Howard *et al.*, 2009), but costly to produce; contribute to climate change (Skjærseth and Skodvin, 2001); increase carbon footprint; (Gentner et *al.*, 2014) and pose waste management problems (Malmasi et *al.*, 2010). All these result in an increased demand for polymeric composites produced from sustainable and ecologically friendly raw material and not from petrochemicals (Kim and Netravali, 2010; Mukherjee and Kao, 2011).

Polylactide or polylactic acid (PLA) is a biodegradable, thermoplastic aliphatic polyester obtainable from renewable resources such as corn starch (Todo and Takayama, 2011). To produce a fully bio-degradable and renewable nano-composite, cellulose based reinforcement which is renewable and biodegradable is used. Cellulose is cheaply sourced, readily available and has good mechanical properties (e.g. high modulus, ~140 GPa), compared to inorganic reinforcing fillers (Sturcova et al., 2005). Applications of PLA are restricted to low performance articles such as plastic bags, packaging for food, disposable cutlery and cups; slow release membranes for drug delivery; and liquid barrier layers in disposable nappies. The inherent brittleness of PLA leads to relatively poor impact properties performance. The limited supply and higher cost of PLA compared with commodity polymers such as polyethylene and polypropylene are of concern (Perego and Cella, 2010). To address these shortcomings, nano-fibres are added as reinforcements in PLA to form polymer composites. This process often helps to improve the polymer's mechanical and physical properties, making it suitable to a wide range of applications.

PLA is a resorbable polymer which degrades on exposure to body fluid (Armentano et *al.*, 2010). Addition of fibres, coatings and coupling agents can be used to control the degradation rate (Zeeshan et *al.*, 2015). When agro-waste fibres are added to PLA, its load bearing capacity, resorbability and some mechanical properties are enhanced. This makes it suitable for tissue engineering application, since the composite is both biodegradable and biocompatible. Such applications include the development of fracture fixation, interference screws, scaffolds and bone graft material (Zeeshan *et al.*, 2015).

Agro-waste such as rice husk contains natural fibres which are readily available, cheap, and biodegradable. This natural waste can be used to produce nano-fibres that can serve as reinforcing agents in polymer composites, through an electro spinning process (Dashtbani and Afra, 2015). This will lead to the production of polymer composites of improved

mechanical and impact performance with enhanced biodegradability. The advantages of using natural fibres as reinforcement over glass fibres, talc or carbon fibres include lower density of the polymer composite, retention of biodegradability of the composite, superior performance, improved waste management of agrowaste fibres, lower cost and ease of acquisition of the abundant agro-waste fibres (Pertinakis, et *al.*, 2013). The fibrous nature of cellulose is another advantage because it can align and orient along the matrix axis with resultant improvement in mechanical properties and weight reduction. Cellulose is non-abrasive and, easy to process, which allows for high filling levels and this in turn yields significant savings (Eichhorn et *al.*, 2010).

Interfacial interactions or adhesion between polymer matrices and cellulose fibres depend on the strength of the molecular interactions that occur at the interphase between them. The stronger the molecular interaction, the stronger the resulting interfacial adhesion and the optimal load transfer performance. These can be achieved by modifying the surface of the cellulosic fibres through esterification, acetylation, and the use of coupling agents or compatibilisers (Huda et *al.*, 2006). Natural nano-composites can be found in the structure of abalone shell and bone. Interphases in nano-composites play a dominant role and affect their macroscopic properties. The reinforcing material can consist of nano materials in zero, one or two dimensional form.

Electro-spinning has been recognized as an effective technique for the fabrication of polymer-nano-fibres. Various polymers have been successfully electro-spun into ultrafine fibres using either solvent solution method or in melt form. Using solvent solution, PLA can be successfully electro-spun into ultra-fine fibres. Some amazing characteristics such as very large surface area to volume ratio, flexibility in surface functionalities, and superior mechanical performance, are achievable provided the diameters of polymer fibre materials measure nano-meters (Zeng et al., 2003). One of the most promising uses for electro-spun nano-fibres is for developing nano-fibrous cellular scaffolds for tissue engineering. This is based on the biomimetic principle that electro-spun nano-fibres can mimic the physical structure of the native extracellular matrix (ECM), as most tissues and organs are fibrous in form with fibre dimensions down to nanometer scale (Laurencin et al., 1999).

Nano fibrous scaffolds can promote cell growth and also function well in the synthesis of genuine extracellular matrices over time (Laurencin *et al.*, 1999). Dimensional stability of nano-composite fibres for scaffold tissue engineering is useful since they should be able to withstand the stresses of shrinkage and swelling due to changes of temperature and moisture (Matoke et *al.*, 2012).

