Optimization and Properties of Polylactic Acid (PLA) / Nypa Fruticans Husks (NFH) Biocomposite Films Via Central Composite Design (CCD) Method

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Abstract: Chemical treatment is one of the recognized methods that can be implemented to improve the overall performances of biocomposite materials. Unfortunately, trial and error methods were used to determine the optimal ratio between percentage of treatment agent and composite's properties in the past. Hence, this research focuses on the optimization and validation of coupling agent percentage with properties of novel Polylactic Acid (PLA) / Nypa Fruticans Husks (NFH) biocomposite films via Central Composite Design (CCD) Method. Nypa Fruticans husks was grounded to obtain particulate form and mixed with Polylactic acid (PLA) using solvent casting method. Due to the different polarity between Nypa Fruticans Husks and Polylactic Acid, 3-Aminopropyltriethoxysilane was used to enhance the properties of the composite films. Central composite design (CCD) method was used to determine the optimized percentage of 3-Aminopropyltriethoxysilane and analysis of variance various (ANOVA) was performed to develop mathematical model to predict the tensile strength value in the range of factors in this research. Apart from that, the enzymatic biodegradation was also performed to investigate the composite's degradation rate. It was found that, the incorporation of Nypa Fruticans Husks decreased the tensile strength and elongation at break, whereas the modulus of elasticity and degradation rate increased. However, composite films treated with 3% of 3-APE showed increment pattern in tensile strength and modulus of elasticity but decreased in elongation at break and degradation rate, respectively. The enhancement of the mechanical properties after treated with 3-Aminopropyltriethoxysilane was supported by the SEM micro-graphs and FTIR analysis.

Keywords: Polylactic Acid, Nypa Fruticans husk, Central Composite Design, Biodegradability, Biocomposite films.

1. INTRODUCTION

Nowadays, almost all aspects of daily life involve polymeric materials. With increasing environmental awareness around the world, the research and development of biodegradable polymers attracted a great attention [1]. Environmental concerns and a shortage of petroleum resources have driven efforts aimed at the production of biodegradable materials [2]. Polylactide (PLA) is one of the most important marketed biodegradable thermoplastictics [3-5]. Polylactide can be fermented from renewable resources at a relatively low cost and in large volume commodity plastics for various end-use applications, due to its good mechanical properties, thermal plasticity, and facile fabrication [6]. As a result, they are a feasible alternative to petroleum-based polymers. However, some of its applications are limited by its low elongation at break and poor toughness. Moreover, PLA has a glass transition (Tg) temperature ranging between 55 and 65 °C, and it is brittle at room temperature, fracturing via a crazing mechanism [7, 8]. Mechanical brittleness of PLA can be modified by using many strategies such as copolymerization, processing manipulation and blending [9-11].

The use of natural fillers as reinforcement is an emerging practice in the polymer industries to enhance the properties of virgin polymers [12, 13]. These materials usually comprise of an effective polymeric matrix in which natural fibers or small natural filler particles are thoroughly dispersed in composite systems. These natural fillers must be well dispersed within the polymer matrix to avoid zones of weaker cohesion where flaws and other defects will be initiated upon stressing [14]. The different polarity between most polymeric matrix and natural filler had been a cause of poor interfacial adhesion and modification of filler are required to overcome this issue [15]. Among

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many types of available natural plants, Nypa Fruticans (NF) is still not yet discover on its potential. Scientifically, Nypa Fruticans (NF) is a monoecious palm with special and promising characteristics. In Malaysia, NF palm can be found throughout the year and it can be considered an abundant source. Nypa, consisting of frond, shell, husk, and leaf, show the contains of cellulose, hemicellulose, lignin, starch, protein, extractives, and inorganic constituents for its each part [16, 17].

