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Research paper

Effect of Pre-Treatment on the Morphology and Chemical Properties of Polyethylene Terephthalate (PET)/Pineapple Leaf Fiber (PALF) Electrospun Mat

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Abstract

In the past decades, conventional petroleum-based plastics have resulted in environmental and sustainability issues. Thus, there has been significant interest in the utilization of natural materials for nanofibers product such as for filtration media. However, poor compatibility exists between polymers and natural fibers due to natural fibers hydrophilic properties leading to poor nanofibers formation. In this study, Pineapple Leaf Fiber (PALF) remarkable properties were explored. PALF undergo alkaline treatment and bleaching treatment in order to improve its compatibility. Thermal, morphology and structural properties of PALF raw (PR), PALF after alkali treatments (PA) and PALF after alkali + bleaching treatment (PB) were studied. Further, all the samples were diluted using Trifluoroacetic Acid (TFA) as the solvent and Polyethylene Terephthalate (PET) as the polymer carrier and proceed to electrospinning to produce a nanofibers electrospun mats. The electrospun mats were then characterized in terms of its chemical properties using Fourier transform infrared spectroscopy (FTIR) as well as the morphology which using Fields Emission Scanning Electron Microscopy (FESEM). FTIR result shows the electrospun PET does not produce any peak at ~3400cm-1 due to its hydrophobic properties. Nevertheless, with addition of PALF, the peak was significantly increased. FESEM results indicated that the present of fibers led to a tendency of lower average fiber diameter compared to the neat PET. Unconnected and thin fibers were coexited from single fiber of PALF raw electrospun indicated that new fibers were ejected however the bond were collapsed during ejection thus did not produce a complete single fiber. Despite that, more uniform fibers of electrospun mat were produced by pre-treatment of PALF.

Keywords: *Pineapple Leaf Fiber(PALF), Pre-treatments, Polyethylene Terephthalate (PET), Electrospinning, Nanofibers.*

1. Introduction

Recently, researchers start to develop interest on green and sustainable materials to replace synthetic fibers due to the critical drawbacks of synthetic fibers [1]. Natural fibers were claimed to offer environmental advantages such as renewable, biodegradable, green friendly and good mechanical properties [2]. Natural fiber such as sisal fibers, bamboo fibers and pineapple leaf fibers that possesses strong mechanical properties had been used long ago for housework purposes such as for ropes and rattan basket. As time changes, natural fibers have become highly demands in industrial market with varies of applications such as for medical field, industrial and textile [4].

Pineapple leaf fibers (PALF) is one of natural fibers that possess great mechanical properties which still unexplored widely. Pineapple plant is referred as secondary plant which by-product wastes were extracts to obtain cellulose. According to Neto et al (2015), cellulose content act directly proportional with mechanical properties while lignin vice versa. PALF consists of high amount of cellulose (70% -82%) and low lignin content (5-12%) thus made it suitable for industrial purposes [5]. However, lack of good interfacial adhesion, low melting point, and poor resistance towards moisture make the use of PALF less attractive. Pretreatments of the natural fibers can help to improve the performance. Pre-treatment were done in two methods, mechanical or chemical treatment [6].

Among the various pretreatment techniques, chemical treatment was common treatment used for natural fibers [7]. PALF is organized into fibrils, which are surrounded by a matrix of lignin, hemicellulose and pectin. Hemicelluloses were present and located within the structure of cellulose. The strong bond between hemicellulose and cellulose were believed to decrease the average crystallinity of the cellulose fibrils [2]. Reducing lignin and hemicellulose amount help to increased crystalline cellulose content which contributed to improvement on thermal and chemical properties [1]. Nadezda et al (2016) in the studied proved that the thermal stability of wood pulp fibers improved after bleaching treatment thus provide materials with great heat resistant.

However, even there are many papers already been published on PALF, there were only few that were proceed to the PALF nanofibers. Nanofiber materials had a good catch up with industrial requirement due to its large surface area, superior mechanical performances and varieties of surface functionalities [8]. 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 [9]. 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 [10].