The study on the effect of different solvent systems on fibre morphology and diameter of electro-spun PLA nano-fibres done by Casasola et *al.*,(2014) revealed that

only acetone was able to produce a sufficient quantity of fibres to form nano-fibre mats with a minimum mean diameter. The fibre diameter is 757 nm with bead string morphology attributed to its relatively high conductivity and dielectric constant when compared to single solvents like Tetrahydrofuran (THF) and 1, 4-dioxane (DX). The single solvent did not produce continuous nano-fibres but produced droplets probably due to their high surface tension and low conductivity (McCullen et *al.*, 2007).

Green nano-composites composed of cellulose nano- fibre (CNF) and PLA were made using a solvent casting method. The CNF was surface modified and followed by esterification to improve the dispersion and its interfacial adhesion with the PLA. The results revealed uniform distribution of nano-particles in the polymer matrix at 1 and 3wt. %, but at 5wt. % the, CNF was easily agglomerated, thus causing a reduction in the mechanical properties of the nano-composite. The results of water vapour permeability (WVP) tests showed that the use of acetylated nano-fibres had no significant changes on the permeability of the films. Nano-composites with 1wt. % CNF does not produce significant alteration in tensile strength and elastic modulus but over 60% increment in elongation.

However, nano-composites with 3 and 5wt. % CNF showed significant changes in tensile strength, elastic modulus and elongation percentage. There is slight increase in glass transition and melting temperatures of PLA reinforced with CNF (Ali et al., 2014). Baumgarten's (1971) study, of the effect of varying solution and process parameters (solution viscosity, flow rate, applied voltage) on the structural properties of electro-spun fibres using a poly (acrylonitrile) /dimethyl formamide (PAN/DMF) solution, determined that fibre diameter had a direct dependence on solution viscosity. The results indicated that the higher the viscosities, the larger the fibre diameters. The fibre diameter does not monotonically decrease with increasing applied electric field. Although it initially decreases with an increase in the applied field reaching a minimum and then increases when the applied field is further increased.

By varying the solution and processing parameters, electro-spun fibres with diameters ranging from 500 to 1,100 nm were produced. Properties of PLA composites reinforced with microcrystalline cellulose (MCC) from oil palm biomass have also been studied (Haafiz et al., 2013). There was an improvement in the thermal stability of the PLA/MCC composites, while there was no improvement in both tensile strength and elongation at break of the composites when compared to virgin PLA. However, the Young's Modulus increased from 3.9- 4.6 GPa with MCC loading. This was attributed to increase in hydrogen bonding, a stiffening effect, and high crystallinity index of MCC. The decrease in tensile strength of the PLA/MCC composites with MCC loading was attributed to aggregation of the MCC. The aggregation was due to Van der Waal's forces causing pronounced filler-filler interaction than filler-matrix interaction. Poor interfacial adhesion between the matrix and filler generated numerous voids at the filler-matrix interface. Decline in elongation with MCC loading was attributed to the stiffening action of the filler by restricting the segmental chain movement of PLA during tensile testing.

Petinakis et al., (2009) studied the effect of wood flour content on the mechanical properties and fracture behaviour of PLA/wood-flour composites. The results indicated that enhancements in tensile modulus could be achieved, but the interfacial adhesion was poor. The incorporation of ligno-cellulosic materials biodegradable polymer materials, such as PLA, has the effect of improving mechanical properties such as tensile modulus. But the strength and toughness of these biocomposites were not necessarily improved. This was attributed to the hydrophilic nature of natural fillers. The incompatibility with the hydrophobic polymer matrix will cause fibres agglomeration resulting in low impact properties, particularly at high fibre loadings.

The incorporation of 1wt. % cellulose nano-crystals (CNC) loading into electro-spun PLA fibres has resulted into about 37% improvement in strength and Young's Modulus (Xiang *et al.*, 2009). It was suggested that the addition of CNCs could reduce the diameter of electrospun fibres and thus improve fibre uniformity. The enhanced electric conductivity of electro-spinning in the presence of CNCs was given as the propelling force, which tends to increase the mechanical properties of mats. The smaller fibre diameters yielded higher overall relative bonded areas between fibres by increasing its surface area, bonding density and distribution of bonds.

This study was aimed at producing biodegradable, health and environmental friendly, renewable and low cost polylactide nano-composites for application in scaffold tissue engineering using treated and untreated rice-husk particles as fillers. The electro-spun nano-composite fibres were characterized for mechanical, water absorption and morphological responses.

# 2. Experimental Methodology

Industrial PLA obtained from Suzhou, China was used. The agro waste (rice-husk) was from a rice plantation in Abakiliki, South East, Nigeria. The exterior of rice husk is composed of dentate rectangular elements. These elements are themselves composed mostly of silica coated with a thick cuticle and surface hairs. The mid region and inner epidermis contain little silica. Amorphous silica is concentrated at the surfaces of the rice husk and not within the husk. The solvent used in the electro-spinning process was Dichloromethane manufactured by Shandong Jinhao Int'l Trade Co. Ltd, CAS number 75-09-2, 96% pure with concentration of 14.9M.