A coupling agent is a chemical that functions at the interface to create a chemical bridge between the filler and matrix, in order to enhance the behavior of biocomposite materials. The 3-APE has ethoxy groups that hydrolyzed in water or solvent producing silanol and next the silanol reacts with OH group of filler which form stable covalent bond onto the filler surface. Generally, the coupling agent improved the degree crosslinking in the interface region and offers a suitable bonding result, as well as creation of high filler surface area. The amine group from 3-APE can form hydrogen bonds to COO- sites on hydrolyzed PLA backbone [18, 19]. Until recently, there is limited number of studies which are focusing and validating on the correlation between percentage of treatment agent and composite's properties. Therefore, the knowledge is still remains unclear. To overcome these limitations, we had purposefully designed an experiment to optimize and validate the properties of polylactic acid (PLA) / nypa fruticans husks (NFH) biocomposite films via Central Composite Design (CCD) method. Apart from that, all fabricated biocomposite specimens were also tested with enzymatic biodegradation test, morphology analysis and elemental analysis for more conclusive finding.

2. MATERIALS AND METHODS

2.1. Materials

Polylactic Acid (PLA) was supplied by TT Biotechnologies Sdn. Bhd., Penang. The filler was Nypa Fruticans husks (NFH) obtained from a plantation at Simpang Empat, Perlis, Malaysia. Nypa Fruticans was first cleaned, grinded and dried at 80°C for 24 hours. Then, the NFH was sieved to a size of 65µm. The silane coupling agent (3-Aminopropyl-triethoxysilane) was obtained from Fluka, Penang, Malaysia.

2.2. Chemical Modification of PLA/NFH Biocomposite Films with Silane Coupling Agent

The silane coupling agent was first dissolved in 1% of ethanol solution at room temperature. The NFH slowly added into silane coupling agent solution and stirred at a speed of 50 rpm for 1 hour. The treated NFH then been filtered using Whatman filter paper and dried at 80˚C for 24 hours. Similar method was repeated for 2,3,4, and 5% of silane coupling agent.

2.3. Preparation of PLA/NFH Biocomposite Films

Biocomposite films were formulated as in Table **1** using solvent casting method. At first, the PLA was dissolved in 100 mL of chloroform while stirred using a mechanical stirrer at 50 rpm under a constant temperature of 45 °C until completely dissolved. Then NFH was added slowly and mixing continues until NFH was well dissolved in the PLA solution before the mixture was poured in a glass mold and dried in a confined area for 48 hours.

Table 1: Formulation of Biocomposite films

Sample	PLA (php)	NFH (php)	3-APE (%)
Untreated	100	0,5,10,15,20, and 25	-
Treated	100	5,10,15,20, and 25	1, 2, 3, 4, and 5

2.4. Experimental Design Plan

The content of NFH and 3-APE silane coupling agent as chemical modification with the total number of input factors of two. In this research the value of α chosen equal to 2 in order to keep the step of levels constant [20]. This α choice was not far enough apart to be of concern the default is the practical alpha (Design expert 10). Consequently, the factorial levels adopted was 10% to 20% were selected for NFH content and 2% to 4% 3-APE silane coupling agent. The star levels determined with α = 2 and the selected factorial levels for all the factors are shown in Table **2**. And the response output of this study is classified into mechanical testing which involve tensile strength. The factors with their levels and the response were entered in the central composite design of Design-Expert version 10. 0.3.0 to generate the overall design plan matrix for the study.

Table 2: Factorial and Levels in CCD Experimental Design Plan

Materials	Levels				
	-2	-1	0	1	2
NFH (php)	5	10	15	20	25
Silane Coupling Agent (%)	1	2	3	4	5

2.5. Testing and Characterization

2.5.1. Tensile Testing

Tensile tests were carried out according to ASTM D882 using Instron 5566. An average of five samples with dimension of 70 x15 x 1 mm was tested, and crosshead speed for the testing was 10 mm/min. Elongation at break, tensile strength, and Young's modulus were recorded and calculated by the machine software.

2.5.2. Morphological Analysis

The morphological study of the tensile fractured surface of the biocomposite films was carried out by a scanning electron microscope (SEM), model JSM 6260 LE JOEL. The fractured surface of the biocomposite films were mounted on aluminium stubs and sputter coated with a thin layer of palladium to mitigate electrostatic charging. The SEM micrographs was obtained at 10kV.

