FILLER SURFACE NATURE, BEAD, SOLUTION VISCOSITY AND FIBRE DIAMETER OF ELECTROSPUN PARTICLE-REINFORCED POLYLACTIDE

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Abstract

The effect of viscosity of agro particle reinforced polylactide (PLA) solution on the electrospun fibre diameter and bead size produced is examined. Solutions of agro waste particle reinforced PLA were made at varying filler weight fraction and these electrospun into fibres. A scanning electron microscope was used to examine the morphologies of fibres while the fibre diameters were determined using ImageJ software. Results show that solution viscosity does not affect fibre diameter when agro particle fillers are processed by a combination of mechanical, thermal and chemical treatments prior to been used as reinforcement. At lower concentration of reinforcement, beads generated from treated particles were of smaller diameter. High solution viscosity gave rise to large bead diameters for treated and untreated reinforcements. Thus, the effect of solution viscosity on fibre and bead diameters depends largely on surface nature of the agro filler.

Introduction

Electrospinning has recently become the most used method to produce nanofibers from polymer solutions [1 – 4]. These electrospun fibres are widely used as scaffolds in tissue engineering, drug delivery, wound dressings, filtration, enzyme immobilization and biosensors [5]. Studies in this area include electrically conductive nanofibers [6] nanofibrous membranes for the development of high performance batteries [7], piezoelectric nanofibrous devices [8], nanofibers alignment [9], nanofiber crossbars [10], nanotubes [11], fabrication of tubular products to serve as blood vessel prosthesis [12], nanofiber composites [13], electrospun mats for fine filtration [14] and nanofibres for wound dressing [15]. The need for structural fibres prompt studies on electrospinning method of composites production using nano materials in polymer solutions and creating fibres with diameters in the nano to micro scale [16 – 18]. This led to the formation of reinforced fibres with high porosity due to high surface area to volume ratio which is very advantageous in the production of scaffolds for tissue engineering. These are functionalized material with interconnected pores and large surface area that mimics extra-cellular matrix [19, 20]. To satisfy biomedical needs of biocompatible and biodegradable scaffolds, most research in this area has been focused on the use of electrospun polylactic acid (PLA) for tissue scaffold [20]. However, such studies in the use of electrospun PLA focused on the use of carbon and halloysite nanotubes as reinforcing fillers [20, 21 – 23]. Recent works has shown that natural fillers in PLA results in increased crystallinity of electrospun PLA nanocomposite fibres with improved strength and decreased fibre diameter [24]. These nanofibres have qualities that make

them useful as scaffolds in tissue engineering. In the production of electrospun fibres there are key parameters that determine the needed properties of the electrospun fibres. Thus, properties such as fibre morphology, average fibre diameter, bead formation are directly linked to solution viscosity, surface tension, concentration, molecular weight and machine parameters [23, 26-33]. Therefore, for the development of useful applications, thorough knowledge of the interconnection between electrospinning parameters and the final product properties is required.

Most works focused on solving the problem of machine parameters such as voltage, distance between plate and tip of the needle, vertical and horizontal setups, inclination of collector plates, flow rate and pressure. However, very limited studies have been targeted on creating a linkage between the surface property of reinforcing filler, solution viscosity, bead formation, surface morphology and average fibre diameter. The objective of this research is, to create a synergy between surface property of reinforcing filler, solution viscosity, bead formation, surface morphology and average fibre diameter of agro- fibre reinforced PLA electrospun fibres. Preliminary electrospinning parameters for optimum mechanical properties of the fibres have earlier been determined [34].

Experimental Methodology

Preparation of Agro-Wastes Fibres

Rice husk, coconut husk and groundnut shells were collected, washed, sun dried for two weeks and then cut into small pieces. The cut agro-wastes materials were ground to pass 10 mm screen in a mechanical crusher. They were then divided into two parts. One part was used in untreated form and thus termed 'untreated' throughout the presentation. The other part was subjected to mechanical, thermal and chemical treatment as in Akpan et al. [35].

Electrospinning Solution Preparation

Mixtures of PLA and selected agro-wastes particles (treated and untreated) were dissolved in DCM at a constant composition of 12.50% (w/v). The solutions were left in the sealed bottles at room temperature (310C) for 24 hours in order to dissolve the PLA and the particles.

Process Setup and Electrospinning

The electrospinning process was conducted as in Adeosun et al. [34]. Electrospinning process was repeated by varying the weight fractions of reinforcements in the mixture from 0 – 8 wt. %.