# 2.1 Fibre processing for untreated and treated ricehusk

The rice-husks (RH) were collected; washed; dried in sunlight for 5 days at an average daily temperature of 29°C; cut into small pieces; ground to pass a screen of 10 mm in a mechanical crusher; and sieved using a sieve size of 105 µm to get the untreated RH particulate.

For the treated RH particulate, in addition to grounding, it was subjected to steam explosion at a temperature of 175 °C and a pressure of 1bar in an autoclave (SM280 E). The resulting fibre was hydrolysed in 2 % solution of NaOH overnight, neutralized in acetic acid and bleached with 8 % solution of hydrogen peroxide. Further acid hydrolysis was undertaken with a mixture of 10 % (w/w) nitric acid and 10 % (w/w) chromic acid at a temperature of 60°C for 15 minutes. The resultant treated RH was sieved to 105 μm. The RH was treated to remove the lignin, amorphous and hemi-cellulose contents from it. This would also increase the crystallinity of the nano- fibre.

# 2.2 Preparation of PLA - Rice husk composite solution

The pulverized and sieved (treated and untreated) RHs were dissolved in Dichloromethane after they were weighed. Different grams of PLA were also dissolved in dichloromethane solvent to form the polymer solution. The different solutions of PLA- RH were mixed accordingly using 3 - 8wt. % RH as shown in Table 1.

**Table 1.** Solution formulation of PLA: Rice husk nano-composite fibre

S/N	PLA wt.	Rice husk wt. %	PLA (g)	Rice husk (g)
X(control)	100	0	20	0
U1 and T1	97	3	16.2	0.5
U2 and T2	96	4	24	1.0
U3 and T3	95	5	28.5	1.5
U4 and T4	94	6	31.3	2.0
U5 and T5	93	7	33.2	2.5
U6 and T6	92	8	34.5	3.0

# 2.3 Electro-spinning of the rice-husk reinforced polylactide nano-composite fibres

In the trial test it was discovered that above 10 wt.% RH were formed in the PLA droplets instead of fibres on the collector plate independent of the voltage applied (0-30 KV), the flow rate and tip-to-collector distances. Therefore, the optimal level of the rice husk in the PLA is 8 wt. %; as above this content level the chances of droplets formation increases.

The solution samples of PLA- RH in different wt. % (from 3 - 8wt. % in increments of 1wt. %) were poured into a burette inclined at 30° to the horizontal surface. The flow rate was maintained at 0.01ml/s with a constant voltage of 26KV from the high voltage source. The distance from the tip of the spinneret to the collector was kept constant at 24.5cm. During electro-spinning, at a room temperature of 23°C, the PLA- RH solution was

involved in an electric field. The polymer filaments were formed from the solution between two terminals bearing electrical charges of opposite polarity. One of the terminals was placed at the tip of the spinneret attached to the tip of the burette, and the other onto a collector (aluminium foil on a metal sheet and grounded). As the charged polymer composite solution jets were ejected out of the metal spinnerets, the solution jets evaporated to become nano-fibres, which were collected on the aluminium foil collector.

#### 2.4 Characterisation

In this study all tests and measurements were done thrice to ensure reproducibility. Mechanical tensile testing was done using 2cm by 2cm samples on a Double column Instron Universal tensile testing machine model 3369 located at Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria. The computerized mechanical testing machine had a load capacity of 50KN, and the mode of operation was by continuous loading. The loading rate / strain rate used was 5mm per minute. The mechanical properties results were obtained from this test.

The morphology of the nano-fibres were studied using an ASPAX 3230 Scanning Electron Microscope (SEM) operated at an accelerating voltage of 15KV, located in the Materials Laboratory of Kwara State University, Malete, Kwara State, Nigeria. Backscattered electrons were used for the acquisition of the images. The samples were sputter-coated with a thin layer of silver to prevent the material from becoming charged by the electron beam during the analysis. The micrographs of treated and untreated PLA-RH electro-spun nanofibres with 4, 6 and 7wt. % untreated RH and 5, 6 and 7 wt. % treated RH reinforced samples were taken. These were samples with the two highest values and the lowest value in ultimate tensile strength (UTS) respectively. The average diameters of fibres and beads were determined using an image analyser software program called ImageJ. It is a Java-based image processing program which can analyse, process, and read many image formats including TIFF, PNG, GIF, and JPEG.

A water absorption test was done on all samples to know the rate at which the nano-composite fibres absorb water. The samples were first dried; weighed using Unic Bloc Digital weighing balance (UW 1020H) with tolerance of 0.001g; and then immersed in distilled water at room temperature (23°C) and at 70°C. At room temperature, the samples were placed in different beakers containing a constant volume of distilled water for five days (120 hours), with water absorption rates taken at 24 hour intervals. At 70°C, the test was done for two hours with the absorption rate taken at 30 minute intervals. The samples were periodically taken out of the water, wiped with tissue paper to remove surface water, and then weighed. The % water absorption or % weight gained (W %) was calculated using Equation 1:

$$W(\%) = \frac{W_2 - W_1}{W_1} \times 100\% - - - - - - - - (1)$$

Where  $W_2$  and  $W_1$  are weight gained after exposure and dry weight respectively.