2.5.3. Enzymatic Biodegradation

Enzymatic testing performed done according to technique as stated by Yoon *et al*., [21]. The biocomposite films were placed in solution of α-amylase. A buffer solution was prepared by adding 4.8 mL of 0.2 M acetic acid to 45.2 mL of 0.2 M sodium acetate solution to produce 50 mL solution. The samples were then taken out every two days and washed thoroughly, dried in an oven at 50 °C for 24 hours. The average weight loss of the sample was calculated as shown in Equation 1:

$$\%\mathrm{WL} = \frac{W_0 - W_t}{W_0} \quad (1)$$

Where:

%WL: the average weight loss in percentage

W_t: weight of dry specimens after enzymatic biodegradation

W_0: initial weight of dry specimens

2.5.4. Fourier Transmission Infra-Red (FTIR)

FTIR was utilized to characterize and validate the presence of functional groups in untreated and treated PLA/NFH biocomposite films. The FTIR analysis was carried out by using an FTIR spectroscopy, Perkin Elmer, Model L1280044. The attenuated total reflectance (ATR) method was used. The 4 scans were recorded for each sample in the frequency range 650 cm^{-1} - 4000 cm^{-1} with a resolution of 4 cm^{-1}.

3. RESULT AND DISCUSSION

3.1. Modelling the Tensile Strength and Optimization of Silane Coupling agent Amount

According to the experimental design, 13 runs were prepared and characterized respectively. Tensile strength as response and independent variables for each experiment are presented in Table **3**. As shown in Table **3**, tensile strength values varied from 14.1 MPa–20.7 MPa.

Table 3: CCD Design of Two Variables with their Obtained Response

Std	Run	Factor 1 A: NFH php	Factor 2 B: 3-APE %	Response Tensile Strength MPa	
				Mean	S.D
13	1	15	3	17.2	0.6
4	2	20	4	19.3	1.3
1	3	10	2	19.2	0.3
6	4	25	3	14.5	0.6
5	5	5	3	20.7	1.3
9	6	15	3	16.2	0.6
2	7	20	2	14.1	2.4
3	8	10	4	17.9	1.6
7	9	15	1	16.0	2.9
11	10	15	3	18.0	2.1
8	11	15	5	17.2	1.2
12	12	15	3	17.5	1.5
10	13	15	3	17.6	1.7

*The values are mean values of three measurements.

Table 4: Analysis of Variance

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	35.47	3	11.82	18.80	0.0003	Significant
A-NFH	21.60	1	21.60	34.35	0.0002	
B-S.C.A.	3.31	1	3.31	5.26	0.0475	
AB	10.56	1	10.56	16.80	0.0027	
Residual	5.66	9	0.63			
Lack of Fit	3.82	5	0.76	1.66	0.3217	Not significant
Pure Error	1.84	4	0.46			
Cor Total	41.13	12				
R-Squared 0.8624				Adj R-Squared 0.8165		
Pred R-Squared 0.6351				Adeq Precision 14.038		

ANOVA for the fitted two factors interaction (2FI) model for tensile strength of PLA/NFH biocomposite films based on NFH content and 3-APE is presented in Table **4**. The Model F-value of 18.80 denotes the model was significant. There was only a 0.03% chance that an F-value this large could occur due to noise. Values of "Prob > F" less than 0.05 indicate model terms was significant. In this study A (filler content), B (3-APE), AB interaction are significant model terms. The "Lack of Fit F-value" of 1.66 denotes the Lack of Fit is not significant relative to the pure error. There was a 32.17% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit good. The R-Squared 0.8624 was closed to 1, that means the model was fit. The Pred. R-Squared of 0.6351 was in reasonable agreement with the Adj R-Squared of 0.8165; *i.e*., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio 14.038 indicated an adequate signal. A ratio greater than 4 was desirable.

The equation in terms of actual factors can be used to make predictions about the response forgiven levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients were scaled to accommodate the units of each factor and the intercept was not at the centre of the design space.