Electrospun nanofibers have become promising materials for many biomedical applications such as wound dressing, drug delivery and tissue scaffold [11, 12]. Besides, it is also known for industrial purposes such as for reinforcing materials, filtration media and protective clothing [13].

2. Experimental

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. Chemicals which are Trifluoroacetic acid (TFA), Hydrogen Peroxide (H_2O_2), Hydrochloric acid (HCL), Sodium Hydroxide (NaOH), Toluene and Ethanol all were supplied by Aldrich Merck.

2.2. Methods

2.2.1 Dewaxing

PALF were first extracted with toluene/ethanol (2:1v/v) for 6 hours in order to remove organic compounds from the surface thus increase the reaction.

2.2.2. Chemical Treatment of PALF

PALF was treated with 2 M of Hydrochloric Acid (HCL) at 80°C for 2 hours. Later, the sample was treated using 2 M of NaOH at 80°C for 2 hours **(**alkali treatment). Lastly, the sample were soaked with H_2O_2 (bleaching) for 5 hours to reduce amount of lignin in the sample. Figure 1 shows sample of raw PALF and PALF after treatment. Samples were labelled as PR, PA and PB respectively as shown in figure 1.

Fig. 1: (PR) Raw PALF (PA) Alkali Treatment PALF (PB) Alkali + Bleaching Treatment PALF

2.2.3 PALF solution preparation

The samples were diluted using Trifluoroacetic Acid (TFA) as the solvent and Polyethylene Terephthalate (PET) as the polymer carrier and proceed to electrospinning to produce a nanofibers electrospun mats. PALF and PET were dissolved in TFA to obtain 2x10g mL^{-1} solution concentration (9). The samples were stirred for 6 hours at room temperature until the solution become homogenous.

2.2.4. Electrospinning

The electrospinning solutions were placed into a 3 mL syringe with a metallic needle diameter 0.3mm which connected to a pump with 0.5ml/h flow rate. A copper wire connected to the positive charge was inserted into solution. Fibers were collected as a nonwoven fibrous mat by aluminium foil wrapped collecter that were placed 12 cm from the needle tip. Figure 2 shows the electrospinning machine set up.

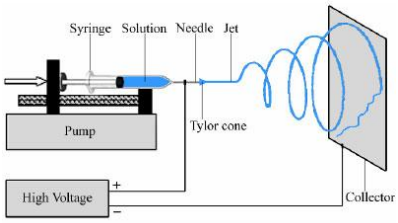

Fig. 2: Electrospinning machine set up

2.3. Characterization

2.3.1. 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-1 with 4 cm^{-1} resolutions.

2.3.2. STA

Simultaneous Thermal Analysis TGA-DTA/DSC measures both heat flow (Differential Scanning Calorimetry) and weight changes (thermogravimetry) in a material as a function of temperature or time in a controlled atmosphere. STA were performed using (Perkin Elmer STA 600) and conducted in a temperature range 30^0C-800^0C with heating rate 10^0C/min. The analysis was carried out under nitrogen atmosphere at a flow rate of 20 mL-min^{-1}.

2.3.3. FESEM

Sample morphology was observed under FESEM at an accelerating volt of 5.0 kV. All samples were coated with a thin layer of gold to reduce charging and produce a conductive surface. The diameters were calculated using Microsoft word.

3. Result & Discussion

3.1. Effect of pre-treatment on the chemical structure of PALF

Figure 3 (a) shows the FTIR spectra of PR, PA and PB respectively. The peak observed at approximately ~3300cm^{-1} that represents O-H bonding comes in the presence of carbohydrate (cellulose + hemicelluloses) and lignin [14]. The peak intensities were increased after each treatment suggested that this is due to the broken hydroxyl group which is alkaline sensitive thus promotes free hydroxyl that caused the addition of extra peak in free hydroxyl bond structure at 2823 cm^{-1} [15].

