

Effect of Pineapple Leaf Fibers (PALF) concentration on nanofibers formation by electrospinning

S N Surip¹, F M Abdul Aziz^{1a)}, N N Bonnia¹ and K A Sekak¹

¹Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia.

Email: fatimahmuyassarah@gmail.com

Abstract. Electrospinning method has been studied widely in producing nanofibers due to its straightforward and versatile method. In this study, Pineapple Leaf Fibers (PALF) solution were electrospinning to obtain mat of PALF electrospun. PALF were diluted in Trifluoroacetic Acid (TFA) into five different concentrations to study the effect of concentration to the nanofibers formation. Raw sample of PALF (PALF_{raw}), PALF after dewax (PALF_{dewax}) and PALF after dilute with TFA (PALF_{TFA}) were analyzed and compared using FTIR to study the structural change occur. TFA solvent has removed and recreated some of the functional group in PALF thus disrupt strong hydrogen bonds that hold hemicellulose, cellulose and lignin together. All the PALF sample has been proceed to electrospinning process. Low concentration of solution cause the solution jet to break up even before reach the collector however high concentration of solution made the solvent volatile faster and the solution dried easily. Therefore, PALF with optimum concentration of 0.02 gml⁻¹ had favors the formation of nanofibers and succeed in forming membrane at the collector.

1. Introduction

Nanofiber materials have develops rapidly due to its large surface area-to-volume properties that enhance its compatibility with other materials [1]. Through the years, fibers have become highly demand in market and often use as reinforcing fibers for composite [2]. As the synthetic fibers has critical drawback such as limited supply, toxicity to surrounding and non-biodegradable, comply with the world policy to conduct a green friendly environment, researchers start to put their interest on natural fibers [3]. Natural fiber come from two sources which is plant fibers (lignocellulosic) and animal fibers [4]. This study focus on the potential of lignocellulosic fibers as replacement for current petroleum-based fibers.

High specific properties that come with lignocellulosic fibers thus contributed to excellence mechanical properties comparable with synthetic fibers. Saheb et al (1999) in his review papers reported that when specific modulus were considered, natural fibers shows comparable values or even higher than glass fibers [5]. In fact, lignocellulosic fibers consist high cellulose content therefore carried high tensile strength that help improves composite properties during interaction with the polymers [6]. Among this fibers, pineapple leaf were one of the potentially unexplored fibers that could offer more to the industry.

Pineapple plant abundantly available especially in tropical country thus provides unlimited supply. Pineapple plant is referred as secondary plant which by-product wastes were extracts to obtain cellulose [7]. Khengketkit et al (2014) compared properties of several parts in pineapple plant and



PALF part shows the best values in mechanical properties [3]. PALF contain high cellulose content that help the leaf to maintain its turgidity thus give great properties [7]. Besides, Neto et al (2015) has study 12 varieties of pineapple leaf fibers in term of its mechanical and thermal properties. His paper stated that increase in cellulose percentage does increase the tensile strength and specific modulus properties [8]. A previous study has been done by Uma Devi et al (2010) on the PALF polyester composite that agreed with this statement. The tensile strength and young modulus increase with cellulose content however the flexural strength shows opposite [9]. However, even there are papers already been published on PALF, there were only few proceed it to the PALF nanofibers size.

Electrospinning method is a convenient with a multi-purpose method that aims on producing fibers with diameter range from several micrometers to tens of nanometers [10]. Through this method, nanofibers size of PALF could be produced. Recently, Guihe and the co workers succeed in produced mats of electrospun PET/PVA with a diameter range 200 μm to 700 μm with higher mechanical properties when compared to pure PET [11]. Not only enhance the mechanical properties, natural fibers also manage to compete with current synthetic fibers. Bodros et al (2006) in his paper reported that PLLA/flux composite show high tensile strength which is almost close to the polyester/glass composite (12).

Electrospinning lignocellulosic biomass using ionic liquid (solvent) had successfully produced nanoscale ultrathin fibers through studied by Ahn et al (2007) using DMF as solvent and the latest studies was from Santos et al (2015) and it is conducted using TFA. Selection of a suitable solvent system for the polymers plays a big role to ensure electrospinning success [14]. Beatriz et al studied on the most effective solvent for PET and found that high percentage of TFA favour the formation of continues nanofibers of PET [10].

2. Experimental procedures

2.1. Materials

Pineapple Leaf fibers were received from local Malaysian company in fibers form. Polyethylene Terephthalate were obtained from Aldrich and received in granular form. The chemicals which are trifluoroacetic acid, cyclohexane and ethanol all were supplied by Aldrich Merck.

