

# The effect of Pineapple Leaf Fiber (PALF) incorporation into Polyethylene Terephthalate (PET) on FTIR, morphology and wetting properties

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**Abstract.** Pineapple Leaf Fibers (PALF) which is rich in cellulose, relatively inexpensive and abundantly available has the potential for polymer reinforcement. In this study, Polyethylene Terephthalate (PET) was added with PALF and electro-spun. The resulting mats were compared with PET neat electrospun. The samples later were examined by Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR) and contact angle (CA). Briefly, SEM results indicated that the present of fibers led to a tendency of lower average fiber diameter compared to the PET neat. Two distinct fiber networks with intersecting fibers were observed in PALF/PET. One networks probably corresponds to PET and the others to PALF. FTIR analysis shows the intensity peak represent carbonyl at  $\sim 3400\text{cm}^{-1}$  and ester at  $\sim 1100\text{cm}^{-1}$  decreased. It is suggested interaction occurred between lone pair of oxygen in the group with hydrogen group in PALF. New peak were observed at  $3400\text{cm}^{-1}$  in PALF/PET that indicated present of hydrogen bonding as well as its hydrophilic tendency. The contact angle of PET signify high average value  $156^\circ$  that comes with hydrophobic properties compared to PALF/PET with average value  $16^\circ$  with more hydrophilic properties.

## 1. Introduction

Nanofiber materials have many potential applications due to its large surface area-to-volume, small pore size and high porosity properties [1]. In the last few decades, natural fibers especially lignocellulosic fibers have attract researcher's attention due to its great mechanical properties as well as the positive contribution to the environment. Through the years, natural fibers have become highly demand in market and often use as reinforcing fibers for composite [2]. This study focuses on the potential of lignocellulosic fibers as replacement for current petroleum-based fibers.

Among these fibers, pineapple leaf was 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. A few studies were conduct to study mechanical properties of PALF and it shows high tensile strength and young modulus value [3-5]. This is due to high cellulose content that help the leaf to maintain its turgidity thus give great properties to PALF [6]. However, even there were papers already been published on PALF, there were only few proceed it to the PALF nanofibers size.

Various ways have been developed to produce high properties of nanofibers such as drawing, template synthesis, phase separation, self-assembly and electrospinning [7-11]. Electrospinning which is straightforward and versatile method with low cost of production has made it used widely to produce nanofibers with lower diameter [11]. Recently, a few studies has successfully produced an



electrospun mats with high mechanical properties after addition of natural fibers [12-13]. Selection of a suitable solvent system for the polymers plays a big role to ensure electrospinning success [14]. Studies has been conducted on TFA and found it could favors the formation of continues nanofibers [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 of PALF)

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 °C for 12 hours until the sample were completely dried.

### 2.3. Dissolution of PALF/PET

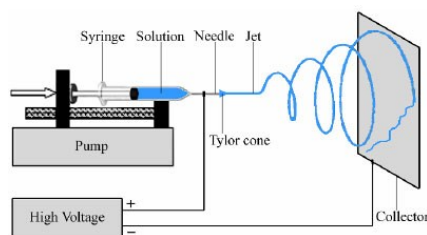
Dried PALF and PET were weight accordingly to table 1. The samples were dilute in the Trifluoroacetic acid (TFA) and stirred for 12 hours until homogenous solution were obtained

**Table 1:** Concentration of PALF

Sample	Conc PET (g mL <sup>-1</sup> )	PET (g)	TFA (mL)	Conc PALF (g mL <sup>-1</sup> )	PALF (g)	TFA (mL)	Total TFA (mL)
PET <sub>neat</sub>	0.2	1	5.0	-	-	-	5.0
PET/PALF	0.2	0.5	2.5	0.02	0.06	3	5.5