Figure 3 (b) illustrates two peaks at 1725cm^{-1} and 1650cm^{-1} that represent C=O (hemicelluloses) and lignin (aromatic C=C) respectively. At 1725cm^{-1} region, hemicelluloses were completely removed after alkali treatment (PA). This happens because hemicellulose become easily hydrolysed in alkaline medium due to the breaking C-O-C bond [17]. Indeed, alkaline treatment is known as effective method to remove hemicelluloses [7, 14]. At 1650 cm^{-1} region which represent lignin, PA peak shift to lower wavenumber indicating weak interaction between the C=C bond. Nevertheless, no significant change in the intensity of the peak were observed. The strong aromatic structure of lignin makes it hard to be removed from the fibers [18]**.**

The peaks at 1373cm^{-1} and 667cm^{-1} represent the C-H bond of cellulose were observed in Figure 4 (b). No significant changes were observed in the intensity of 1373cm^{-1}. However, at peak 667cm^{-1}, peak intensity for PA and PB were increased and the peak shifts to higher wavenumber which is 670cm^{-1} and 673cm^{-1}

respectively. According to M. Le Troedec et al (2008), crystalline cellulose of fiber can be calculated from ratio of the band at 1373cm^{-1} and 667cm^{-1} [18]. Treatment fibers shows high crystalline cellulose contributed to thermal properties enhancement. Despite that, peak that come from raw PALF at 1250 cm^{-1} that represent pectin and lignin, were completely removed after alkali treatment indicating removal of pectin during treatment. Removal of hemicellulose, pectin and waxes lead to the rearrangement of crystalline cellulose chains in a particular order that contributed to strong mechanical properties [7]. Furthermore, at region 1030cm^{-1} to 1060cm^{-1}, single peak of PR has become combinations of two different small peak of 1037cm^{-1} and 2053cm^{-1} respectively after alkali and bleaching treatment. Cao et al suggest that both of this peak come from C-O stretching bond of functional group of glycoside linkage.

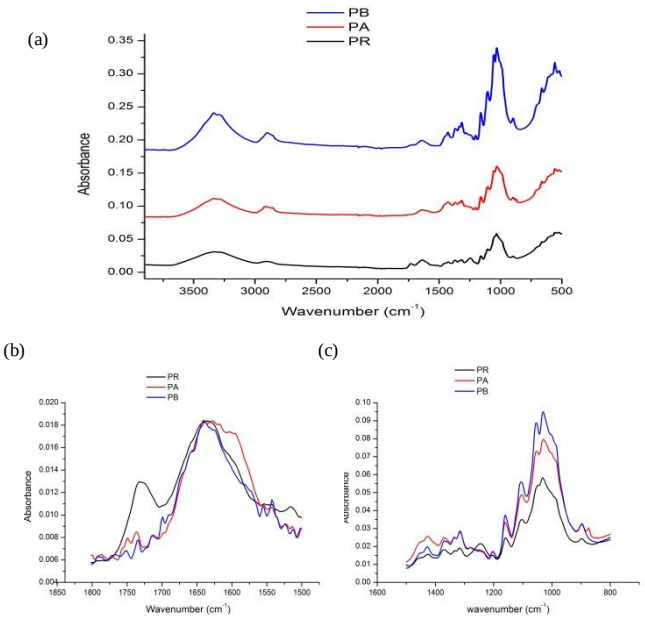

Fig. 3: (a) FTIR spectra of PR, PA and PB (b) zoom in at 1500-1800 cm^{-1} (c) zoom in at 800-1500 cm^{-1}

3.2. Effect of pre-treatment on thermal properties (TGA) of PALF

Figure 4(a) and 4 (b) shows TGA and DTG results for PR, PA and PB respectively. TGA result (Figure 4(a)) shows that initial weight losses were observed at temperature 20^{0}C-100 ^{0}C resulting from moisture evaporation. This common loss mass depends on the initial moisture content of the fibers. PR shows lower moisture content, 2.3% compared to PA and PB which were 5.4% and 7.6% respectively. Second stage loss for PR occurred at temperature between 282 ^{0}C to 367 ^{0}C and likely contributed by degradation of hemicellulose and initial broken glycosidic linkages of cellulose [2]. Nevertheless, this stage lose were completely absent for PA and PB indicating completely removal of hemicellulose during treatment. Low thermal stability of hemicellulose made it easily degraded before cellulose and lignin**.** According to Asim et al (2016), thermal stability of a fiber was determined using initial degradation temperature of hemicellulose.