#### 3. Results and Discussions

### 3.1 Microstructural responses

The extent of dispersion of the fillers into the PLA- RH nano-composite fibres, bead formation and diameter in nanometres of the fibres, were observed using the SEM. The presence of numerous beads in the morphologies is attributed to low solution viscosity and agglomeration of fillers as shown in Figure 1. This is in keeping with the studies done by Zeng et *al.*, (2003). The 6 wt. % treated RH and 7 wt. % untreated RH- PLA nano-fibres exhibited the least UTS due to large diameters.

The 4 wt. % untreated RH showed the best dispersion of filler and less bead formation, with the highest UTS, Young's Modulus and fracture stress due to efficient load transfer from PLA to filler irrespective of its diameter size (see Figure 2). This agrees with the work of Seong et al., (2012). The larger nano-fiber diameter at 6 and 7 wt. % untreated RH and 5 and 6 wt. % treated RH (see Figure 3) is attributed to solution viscosity, as higher viscosities gave larger fibre diameters. Baumgarten (1971) reported the effect of varying solution concentration and process parameters on the structural properties of electro spun fibres using a poly (acrylonitrile) /dimethyl formamide (PAN/DMF) solution. It was deduced that fibre diameter had a direct dependence on solution viscosity as higher viscosities gave larger fibre diameters.

#### 3.2 Mechanical Responses

The effect of treated and untreated RH on the tensile strength of electro-spun PLA nano-composite fibres are shown in Figure 4. The tensile strength for untreated RH decreased for 3, 7 and 8 wt. % RH loading of the reinforced nano-composite fibre. However, a 95% and 43% increase in strength occurred at 4 and 6wt. % RH loading compared to the virgin PLA. The tensile strengths decreased for treated RH reinforced PLA nanofibres that are 45, 13 and 45% for 3, 4 and 6 wt. % RH loading respectively. But slight strength increases occurred at 5, 7 and 8 wt. % RH loading, which is inferior to the virgin PLA. Lignin content in the untreated RH filler is capable of enhancing adhesion between the hydrophilic natural fibre and the hydrophobic matrix polymer (Salmah et al., 2013). The removal of the amorphous and lignin contents from the filler led to an increase in crystallinity and decrease in tensile strength of the rice-husk (Akpan et al.., 2014).

The morphological observation indicates better dispersion of the filler at 4 and 6 wt. % untreated RH loading with less beads or agglomeration of the fillers as

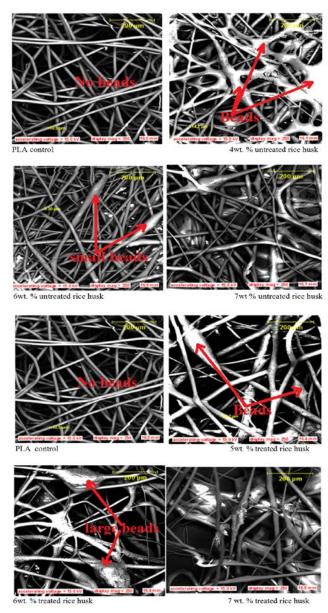


Figure 1. SEM micrographs of reinforced PLA nan-composite fibres at 250x magnification

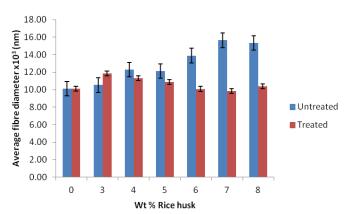
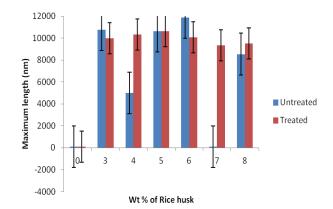


Figure 2. Comparison of average diameter of nano-composite fibres



**Figure 3.** Comparison of maximum length of nano-composite fibres

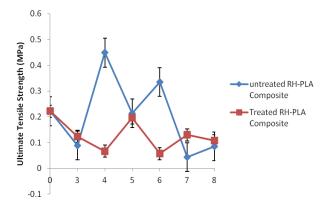
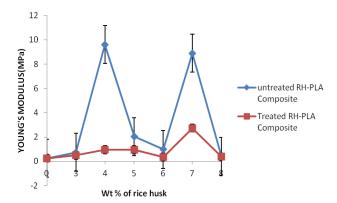


Figure 4. Ultimate Tensile Stress of rice-husk reinforced PLA nano-composite fibres

compared to 7 wt. % untreated RH which had more beads and agglomeration of filler as shown in Figure 2. Thus, there is poor filler-matrix interface alignment and reduction in stress transfer to the filler. This finding agrees with studies by Haafiz et *al.*, (2013).