Viscosity of the Composite Fibres

Solution viscosity was analytically determined using the relationship in Mituppatham et al. [36].

$$\mu = (1/0.00137)\ln((d - 88.7)/0.804) \quad (2)$$

Scanning Electron Microscopy (SEM)

Morphological features of the electrospun composite fibres were acquired using a scanning electron microscope (Model: ASPEX 3020) located at the Materials Science and Engineering

Laboratory of Kwara State University, Nigeria. It was operated at 15kV to determine the fibre morphology of the electrospun samples. The electrospun samples were coated with conducting carbon tape. The Digital SEM images of the samples were captured at 100x and 250x magnifications. The average diameters of fibres and beads were determined using ImageJ software.

Results and Discussion

PLA Reinforced Coconut Particles Electrospun Fibres

Table 1 and Figures 1 – 2 show the characteristics of composite fibres with coconut filler particles. Table 1 shows the variation in average fibre diameter for the composite fibres. Composites with treated fillers show higher average fibre diameters compared to that with untreated filler. Similarly, the viscosities of composites fibres with treated fillers are higher than that with untreated filler. This is an indication that the higher the viscosity the higher the fibre diameter. This phenomenon had earlier been observed by Chien and Wang [23] that decrease in solution viscosity of fibres facilitates reduction in fibre diameter. Figure 1a compared to 1b shows that the fibre surfaces of the untreated fillers look smooth than those with treated filler particles. It is also apparent from Table 1 that increase in filler weight fraction promotes increase in fibre viscosity and diameter. The SEM images show that composites with treated filler particles have more beads than that with untreated filler. It is suggested that the treated filler particle forms a good surface adhesion to the matrix leading to increased viscosity and consequently increased fibre diameter and number of beads. It has been stated in an earlier study that using treated fibre fillers led to increase in viscosity of the composite [35]. It is noted that the average fibre diameter and viscosity of composites with 4 wt. % of untreated filler are lower than that of virgin PLA and other composite fibres.

Table 1: Average fibre diameter and solution viscosity of composite fibres (fourteen readings)

	Rice Husk			Groundnut shell		
Weight fraction (wt. %)	4	5	8	4	5	8
Fibre diameter (untreated filler) µm	9.85±4.1	10.08±5.2	10.89±4.2	9.26±3.4	10.96±4.8	12.46±5.9
Viscosity (untreated filler) cP	6864±351	6881±509	6938±388	6818±275	6943±471	7037±490
Fibre diameter (Treated filler) µm	15.65±5.86	13.89±4.0	12.28±4.8	12.61±5.9	11.59±5.8	10.06±4.1
Viscosity (Treated filler) cP	7204±318	7117±219	7026±346	7046±584	6984±491	6880±468
	Coconut husk					
Weight fraction (wt. %)	Control	4	5	8		
Fibre diameter (untreated filler) µm	10.11±1.34	9.46±2.3	10.41±3.8	11.23±3.9		
Viscosity (untreated filler) cP	6883±317	6834±196	6905±317	6961±304		
Fibre diameter (untreated filler) µm		11.52±3.5	13.01±5.7	11.25±4.8		
Viscosity (untreated filler) cP		6979±224	7069±336	6962±367		

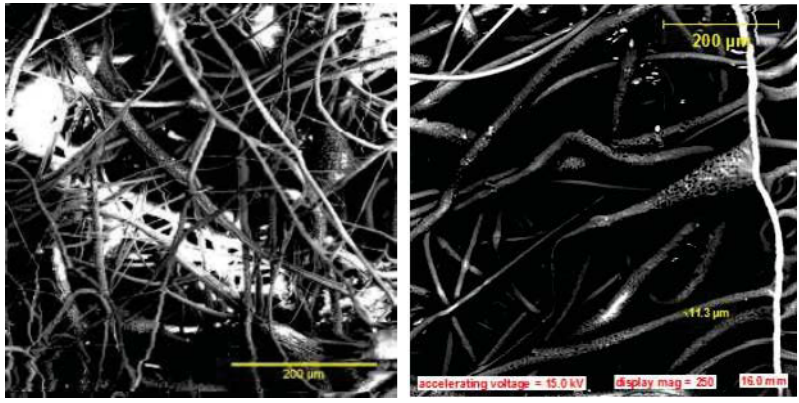

Figure 1. SEM of electrospun composite with 4 wt. % (a) untreated (b) treated coconut fibres