Weight losses for PR, PA and PB at temperature 367 ^{0}C - 415 ^{0}C are 27%, 39% and 47% respectively. These results are indicating of a fast rate of fiber degradation and increased with treatment PALF. PR shows low percentage mass loss compared to PA and PB. This is because raw PALF (PR) cellulose was surrounded by lignin, hemicellulose and pectin. Hemicellulose were strongly connected to the cellulose thus is believed to decreased the average crystallinity of cellulose [2]. At 415 ^{0}C to 600 ^{0}C, only 4.3% - 5.0% lignin weight losses were observed. This small percentage loss occurs due to broken of lignin and formation of aromatic in nitrogen atmosphere [14]. There is also a distinction between the amounts of the residue of PALF which is 14.0%, 13.26% and 7.52%.

In figure 4 (b), it can be seen that PALF has become slightly hydrophobic after treatment as the water losses increased. Besides, the moisture loss peak shifted to higher temperature for PB indicated improvement of structure of water that made it become crystalline thus facilitates the moisture evaporation at higher temperature [2]. Maximum degradation occurs at temperature of about 367 ^{0}C - 370 ^{0}C which is mainly expected due to the contribution of cellulose. Cellulose molecule is a very long polymer of glucose units and its crystalline region improved the thermal stability. This supported by how degradation temperature of cellulose shifted to higher temperature for PA and PB. Increase in hydrogen bond between cellulose chains can lead to more organized and packed cellulose region thus help in increasing thermal decomposition of cellulose [1].

Table 1 summarized thermal behaviour of PR, PA and PB. It can be concluded that pre- treatment helps to enhance the thermal stability of PALF thus improved others thermal behaviour of PALF.

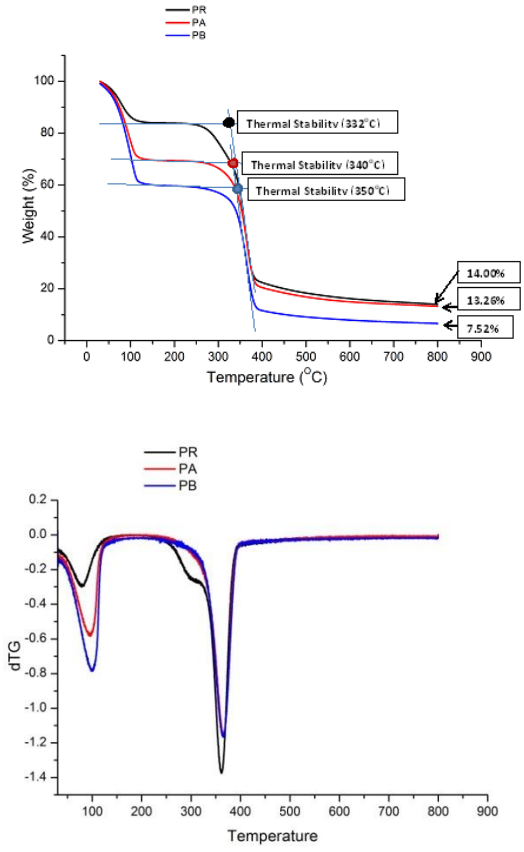

Fig. 4: Thermal graph of PR, PA, PB (a) TGA graph (b) DTG graph

Table 1: Thermal behaviour of raw and variously treated PALF

PALF	Initial Thermal Stability (^{O}C)	Peak Temperature (^{O}C)	% of the maximum degradation	Ash content at 800 ^{O}C (%)
PR	332	83	47.5	14.00
PA	340	95	41.86	13.26
PB	350	100	41.86	7.52

The DSC curves in nitrogen atmosphere of PR, PA and PB were presented in figure 5. The DSC curves for all samples shows

evaporation of water at temperature 110 ^{0}C -120 ^{0}C and cellulose degradation at around 330 ^{0}C -380 ^{0}C. Treated PALF exhibits higher entalphy values than untreated PALF. Different chemical processes increase the amount of crystalline cellulose thus increased the H-bonding that resulted in structure stabilized [1].