### 2.4. Electrospinning

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



**Figure 1.** Electrospinning set-up

### 2.5. Characterization

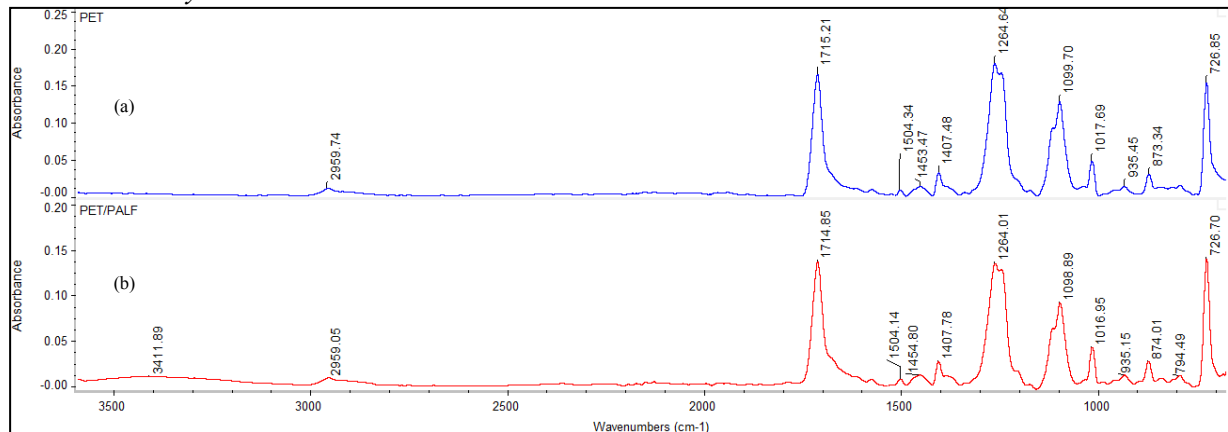
**2.5.1. FTIR.** FTIR spectroscopy was carried out in order to study the interaction that occurred in TFA and PALF. This kind of interaction can be proven through frequency shifts, changes in band intensity, and shape of the FTIR spectra. The spectra were recorded by FTIR (Thermo Fisher Scientific Nicolet iS 10) equipped with Attenuated Total Reflectance (ATR) in the transmittance mode over a frequency range 500-4000 cm<sup>-1</sup> with 4 cm<sup>-1</sup> resolution.

2.5.2. *FESEM*. The surface morphology and size distribution were determined by FESEM.

2.5.3. *Contact Angle (CA)*. The wettability of PET and PET/PALF electrospun was analyzed through a digital camera positioned on a static contact angle analyzer then analyzed with Image J 1.34S.