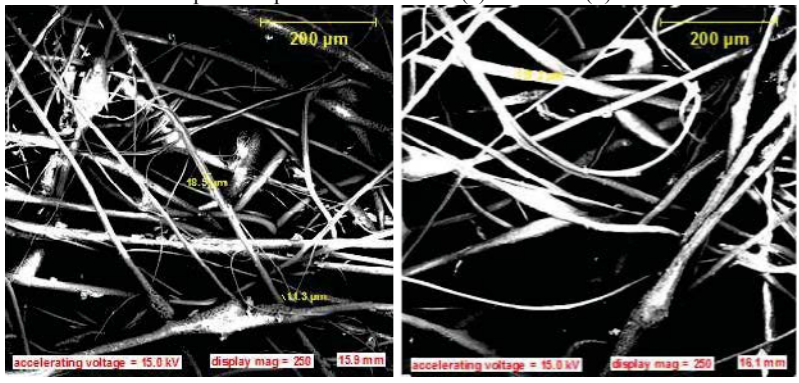

Figure 2. SEM of electrospun composite with 8 wt. % (a) untreated (b) treated coconut fibres

PLA Reinforced Groundnut Particles Electrospun Fibres

The average fibre diameter of composite fibres with groundnut shell filler is shown in Table 1. Here increase in fibre diameter occurred with increase in weight fraction of the filler with the lowest (9.26 µm) recorded at 4 wt. % untreated filler. Average fibre diameter for treated filler filled PLA decrease with increasing weight fraction of fillers. This trend is repeated for fibre viscosity as displayed in Table 1, showing that increase in viscosity of the solution leads to increase in the fibre diameter of electrospun fibres. Contrary to that obtained in composites with coconut shell filler particles, the fibres with treated groundnut shell particles show smooth surface with similar fibre diameters compared to the untreated filler (see Figures 3 and 4). However, higher fibre diameter and viscosity are shown except at 8 wt. % filler where fibre diameter and viscosity are better in untreated filler PLA fibre. In Figures 3 and 4 there are more beads formed with untreated filler-PLA than with treated filler composites. Increase in weight fraction of filler is also found to lead to growth in bead and fibre diameter. Pillay et al. [32] had shown that increase in viscosity leads to increase in fibre diameter and it is also known that

beads are formed as a result of agglomeration of fibres [23] as 1 wt. % of carbon nanotubes in PLA yielded uniform fibre size with fewer beads. However, addition of up to 5 wt. % increased the number of beads. Studies have shown that beads are undesirable in electrospun fibres as these act as defects resulting to inferior mechanical properties of composite fibres [34, 37]. In this study it is noted that untreated filler catalyzes the formation of beads. Thus, bead formation is dependent on surface quality of reinforcement and solution viscosity.

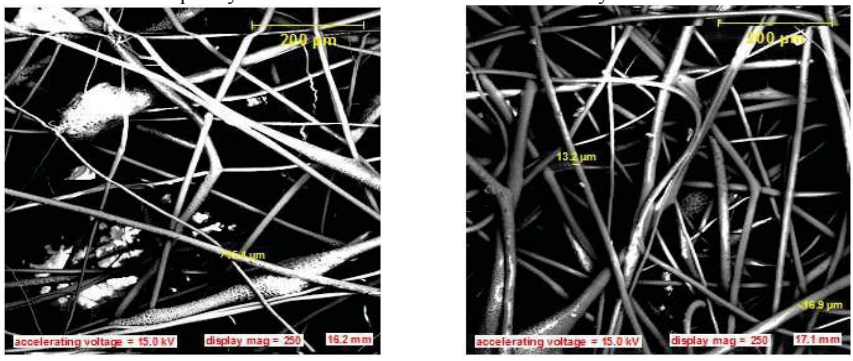

Figure 3. SEM of composite fibres with 4 wt. % (a) untreated (b) treated groundnut shell fibres

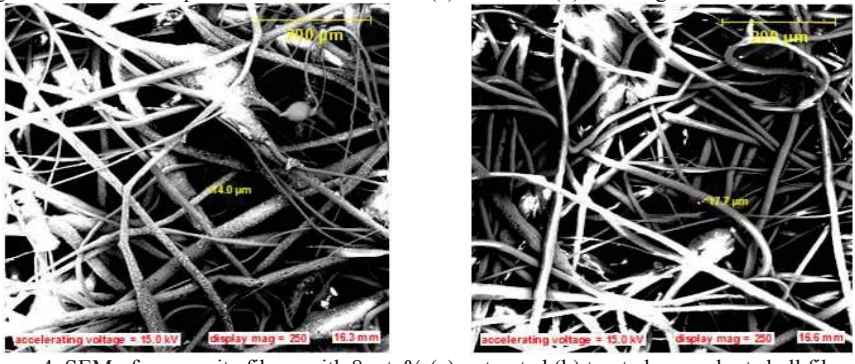

Figure 4. SEM of composite fibres with 8 wt. % (a) untreated (b) treated groundnut shell fibres