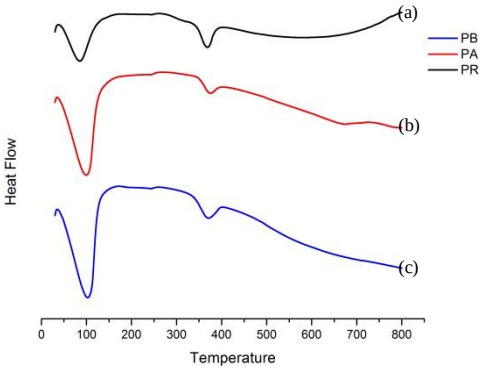

Fig. 5: DSC result of (a) PR (b) PA (c) PB

3.3. Effect of pre-treatment the morphology of PALF

Figure above shows surface morphology result for PR and PB samples. PALF contained cylindirical surface that surround bound of assembly microfibrils. Cellulose is organized into fibrils, which are surrounded by matrix of lignin [9] with layer of subtances which may include pectin, lignin, and other impurities [13]. However, alkali and bleaching treatment was believed manage to breakdown the outer surface of PALF fiber (lignin) and hemicelluloses thus produced more separate and singular unifibril PALF such as shown in figure 6 (b).

Figure 6 (c) and 6 (d) shows the SEM result using bigger magnification at 5K. PB modified the fiber surface thus made it more smooth than those of untreated one due to the hemi, pectin and lignin partially removal. During bleaching treatment, most of the impurities, hemicelluloses and lignin were diminished thus enlighten hidden cellulose fibers to the surface producing crystalline cellulose. On the other half, there were also reduction in the diameter of the fibers from an average of 15µm to 6 µm.

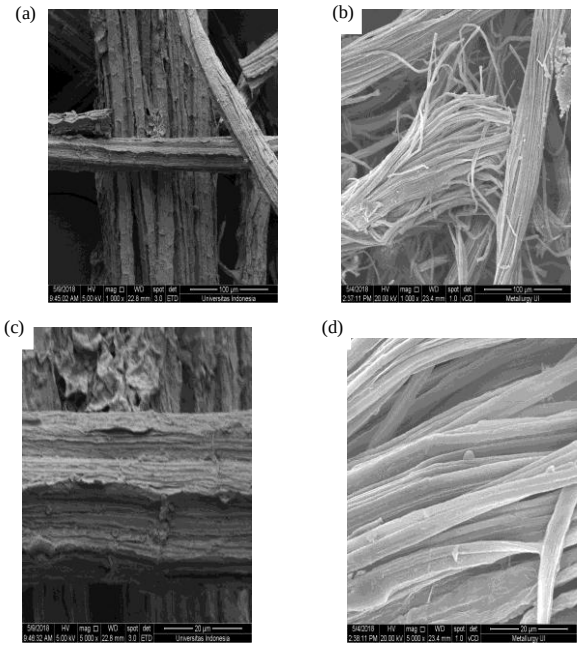

Fig. 6: Surface morphology result of (a) PR (1K x mag), (b) PR (5K x mag) (c) PB (1K x mag) (d) (5K x mag)

3.4. Effect of pre treatment on chemical structure of electrospun PALF/PET

Based on few paper written on lignocellulosic fibers [8,9] a peak usually presented at ~1595 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 treatment PALF followed by dissolve in TFA that plays role on disrupted the covalent bond that hold the cellulose (lignin) as well eliminates it. Peak at ~1715cm^{-1} and ~1099cm^{-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 cm^{-1} representing the hydroxyl group resulted from the interaction of PET/PALF contributed to the hydrophilic tendency of the fiber.