Tensile strength = 34.41346 -1.24333* (NFH) - 4.35000* (3-APE) + 0.32500* (NFH * 3-APE) (2)

3.1.1. Confirmation Experiments

Confirmatory experiments were conducted to validate the process parameters condition to verify the model predictability. The tensile strength as response selected at 10 and 20 NFH using 3% 3-APE of the input process parameters were termed as the predicted response, while the experimental observations were the actual response obtained by per-forming the tensile test at the predicted conditions. The experiments were conducted three times at 10 and 20 NFH using 3% 3-APE for accuracy of the confirmation results. The actual experimental observations compared with the predicted outcome and the percentage errors were computed. The percentage errors and confirmation test report in Table **5** revealed that the percentage error in

Table 5: Analysis of Confirmation Report for Tensile Strength

Sample	Pred. Mean	n	Confirmation Test Data	% Error	95% PI low	Confirmation Data Mean	95% PI high
10 NFH 3% 3-APE	18.68	3	17.3	7.4	17.42	18.3	19.94
			19.1	2.3			
			18.5	1.0			
20 NFH 3% 3-APE	15.997	3	15.4	3.7	14.74	15.5	17.26
			15.6	3.5			
			15.5	3.1			

the response was within the range of 1% to 7.4 % at 10 NFH, 3% 3-APE and 3.1% to 3.7% at 20 NFH, 3 3-APE. With these confirmations and validation of the percentage error, it can be concluded that the model was adequate for predicting the response using the process parameter conditions for NFH/PLA biocomposite films.

3.1.2. Effect of Factors Interaction

Figure **1** shows the interaction between the NFH content and 3-APE concentration as input factors and tensile strength as a response. It can be seen that at 1% 3-APE the tensile strength decreased with increasing NFH content. This effect gradually be inverted by increasing the 3-APE concentration. At 5% 3-APE concentration the tensile strength increased with NFH content increasing. On other hand at 3% 3-APE the tensile strength did not affect by change on NFH content. Therefore, the optimum value of silane coupling agent 3-APE was determined at 3%.

3.2. Tensile Properties

The tensile strength of the untreated and treated PLA/NFH biocomposite films with 3-APE is illustrated in Figure **2**. It can be seen that the tensile strength of untreated and treated biocomposite films reduced with increasing NFH content. The decreasing of tensile strength was due to the incompatibility among the PLA matrix and NFH filler [22]. The incompatibility resulted because of the poor wettability, dispersion and filler-matrix interaction of NFH and PLA matrix. Furthermore, as the filler content increased the dispersion of the filler through the matrix become poorer. The poor dispersion of filler at higher NFH content caused by agglomeration of filler thus decreased the tensile strength [23].

At similar NFH content, the treated biocomposite films with 3-APE had higher tensile strength compared to untreated biocomposite films. The average tensile strength of treated PLA/NFH biocomposite films with 3-APE was around 6.8 % higher than that of untreated PLA/NFH biocomposite films. This attributed to the 3-APE treatment increased the interfacial adhesion between NFH filler and PLA matrix [18]. The silane treatment 3-APE improving the compatibility between NFH filler and PLA matrix [24].

Figure **3** shows the elongation at break of untreated and treated PLA/NFH biocomposite films with 3-APE. The figure illustrates that the elongation at break of the untreated and treated PLA/NFH biocomposite films decreased as the NFH content increased. The decreasing of elongation at break with increasing NFH content impute to the stiffening effect of NFH because of the NFH rigid surface restricting the mobility of the matrix molecular chain [9]. The increasing of NFH content cause more weak interfacial regions among filler and matrix occur. Thus, cracks were easier to merge through the weak interfacial regions and