PLA Reinforced Rice Husk Particles Electrospun Fibres

Fibre diameter, viscosity and SEM images of rice husk filled electrospun PLA composite fibres are shown in Table 1 and Figures 5 – 6. Table 1 shows increase in fibre diameter with increase in weight fraction of the filler particles. All composites with treated filler show higher average fibre diameter compared to that with untreated filler. However, it is observed that the composite with 4 wt. % untreated filler has the smallest fibre diameter. This indicates that lower composition of the filler results into lower fibre diameter. This is in contrast to the response of composites with treated filler showing decrease in fibre diameter as the weight fraction increases. Viscosity of the composite fibres displays similar trend (see Table 1). All composites with treated filler have higher viscosities than those with untreated filler. Increase in weight fraction of untreated filler in

PLA composite also leads to increase in viscosity except at 4 wt. % filler. In composites with treated filler the viscosities decrease with increase in fibre weight fraction. The SEM images show that composites with treated filler have larger beads compared to those with untreated filler. The beads are observed to increase as filler weight fraction increases. Pores are found mostly on the surface of composites with treated filler (see Figure 5b). It is generally observed that increase in viscosity leads to increase in fibre diameter and bead size. In an earlier study [38] it was observed that treatment of filler before use promoted increase in melt viscosity of compounded PLA – rice husk composites. This was attributed to good surface adhesion of the treated filler resulting in the development of cohesive, plastic and sticky dough during compounding.

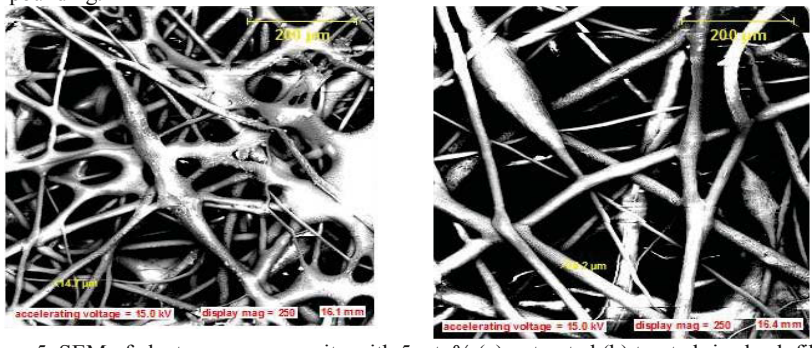

Figure 5. SEM of electrospun composite with 5 wt. % (a) untreated (b) treated rice husk fibres

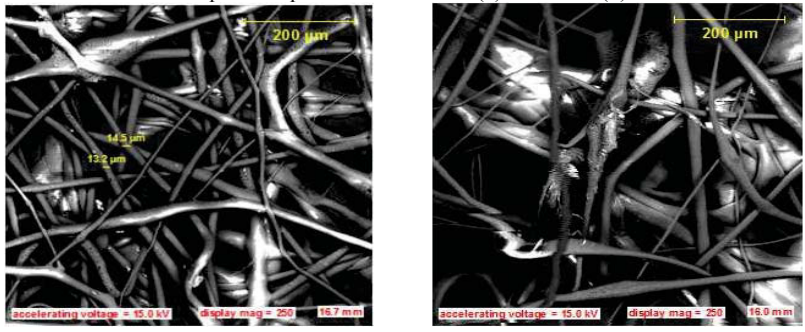

Figure 6. SEM of electrospun fibres with 8 wt. % (a) untreated (b) treated rice husk fibres

Conclusion

From this investigation, it is observed that electrospun fibre properties such as average fibre diameter, fibre morphology and bead formation are related to solution viscosity and surface quality of the reinforcing filler. Poor surface quality of reinforcing filler is found to cause beads formation, which is detrimental to mechanical properties of the composite fibres. Average solution viscosity with improved filler surface quality is desired for small fibre diameter and good fibre morphology. Agro-fillers can be used to develop electrospun fibres for tissue engineering with the correct combination of surface quality and solution viscosity.

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