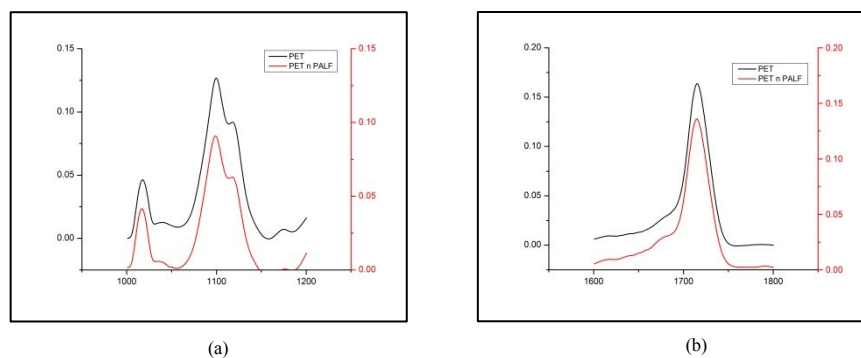
### 3. Results and Discussion

#### 3.1. FTIR analysis



**Figure 2.** FTIR result for (a) PALF<sub>neat</sub>, (b)PALF/TFA

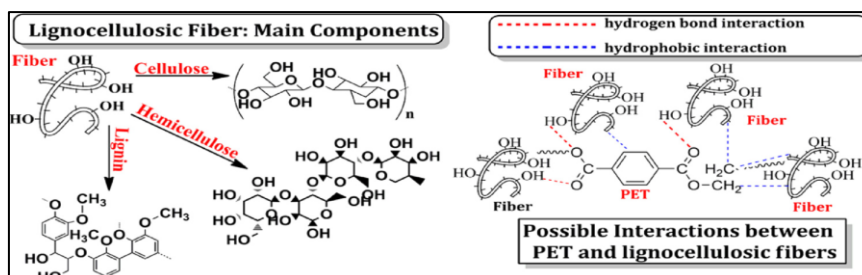
Figure 2 showed FTIR spectra of (a)PET and (b)PET with PALF addition (PET/PALF) (b) at (600–3500)  $\text{cm}^{-1}$  region. For both PET and PET/PALF sample, peaks approximately at 2900  $\text{cm}^{-1}$  were observed. This is due to the vibration of CH<sub>2</sub>, CH<sub>3</sub> and CH bond in the PET structure. At peak  $\sim 1715 \text{ cm}^{-1}$ , stretching of C=O bond were appeared indicated the conjugated ester group in the chemical structure of PET as well as acetyl group that present in the hemicellulose. C=C stretching that attribute to vibration of benzene and aromatic lignin of the skeletal vibration were observed in both sample at peak  $\sim 1050 \text{ cm}^{-1}$  wavelength. At peak  $\sim 725 \text{ cm}^{-1}$ , peak signifies the present of C-H bond from glucose ring of the cellulose were observed. However, most of the peak shows a decreased intensity after PALF addition thus suggested there were interactions occurred between PET and PALF.



**Figure 3.** Intensity of (a)C=O bond spectra and (b)C-C-O spectra for PET and PET/PALF

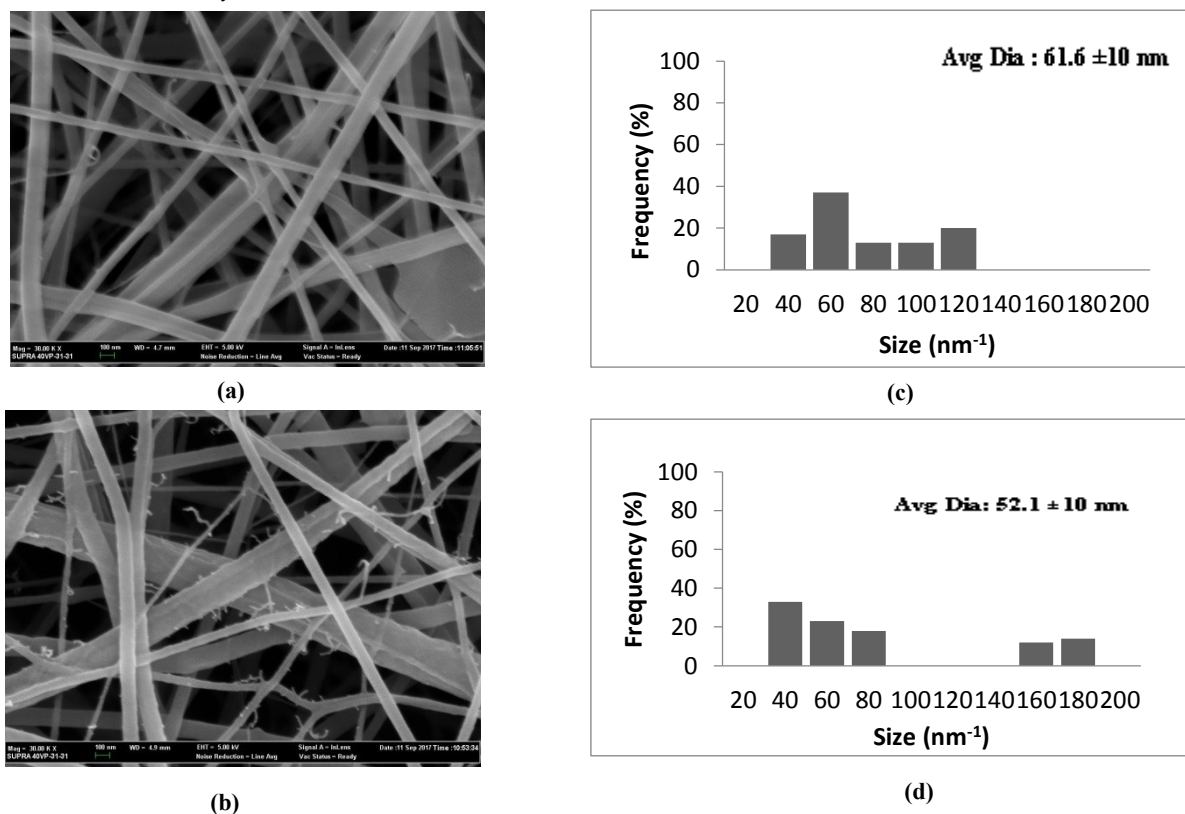
Based on few paper written on lignocellulosic fibers [14,15] a peak usually presented at  $\sim 1595 \text{ cm}^{-1}$  represent the lignin however were absent at PET/PALF spectrum. This could indicate the reducing amount of lignin in the sample. It is suggested that this is due to the addition of TFA that plays role on disrupted the covalent bond that hold the cellulose (lignin) as well eliminates it. Peak at  $\sim 1715 \text{ cm}^{-1}$  and  $\sim 1099 \text{ cm}^{-1}$  shows a decreasing intensity as shown in figure 3. This indicated there is interaction