Young's Modulus of the PLA-RH nano-composite fibers increased for both treated and untreated RH loading, compared to the unreinforced PLA. The untreated filler nano-fibre composite showed 1000, 700 and 350% increase at 4, 5 and 6 wt. % RH loading respectively. There were 125, 100, 212, and 174% increases in Young's Modulus for 3, 4, 5 and 7 wt. % RH loadings respectively as shown in Figure 5. This increase in Young Modulus is attributed to the stiffening effect and high crystallinity index of the filler due to the presence of cellulose in the RH fillers, with significant increase in untreated ones due to amorphous content (Haafiz et al., 2013; Akpan et al., 2014). The high increase in Young's Modulus at 4 and 5wt. % untreated RH and 5wt. % treated RH loadings was as a result of efficient stress/load transfer from the PLA matrix to the filler material due to good dispersion and adhesion between the matrix and the filler.



**Figure 5.** Young's Modulus of rice-husk reinforced PLA nanocomposite fibres

Gorga and Cohen (2004) reported that as the content of the filler is increased in a polymeric matrix above a critical level, the filler aggregates and reduces the effective stress transfer resulting in a modulus decline. This was also observed in the SEM micrographs in Figure 1; with 4wt. % untreated and 5wt. % treated RH reinforced nano-composite fibres showing less bead formation, which could be caused by adequate filler-matrix adhesion and dispersion with subsequent increase in the Young's Modulus.

Figure 6 shows the ductility for 3- 8 wt. % treated and untreated RH reinforced PLA nano-composite fibres. There was a drastic decrease in ductility for both treated and untreated RH fillers when compared with the unreinforced PLA. There were 89, 91, 89, 61, 100 and 77 % decrease at 3-8 wt. % untreated RH respectively. For the treated 3- 8wt. % RH loadings there were 72, 91, 77, 83, 94 and 66 % decrease in ductility respectively.

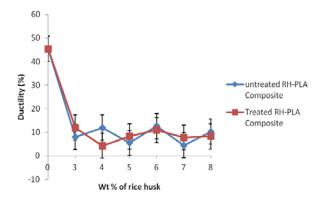
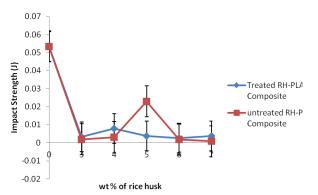


Figure 6. Ductility of rice- husk reinforced PLA nano-composite fibres

This result could be attributed to the stiffening action of the RH filler by restricting segmental movement of PLA during tensile testing and/or poor dispersion / interaction between PLA and RH. These led

to agglomeration and substantial local stress concentrations, with subsequent reduction in ductility of the nano-fiber composites. The study by Pei et *al.*, (2005), reported that ductility can be affected by the filler volume fraction; the level of the dispersion of the reinforcement in the matrix; and the interaction/adhesion between the reinforcement and the matrix.

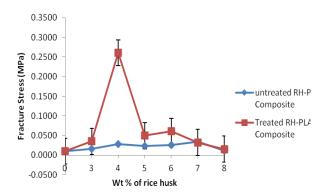
Impact, given by the energy at break, also decreased drastically for both treated and untreated RH reinforced nano-composite fibres at all wt. % and is inferior to virgin PLA (see Figure 7). There were 90, 91, 91, 56, 90 and 89 % decline at 3, 4, 5, 6, 7 and 8wt. % untreated RH respectively. For treated RH, there were 96, 89, 87, 91, 90 and 91% decline for 3, 4, 5, 6, 7 and 8wt. % respectively. There was a slight increase in energy at break at 6 wt. % untreated RH, possibly due to better filler-matrix adhesion which was observed in the micrograph, with very few beads or agglomeration of the filler. The drastic reductions in impact resistance for both filler types could be attributed to the stiffening action of the fillers through segmental chain movement restriction of the PLA, including possible agglomeration of filler thus leading to substantial local stress concentrations with resultant decrease in energy at break (Pie et al., 2005).



**Figure 7.** Impact responses of rice-husk reinforced PLA nanocomposite fibres

Fracture stress (Tensile stress at breaking) increased for both treated and untreated RH reinforced PLA nanocomposite fibres. Results show that the untreated RH PLA nano-composite fibre being higher, when compared with treated RH reinforced PLA and the virgin PLA (see Figure 8). There were 67, 1250, 400, 500, 150 and 10% increase in fracture stress at 3, 4, 5, 6, 7 and 8wt. % untreated RH respectively. For 3 - 8 wt. % untreated RH reinforced PLA there were 10, 150, 100, 150, 150 and 10% increase in fracture stress respectively compared to the unreinforced PLA.

This result was attributed to the dispersion and adhesion properties between the filler and PLA and this was higher in the untreated fibers especially at 4wt. % (see Figure 1).