2.2. Soxhlet method (Dewaxing)

PALF were first dewax using soxhlet instrument to remove wax and terpenes thus increase its surface interaction with others chemicals. 10 g of PALF were put into the thimble and rinse with 200ml of ethanol:cyclohexane 1:1 ratio for 6 hours. Then, the remaining sample were rinse using distilled water and put in the oven with temperature 40 $^{\circ}\text{C}$ for 12 hours until the sample were completely dried.

2.3. Dissolution of PALF

Dried PALF were weight accordingly to table 1. Four different concentrations were made in order to find out the best concentration for the electrospinning process. All samples were dilute in 3mL of Trifluoroacetic acid (TFA) and stirred for 12 hours until homogenous solution were obtained.

Table 1: Concentration of PALF

NO	CONC. (gml^{-1})	FIBERS (WEIGHT) (g)	TFA (VOLUME) (mL)
1	0.01	0.03	3
2	0.02	0.06	3
3	0.03	0.09	3
4	0.04	0.12	3

2.4. Characterization (FTIR)

FTIR spectroscopy was carried out in order to study the interaction that occurred in TFA and PALF. This kind of interaction can be proven through frequency shifts, changes in band intensity, and shape of the FTIR spectra. The spectra were recorded by FTIR (Thermo Fisher Scientific Nicolet iS 10) equipped with Attenuated Total Reflectance (ATR) in the transmittance mode over a frequency range $500\text{-}4000\text{ cm}^{-1}$ with 2 cm^{-1} resolution.

2.5. Electrospinning

Electrospinning set up were mainly consists of power supply, syringe pump, syringe, needle and collector (figure 1).

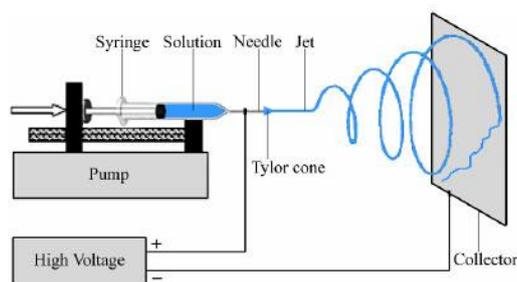


Figure 1: Electrospinning set-up

3. Results and Discussion

3.1. Solvent effect on functional group of PALF

Figure 2 shows FTIR spectra after zoom in at $(500\text{-}2000)\text{ cm}^{-1}$ region. Peak at $1630\text{-}1640\text{ cm}^{-1}$ suggested from lignin aromatic structure [14]. It can be seen in sample (a) and (b) spectrum however, after addition of TFA the peak were completely absent. At sample (a) and (b) region, a peak approximately at $1730\text{-}1740\text{ cm}^{-1}$ were observed attribute to the C=O of the acetyl group present in hemicellulose however dissolve at (c) region. Thus, it is suggested that TFA addition favors the elimination of lignin and hemicellulose. At peak $1020\text{-}1050\text{ cm}^{-1}$, a C=O stretching vibration indicated on the cellulose backbone were present in all sample thus suggested the remain of cellulose in the sample. Although a small peak can be observed at peak 1774 cm^{-1} in sample (c) that indicated the present of trifluoroacetyl group it is well known that constant exposure to air could lead to the complete hydrolysis of trifluoroacetic group [18]. Disrupt of lignin usually needed to break the high covalent bond that hold the hemicellulose, cellulose and lignin together. Thus, TFA addition favors the elimination of lignin and hemicellulose. The present of C=O in TFA structure make it susceptible for esterification reaction take place as shown in fig 3. Recently, a study on electrospinning from TFA of sisal pulp were conducted by Santos et al (2015) and the FTIR result also showed the possibility of the reactions occur (figure 3).