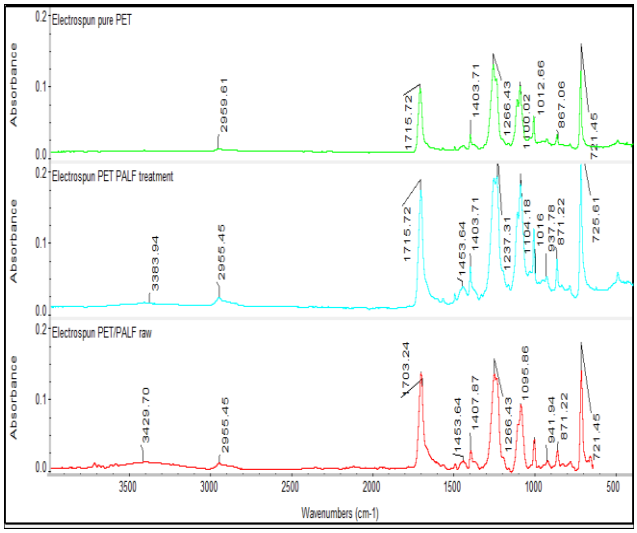

Fig. 7: FTIR result of (a) Electrospun PET, (b) Electrospun PET/PR (c) Electrospun PET/PB

3.5. Effect of pre-treatment on the morphology of electrospun PALF/PET

FESEM images of electrospun nanofibrous structures of (a) PET and (b) PET/PR and (c) PET/PB shown in Figure 8 revealed that nano-scale of spider web structures were successfully created via electrospinning method. The fibers were found randomly oriented with interconnected pores in between to form a 3D scaffold. Electrospun PET (figure 8(a)) sample shows diameter range between 40-120 nm with average 91.6 nm while electrospun PET/PR (figure 8(b)) and electrospun PET/PB (figure 8(c)) shows lower fiber average diameter which is 52.1 nm and 51.6 nm respectively.

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 PET/PALF. It is suggested that one networks with bigger diameter probably corresponds to PET and the others with smaller diameter correspond to PALF. Thicker diameter might due to the increasing solution concentration after adding PALF.

As shows in fig 8 (b), a thin fibers coexited among the electrospun fibers were present. A thin fiber was coexited from single fiber indicated that new fibers were ejected however the bond were collapsed during ejection thus did not produce a complete single fiber**.** Nevertheless, electrospun PET/PB with treatment shows improvement in the morphology. Smooth single fiber was produced. Fiber without defect could lead to a good mechanical properties of the sample [8]. It may be due to the reducing and removal of lignin, hemicellulose and pectin from PALF that help increase the amount of crystalline cellulose from PALF.

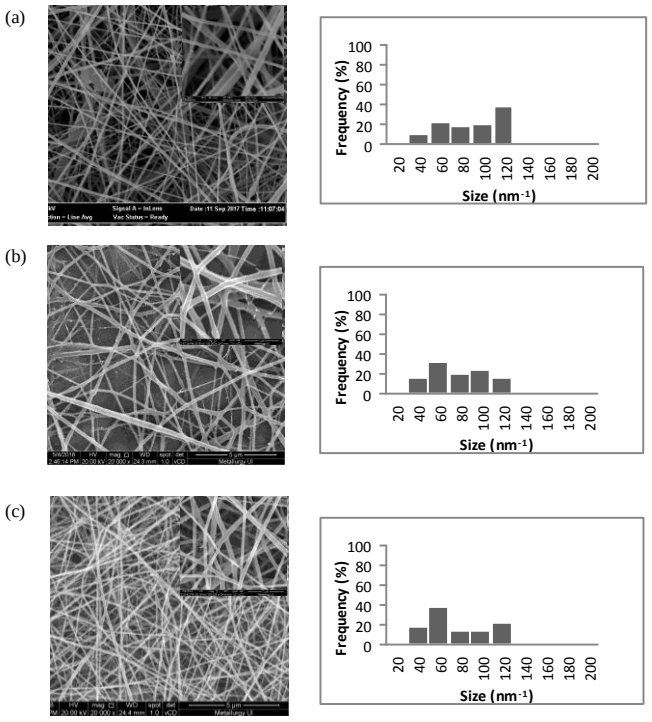

Fig. 8: FESEM result of (a) Electrospun PET, (b) Electrospun PET/PR (c) Electrospun PET/PB

4. Conclusion

As a conclusion, FTIR, TGA and DSC studies shows reducing amount of hemicellulose, pectin and lignin thus improve crystalline structure of PALF. FESEM morphology shows decreasing in treated PALF size compared to PR. Thus, pre-treatment PALF favors the formation of smooth fine nanofibers electrospun mats.

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