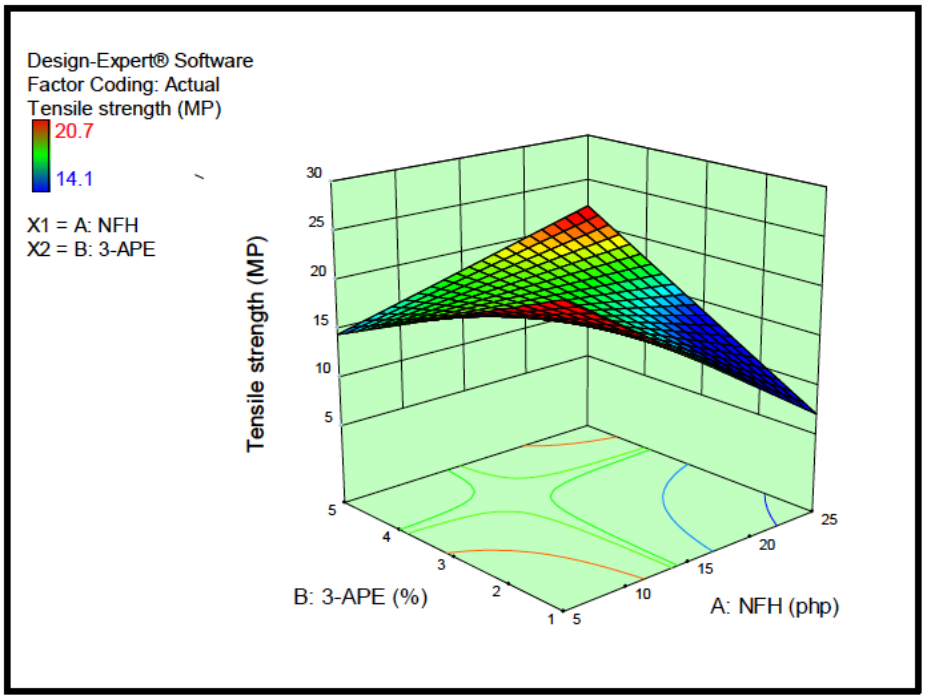

Figure 1: 3D surface and contour plots of tensile strength (MPa) with NFH content (php) and 3-APE (%).

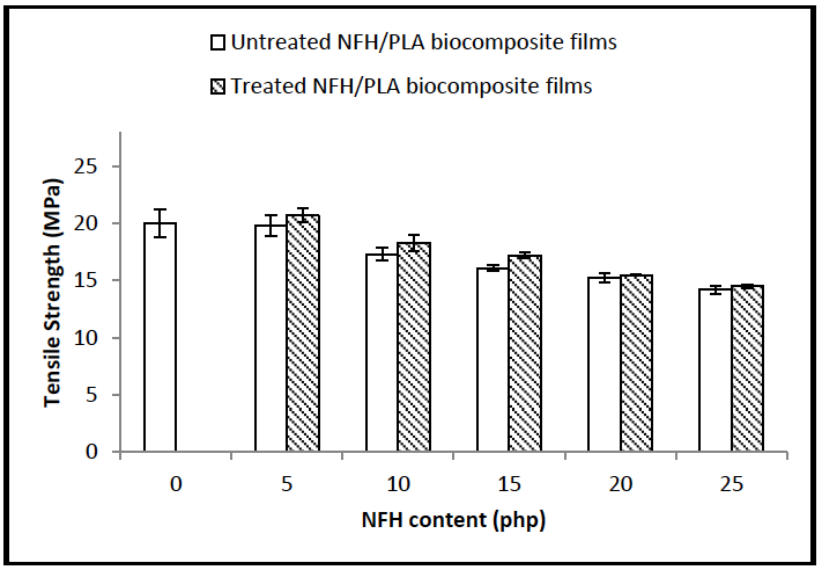

Figure 2: Effect of NFH content (php) on tensile strength (MPa) of untreated and treated PLA/NFH biocomposite films.