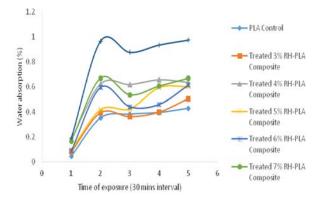


**Figure 8.** Fracture stress of rice-husk reinforced PLA nanocomposite fibres

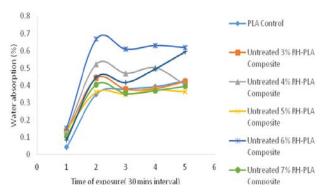
Thus, there was increased filler-matrix interface with efficient load/stress transfer to the filler (Haafiz et al., 2013; Zhou and Wu, 2012). The slight increase in fracture stress for treated RH reinforced PLA nanocomposite fibres compared to the virgin PLA and the untreated RH could be attributed to the removal of the amorphous content from the treated RH, thus increasing its crystallinity with subsequent reduction in its toughness (Akpan et al., 2014).

#### 3.3 Water absorption of nano-composite fibres

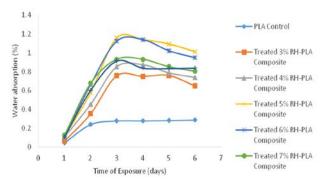
The effect of water absorption is important where the application requires the material to be in contact with water like in tissue engineering and drug delivery systems. The effects were observed for both treated and untreated RH reinforced PLA nanocomposite fibers at 23°C and 70°C as shown in Figures 9-12. It was observed that water absorption increased with increase in RH filler loading for both treated and untreated RH. As the filler loading increases, the formation of agglomerations increases which subsequently increases the water absorption of the fibers.



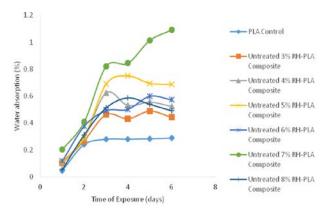
**Figure 9.** Water absorption of treated rice-husk reinforced PLA nano-fibres at 70<sup>o</sup>C



**Figure 10.** Water absorption of untreated rice- husk reinforced PLA nano-fibres at 70°C



**Figure 11.** Water absorption of treated rice-husk reinforced PLA nano-fibres at 23<sup>0</sup>C



**Figure 12.** Water absorption of untreated rice- husk reinforced PLA nano-fibres at 23°C

Dimensional stability of nano-composite fibres for scaffold tissue engineering is relevant since they should be able to withstand the stresses of shrinkage and swelling due to changes of temperature and moisture (Matoke et *al.*, 2012).

#### 3.4 Summary

As a biopolymer the studied composites demonstrate low solubility in water and high water uptake characteristics that are very important for use as absorbent materials in horticulture, healthcare and agricultural applications (Petersen et al., 1999). Scaffold design and fabrication are subjects of biomaterial research, tissue engineering and regenerative medicine research (Langer and Vacanti, 1993). Scaffolds play a unique role in tissue regeneration and repair. Scaffolds are porous solid biomaterials designed to promote cellbiomaterial interactions, cell adhesion, and ECM deposition. They permit adequate transport of gases; and for cell survival, proliferation, differentiation. Scaffolds, sustain biodegradation at a controllable rate similar to the rate of tissue regeneration with minimal or no inflammation or toxicity (Langer and Tirrell, 2004).

The results of this study on polylactide rice-husk nano-fibre composites indicate that this material can be considered for use in scaffolds as their strength, rate of degradation, porosity, and microstructure, as well as their shapes and sizes, can be more readily and reproducibly monitored (Fuchs, Nasseri, and Vacanti,2001).

In view of the properties studied and discussed in this work an optimal level of properties performance was achieved with the rice-husk reinforced PLA nanocomposite fibre at 4 wt. % and 5 wt. % for untreated and treated rice-husk reinforcement respectively.

#### 4. Conclusion

The study on the reinforcement of PLA using rice-husk as filler for the production of nano-composite fibres has shown that the mechanical properties of electro-spun PLA nano-fibre can be improved by reinforcing with 3 - 8 wt. % rice-husks. Untreated rice-husk fillers improved the mechanical properties than the treated ones due to the presence of amorphous content together with the cellulosic content. Improved dispersion and adhesion between 4 -6 wt. % untreated rice-husks as seen in the micrographs led to more efficient stress transfer to the filler which is the load bearing entity, with subsequent improved mechanical properties.

Water absorption also improved with increase in wt. % for both the treated and untreated rice-husk reinforced PLA nano-composite fibres. Thus the mechanical properties and biodegradability of scaffolds for tissue engineering, can be improved by reinforcing PLA with rice-husk in place of petroleum based polymeric nanofibre composites, thereby reducing their adverse effect on the environment.