between oxygen in the C=O and C-C-O group of PET with hydrogen bond of PALF. It is supported by the appearance of broad peak at  $3400\text{ cm}^{-1}$  representing the hydroxyl group resulted from the interaction of PET/PALF contributed to the hydrophilic tendency of the fiber. Figure 4 shows the possible reactions occurred during PET and PALF interaction.



**Figure 4.** Main components of a lignocellulosic fiber and their reactive sites susceptible for interaction (R.P.O Santos et al., 2015)

### 3.2. FESEM analysis



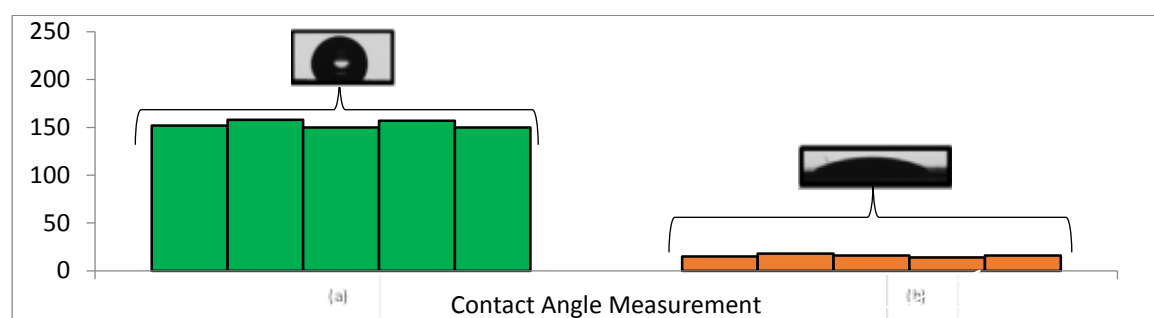
**Figure 5.** FESEM result for (a) PET (b) PET/PALF with magnification of X15K and frequency percentage size distribution for (c) PET (d) PET/PALF

FESEM images of electrospun nanofibrous structures of (a) PET and (b) PET/PALF shown in Figure 5 revealed that nano-scale of spider web structures were successfully created via electrospinning method. The fibers were found randomly orientated with interconnected pores in between to form a 3D scaffold. PET sample shows diameter range between 40-120 nm with average  $61.6 \pm 10\text{ nm}$  while PET/PALF shows lower fiber average diameter which is  $52.1 \pm 10\text{ nm}$ , with

uniform size while PET/PALF shows diameter one with thicker fibers range between 160-180 nm while others shows thinner fibers range between 40-80 nm with average  $52.1 \pm 10$  nm.