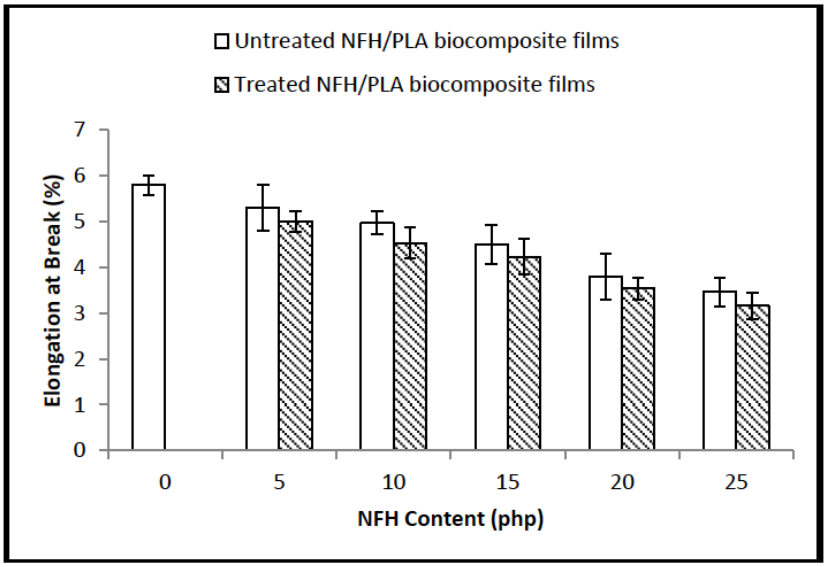

Figure 3: Effect of NFH content (php) on elongation at break (%) of untreated and treated PLA/NFH bio-composite films.

contributed to fracture at lower degree of elongation at break. Moreover, the elongation at break of treated PLA/NFH biocomposite films with 3-APE decreased around 6 % in comparison with untreated PLA/NFH biocomposite films. The decreasing of the elongation at break of treated PLA/NFH biocomposite films was due the 3-APE treatment has improved the tensile strength of biocomposite films with the enhancement in rigidity and decrement of the ductility of biocomposite films [25].

Figure **4** exhibits the modulus of elasticity of untreated and treated PLA/NFH bio-composite films. It was found that the modulus of elasticity of both PLA/NFH biocomposite films increased with increasing NFH content. The increment of the modulus of elasticity of untreated PLA/NFH biocomposites films was due to the reduction in PLA chain mobility which provided high brittleness. Modulus of elasticity of filled composites was influenced by filler content and filler aspect ratio [26]. The aspect ratio played an important role in determining the properties of stiffness and strength in composites, because the particulate aspect ratio was lower than the fiber, and the effectiveness in improving the mechanical properties of particulate matter was not obvious. Moreover, the modulus of elasticity of treated PLA/NFH biocomposite films with 3-APE was higher as compared with untreated PLA/NFH

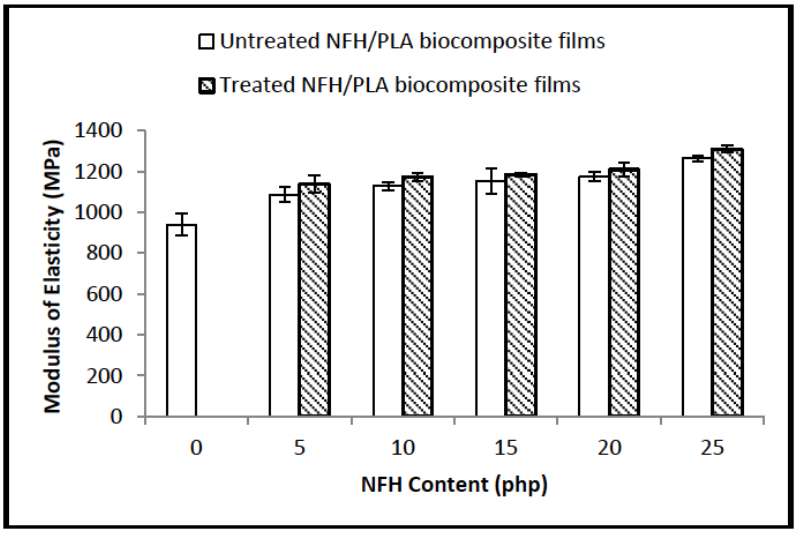

Figure 4: Effect of NFH content (php) on modulus of elasticity (MPa) of untreated and treated PLA/NFH biocomposite films.

biocomposite films. This attributed to the 3-APE silane coupling agent treatment of NFH improved the stiffness of PLA/NFH biocomposite films due to improvement of the interfacial adhesion between NFH and PLA matrix.

3.3. Morphology Analysis

A scanning electron microscope (SEM) was used to study the tensile fracture surface of PLA/NFH biocomposite films. Figure **5** illustrates the scanning electron micrograph of PLA films presented a smooth surface with matrix tearing at a magnification of X500. Tensile fracture surfaces of untreated PLA/NFH biocomposite films with NFH content of 10 php and 20 php are showed in Figure **6 a** and **b**, respectively. The micrographs display poor interfacial adhesion and dispersion of NFH content in the PLA matrix. The micrograph of untreated PLA/NFH biocomposite films containing 20 php NFH exhibited NFH detachment and pull out from matrix. Higher NFH content increased the tendency of filler-filler interaction to form agglomerates and caused poor dispersion of NFH as shown in Figure **6**. This resulted in higher level of dewetting of filler in the matrix. Besides that, from the micrograph, the surface of untreated PLA/NFH biocomposite films appeared to be rough than the surface of neat PLA due to the incorporation of NFH content.