#### References:

- Akpan, E.I., Adeosun, S.O., Lawal, G.I., Balogun, S.A. and Chen, X.D. (2014), "Structural characteristics of batch processed agrowaste fibres", *International Journal of Chemical, Nuclear, Metallurgical and Materials Engineering*, Vol 8, No 3, pp.223-230.
- Ali, A., Jaber, H., Alireza, A., Saeed, D. and Zahra, T. (2014), "Preparation and characterization of modified cellulose nano-

- fibres reinforced polylactic acid nano-composite", *Polymer Testing*, Vol. 35, pp. 73-79.
- Armentano, I., Dottori, M., Fortunati, E., Mattioli, S., and Kenny, J. (2010), "Biodegradable polymer matrix nano-composites for tissue engineering: A review", *Polymer Degradation and Stability*, Vol 95, pp 2126–2146.
- Baumgarten, P.K. (1971), "Electrostatic spinning of acrylic microfibers", *Journal of Colloid and Interface Science*, Vol 36, pp.71-79.
- Casasola, R.., Thomas, N. L., Trybala, A. and Georgiadou, S. (2014), "Electro-spun polylactic acid (PLA) fibres: Effect of different solvent systems on fibre morphology and diameter", *Polymer*, Vol.55, pp 4728 4737.
- Dashtbani, R. and Afra, E. (2015), "Producing cellulose nano-fiber from cotton wastes by electro-spinning method", *International Journal of Nano Dimension*, Vol 6, No.1, pp.1-9.
- Eichhorn, S.J., Dufresne, A., Aranguren, M., Marcovich, N.E., Capadona, J.R., Rowan, S.J., Weder, C., Thielemans, W., Roman, M., Renneckar, S., Gindl, W., Veigel, S., Keckes, J. Yano, H., Abe, K., Nogi, M., Nakagaito, A.N., Mangalam, A., Simonsen, J., Benight, A.S., Bismarck, A., Berglund, L.A. and Peijs, T. (2010), "Review: Current international research into cellulose nano-fibres and nano-composites", *Journal of Materials Science*, Vol.45, No.1, pp.1-33.
- Fuchs, J.R., Nasseri, B.A. and Vacanti, J.P. (2001), "Tissue engineering: a 21st century solution to surgical reconstruction", *Annals of Thoracic Surgery*, Vol. 72, No.2, pp.577–591.
- Gentner, D.R., Ford, T.B., Guha, A., Boulanger, K., Brioude, J. Angevine, W.M., Gouw, J.A., Warneke, C., Gilman, J.B., Ryerson, T.B., Peischl, J., Meinardi, S., Blake, D.R., Atlas, E., Lonneman, W.A., Kleindienst, T.E., Beaver, M.R., Clair, J.M., Wennberg, P.O., VandenBoer, T.C., Markovic, M.Z., Murphy, J.G., Harley, R.A. and Goldstein, A.H. (2014), "Emissions of organic carbon and methane from petroleum and dairy operations in California's San Joaquin Valley", *Atmospheric Chemistry and Physics*, Vol.14, pp.4955-4978.
- Gorga, R.E., and Cohen, R.E. (2004), "Toughness enhancements in poly(methyl methacrylate) by addition of oriented multiwall carbon nanotubes", *Journal of Polymer Science Part B-Polymer Physics*, Vol.42, pp.2690–2702.
- Haafiz, M.K.M., Azman, H., Zainoha, Z., Inuwa, I.M. and Islam, M.S. (2013), "Properties of Polylactic acid composites reinforced with oil palm biomass microcrystalline cellulose", *Carbohydrate Polymers*, Vol.98, pp.139-145.
- Howard, F., Jeremy, H. and Stephen, V. (2009), "Energy and public health: The challenge of peak petroleum", *Public Health Reports*, Vol 124, No.1, pp.5-19.
- Huda, M.S., Drzal, L.T., Misra, M. and Mohanty, A.K. (2006), "Wood-fibre reinforced polylactic acid composites: Evaluation of the physicomechanical and morphological properties", *Journal of Applied Polymer Science*, Vol.102, pp.14.
- Kim, J.T. and Netravali, A.N. (2010), "Mechanical, thermal, and interfacial properties of green composites with ramie fibre and soy resins", *Journal of Agricultural and Food Chemistry*, Vol.58, No.9, pp.5400-5407.
- Langer, R. and Tirrell, D.A. (2004), "Designing materials for biology and medicine", *Nature*, Vol. 428, No.6982, pp.487–492. Langer R. and Vacanti, J.P. (1993), "Tissue engineering", *Science*, Vol. 260, No.5110, pp. 920–926.
- Laurencin, C.T., Ambrosio, A.M.A., Borden, M.D. and Cooper, J.A.Jr. (1999), "Tissue engineering: Orthopedic applications", *Annual Review of Biomedical Engineering*, Vol.1, pp19–46.
- Malmasi, S., Jozi, S., Monavari, S.M. and Jafarian, M.E. (2010), "Ecological impact analysis on mahshahr petrochemical industries using analytic hierarchy process method", *International Journal of Environmental Research*, Vol.4, No.4, pp.725-734.