FESEM results indicated that the present of fibers led to a tendency of lower average fiber diameter however has random diameter distribution. Two different fiber networks with intersecting fibers were observed in PALF/PET. It is suggested that one networks with bigger diameter probably corresponds to PET and the others with smaller diameter correspond to PALF. Diameter with thicker fibers range between 160-180 nm while the thinner fibers range between 40-80 nm. Thicker diameter might due to the increasing solution concentration after adding PALF. As shows in fig 5 (b), a thin fibers coexited among the electrospun fibers were present. It is suggested that a reaction has occurred during addition of PALF into PET.

### 3.3. Contact Angle (CA) analysis



**Figure 6:** Contact Angle result for (a) PALF (b) PALF/TFA

Figure 6 shows contact angle results obtained from PET and PET/PALF electrospun mats. The contact angle of PET signify high average value  $156^\circ$  that comes with hydrophobic properties however decrease drastically after added with PALF with average value  $16^\circ$  thus made it more hydrophilic properties. This change indicates the presence of polar chemical groups onto the PET surface, increasing the surface energy of polymer and thereby decreasing in surface contact angle. Thus, it suggested PALF were successfully electro-spun with PET polymer and PALF favored the changed of PET hydrophobic properties.

## 4. Conclusion

As the conclusion, PALF were successfully electro-spun together with PET and produced lower average finer diameter compared to PET electro-spun alone. Besides, contact angle result shows the ability to controls the hydrophilic/hydrophobic materials properties by tuning the PET/PALF ratio thus made it useful for many applications.

## 5. Acknowledgement

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## 6. References

- [1] Huang Z M, Zhang Y Z, Kotaki M and Ramakrishna S 2003 *Composite Science and Technology* **63** pp 2223-2253
- [2] Kaewpirom S and Worrarat C 2014 *Fibers and Polymers* **15** pp 1469-1477
- [3] Khengketkit N and Amornsakchai T 2014 *Materials and Design* **55** pp 292-299
- [4] Neto A R S, Araujo M A M, Souza F V D, Mattoso L H C and Marconcini J M 2013 *Industrial Crops and Products* **43** 529-537

- [5] Dewi L U, Bhagawan S and Thomas S 1997 *Polymer Composite* (Wiley Inter-Science)
- [6] Asim M, Abdan K, Jawaid M, Nasir M, Dashtizadeh Z, Ishak M R, Hoque M E 2015 *Int. Journal of Polymer Science* ID 950567
- [7] Bajakova J, Chaloupek J, Lukáš D and Lacarin M 2011 *Proceedings of the 3rd International Conference on Nanotechnology-Smart Materials (NANOCON'11)*.
- [8] Wang Y, Zheng M, Lu H, Feng S, Ji G and Cao J 2010 *Nanoscale research letters* p 5 913.
- [9] Huang W, Wang M J, Liu C L, You J, Chen S C, Wang Y Z, and Liu Y 2014 *Journal of Materials Chemistry A* **22** pp 8416-8424
- [10] Suvannasara P, Praphairaksit N and Muangsin N 2014 *RSC Advances* **102** pp 58664-58673
- [11] Veleirinho B, Rei M F and Lopes J A 2007 *Journal of Polymer Science* (Wiley Inter-Science)
- [12] Li G, Zhao Y, Lv M, Shi Y and Cao D 2013 *Colloids and surfaces A :Physicochem. Eng. Aspects* **436** pp 417-424
- [13] Ahn Y, Lee S H, Kim H J, Yang Y H, Hong J H and Kim Y H 2012 *Carbohydrate Polymers* **88** pp 395-398
- [14] Santos R P O, Rodrigues B V M, Ramires E C, Ruvolo A C and Frollini E 2015 *Industrial Crops and Products* **72** pp 69-76
- [15] Chirayil CJ, Joy J, Mathew L, Mozetic M, Koetz J, Thomas S 2014 *Industrial Crops and Products* **59** pp 27-34