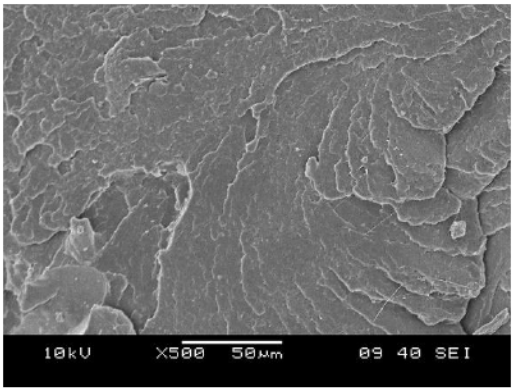

Figure 5: Scanning electron micrograph of tensile fracture surface of PLA films.

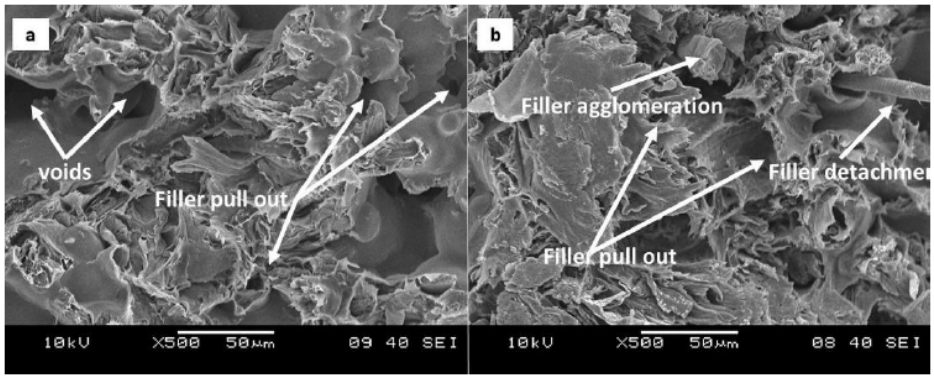

Figure 6: Scanning electron micrographs of tensile fracture surface of PLA/NFH biocomposite films (**a**) 10 php NFH; (**b**) 20 php NFH.

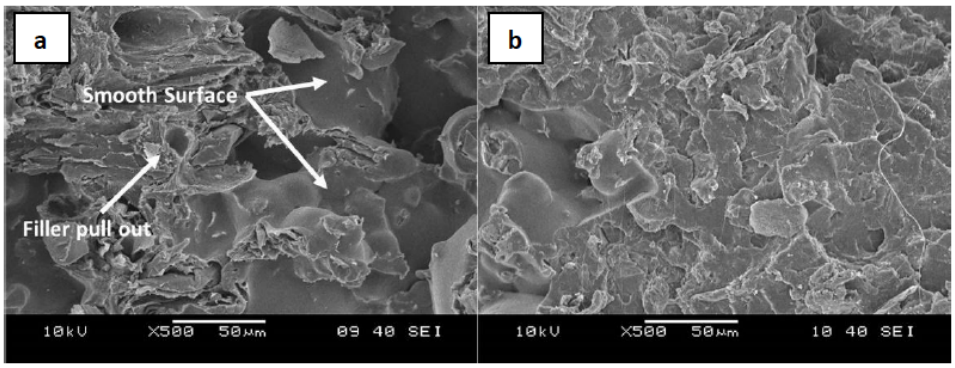

Figure 7: Scanning electron micrographs of tensile fracture surface of treated PLA/NFH bio-composite films with 3-APE (**a**) 10 php NFH; (**b**) 20 php NFH.