- Matoke, G.M., Owido, S.F. and Nyaanga, D.M. (2012), "Effects of production methods and materials ratios on physical properties of the composites", *American International Journal of Contemporary Research*, Vol 2, No.2, pp1-8.
- McCullen, S.D., Stevens, D.R., Roberts, W.A., Clarke, L.I., Bernacki, S.H., Gorga, R.E. and Loboa, E.G. (2007), "Characterization of electro-spun nano-composite scaffolds and biocompatibility with adipose-derived human mesenchymal stem cells", *International Journal of Nanomedicine*, Vol.2, No.2, pp 253-263.
- Mukherjee, T. and Kao, N. (2011), "PLA based biopolymer reinforced with natural fibre: A review", *Journal of Polymers and the Environment*, Vol.19, No.3, pp.714-725.
- Perego, G. and Cella, G.D. (2010), *Mechanical Properties*. *Polylactic Acid*, John Wiley & Sons, p.141-153.
- Petersen, K., Nielsen, P.V., Bertelsen, G., Lawther, M., Olsen, M.B., Nilsson, N.H., and Mortensen, G. (1999), "Potential of biobased materials for food packaging", *Trends in Food Science and Technology*, Vol.10, pp.52-68.
- Petinakis, E., Yu, L., Edward, G., Dean, K., Liu, H. and Scully, A. (2009), "Effect of matrix-particle interfacial adhesion on the mechanical properties of polylactic acid/wood-flour microcomposites", *Journal of Polymers and the Environment*, Vol.17, No.2, pp.83-94.
- Pertinakis, E., Yu, L., Simon, G. and Dean, K. (2013), "Natural fibre bio-composites incorporating poly (lactic acid)", Accessed August 5th, 2014, from http://dx.doi.org/10.5772/52253.
- Pie, A., Qi, Z., and Berglund, L.A. (2005), "Functionalized cellulose nano-crystals as bio-based nucleation agents in PLLA-crystallization and mechanical property effects", *Composites Science and Technology*, Vol.70, pp.815-821.
- Salmah, H., Marliza, M. and Teh, P.L. (2013), "Treated coconut shell reinforced unsaturated polyester composites", *International Journal of Engineering and Technology (IJET IJENS)*, Vol.13, No.2, pp 94-103.
- Seong, O.H., Karevan, M., Sim, I.N., Bhuiyan, M. and Jang, Y.H. (2012), "Understanding the reinforcing mechanisms in kenaf fiber/PLA and kenaf fiber/PP composites: A comparative study", *International Journal of Polymer Science*, Article ID 679252, pp 1-8.
- Skjærseth, J.B. and Skodvin, T. (2001), "Climate change and the oil industry: Common problems, different strategies", *Global Environmental Politics*, Vol.1, No.4, pp.43-64.
- Sturcova, A., Davies, G.R., and Eichhorn, S.J. (2005), "Elastic modulus and stress-transfer properties of tunicate cellulose whiskers", *Bio Macromolecules*, Vol.6, No.2, pp.1055-1061.

- Todo, M. and Takayama, T. (2011), "Fracture mechanisms of biodegradable PLA and PLA/PCL blends", in: Pignatello, R. (ed), *Biomaterials Physics and Chemistry*, Publisher InTech (ISBN 978-953-307-418-4), November, 490 pages
- Xiang, C.H., Joo, Y.L., and Frey, M.W. (2009), "Nano-composite fibres electro-spun from polylactic acid/cellulose nano-crystals", *Journal of Bio-based Materials and Bio-energy*, Vol.3, No.2, pp 147-155.
- Zeeshan, S., Shariq, N., Zohaib, K., Vivek, V., Haroon, R. and Michael, G. (2015), "Bio-degradable materials for bone repair and tissue engineering applications", *Materials*, Vol.8, pp.5744-5794
- Zeng, J., Xu, X. and Chen, X, (2003), "Biodegradable electro-spun fibres for drug delivery", *Journal of Controlled Release*, Vol.92, pp.227–231.
- Zhou, C. and Wu, Q. (2012), "Recent developments in application of cellulose nano-crystals for advanced polymer-based nano-composites by novel fabrication strategies", Accessed September 2015, from http://dx.doi.org/10.5772/46512.

#### **Authors' Biographical Notes:**

Samson Oluropo Adeosun is an Associate Professor/Reader in the Department of Metallurgical and Materials Engineering, University of Lagos, Nigeria. His works are in the area of materials development, processing and characterization. He currently works on biodegradable composites for orthopedic applications and composites for high temperature applications.

Abraham Kehinde Aworinde is a lecturer in the Department of Mechanical Engineering, Covenant University, Ota, Ogun State, Nigeria. His research interest is in Materials behaviour under loading. He is currently working on modeling and simulation of Fracture Behaviour of biodegradable Polymer - Composite Fiber for orthopedic applications.

Ihuoma Vivian Diwe is a graduate student in the Department of Metallurgical and Materials Engineering, University of Lagos, Nigeria. Her area of research is in Polymer composites and Environmental Management.

Samuel Adebayo Olaleye is a Senior Technologist in the Department of Mechanical Engineering, University of Lagos, Nigeria. He is in charge of the Stress Analysis Laboratory in the Department of Mechanical Engineering.