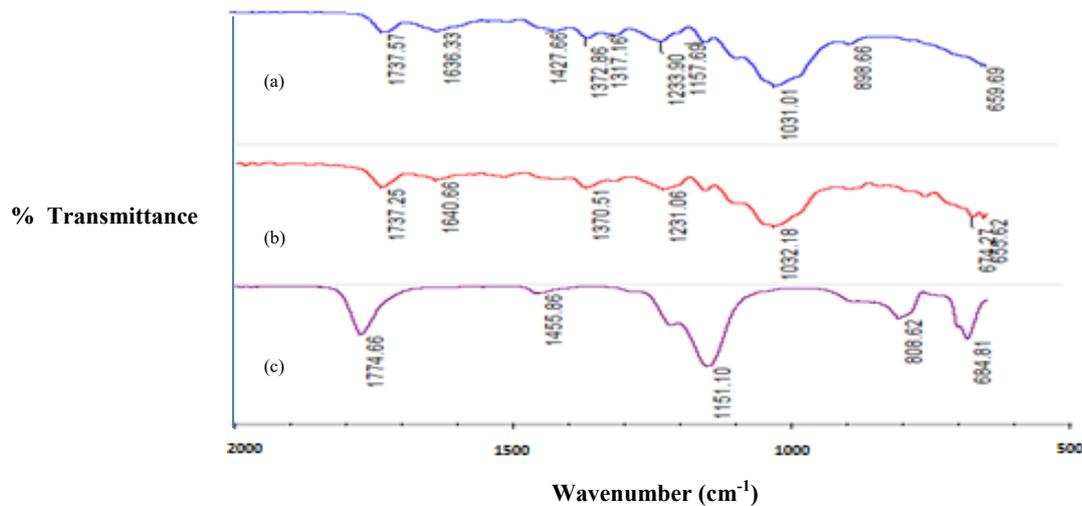


Figure 2: FTIR result for (a) PALF_{raw}, (b) PALF_{dewax} and (c) PALF_{TFA}
Zoom in for (500-2000) cm⁻¹ region

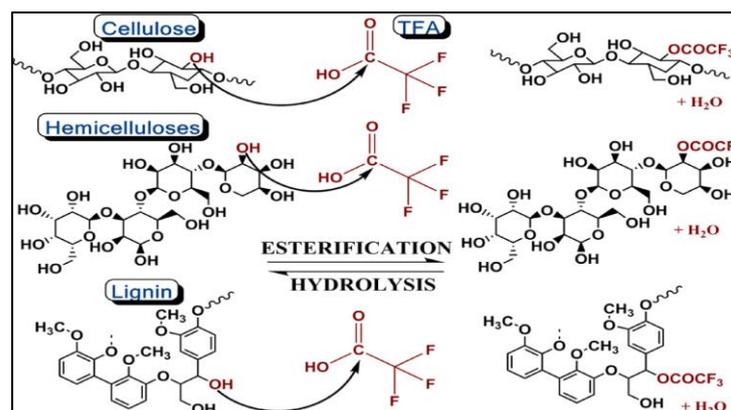


Figure 3 : Main components of a lignocellulosic fiber and their reactive sites susceptible to esterification by TFA (*R.P.O Santos et al., 2015*)

3.2. Concentration effect on nanofibers formation

Table 2 shows the result of PALF nanofibers formation. Nanofibers formation via electrospinning were highly related with the concentration, viscosity and surface tension of the solution. As the concentration increase, the viscosity also increase caused improvement to the polymer entanglement [15]. During 0.01gml⁻¹ solution jet, only electrospayed were formed and no membrane produced at the collector. Low viscosity attributed to the low viscoelastic force thus made the fibers jet easily break up even before reached the collector [16]. Therefore, increasing the concentration helps to prevent the break up due to the improvement in the chain entanglement as can be seen at concentration 0.02gml⁻¹. Membranes were successfully formed at the collector. However, increasing the concentration higher has cause the solution dry faster and did not form any fiber jet as can be seen during 0.04gml⁻¹ of solution. TFA has a high volatile values compare to other solvent [17]. Costa et al (2010) suggested high volatile of solvent should set up with low concentration to prevent fast volatilization [10].

Table 2: PALF nanofibers formation by electrospinning

Concentration (gmL ⁻¹)	Condition	
	Jet formation	Membrane formation
0.01	-Solution were electro sprayed	-No membrane formed at collector
0.02	-Solution successfully electrospinning	-Membrane were formed at the collector
0.03	-Solution start dry at 4 th second -No solution were eject afterward	-No membrane formed at collector
0.04	-Solution hardly eject and dried at the tip of metallic needle and block the solution	-No membrane formed at collector

4. Conclusion

As the conclusion, TFA used as solvent helps PALF to achieve homogenous solution. FTIR result shows addition of TFA help to disrupt the hydrogen bonding thus eliminate lignin while keep remain the cellulose content. PALF concentration of 0.02 gmL⁻¹ was the optimum concentration need to electrospin PALF. Low concentrations of PALF produce an electro sprayed rather than electrospinning fibers while high concentration caused solution to dry faster.

Acknowledgement

The authors would like to acknowledge University Technology Mara for providing grant to carry out this research under Nanocomposite Material & Industrial Application Research Group (600-IRMI/DANA 5/3/REI (0001/2016)).

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