The SEM micrographs of the tensile fracture surface of treated PLA/NFH biocomposite films with 3-APE at 10 php and 20 php NFH content are shown in Figure **7 a** and **b** respectively. The micrographs of treated PLA/NFH biocomposite films showed a smooth surface compared to untreated PLA/NFH biocomposite films. The micrographs of treated PLA/NFH biocomposite films displayed good interfacial adhesion among the PLA matrix and NFH. Moreover, the morphology of treated PLA/NFH biocomposite films exhibited less NFH detachment and less pull out from PLA matrix. It was clear that the presence of 3-APE silane led to improve of interfacial interaction between NFH and PLA matrix.

3.4. Enzymatic Biodegradation

The weight loss percentage due to enzymatic biodegradation of PLA/NFH for untreated and treated biocomposite films is shown in Figure **8**. It is observed that the weight loss of untreated and treated PLA/NFH biocomposite films increased with increasing in filler content and immersion time. A higher weight loss was observed for untreated PLA/NFH biocomposite films than treated PLA/NFH biocomposite films after 14 days. This trend was due to the poor interfacial adhesion existing in PLA/NFH which facilitated the absorption of enzymes into the biocomposite films. At high filler content, the PLA/NFH biocomposite films absorbed more of the amylase solution because of excess hydroxyl group on NFH filler. Therefore, the NFH filler content affected the weight loss of the biocomposite films. In contrast the treated PLA/NFH biocomposite films with 3-APE silane coupling agent exhibited lower percentage of total weight loss in α-amylase buffer solution than untreated PLA/NFH biocomposite films. The treated PLA/NFH biocomposite films with 3-APE showed more resistance to hydrolysis in the α-amylase buffer solution that untreated form. This due to the chemical modification of NFH and PLA biocomposite films with 3-APE, which exhibited a lower moisture absorption compared to the untreated biocomposite films. Furthermore, the present of 3-APE resulted in the improvement of the interfacial between matrix and the filler, as well as the formation of imine

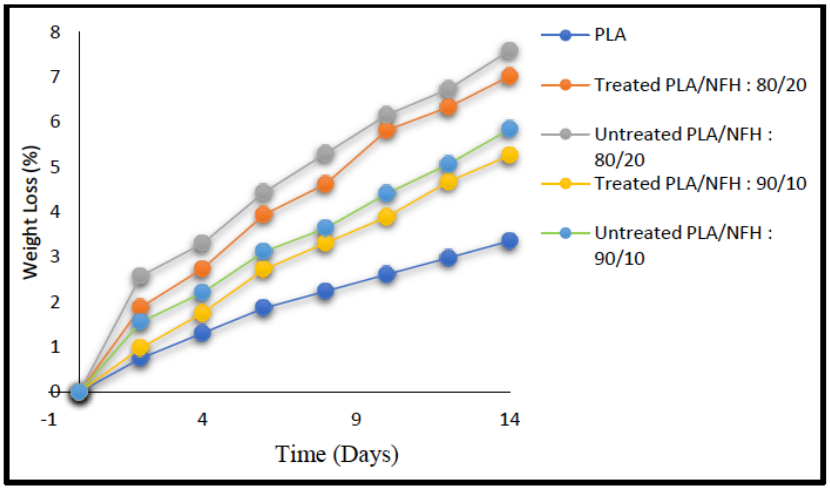

Figure 8: Weight loss (%) of untreated and treated PLA/NFH biocomposite films on enzymatic bio-degradation.

linkages, which led to a reduction in the enzymatic biodegradation.

3.5. Fourier Transform Infrared Analysis

The FTIR spectra of untreated and treated PLA/NFH biocomposite films is shown in Figure **9**. It can be seen on the IR spectrum of untreated biocomposite films at peak 3370.99 cm^{-1} assigns to OH group belonging to NFH. The peaks at 1751.34 cm^{-1} and 1637.97 cm^{-1} attributed to carbonyl (C=O) and C=C stretching from hemicellulose, respectively. Meanwhile, peaks at 1537.5 cm^{-1} and 1452.48 cm^{-1} were C=C and C-H deformation from lignin, respectively. The C-H and C-O groups at peaks 1373.4 cm^{-1} and 1193.49 cm^{-1} were contributed from cellulose and lignin. Furthermore, the peak 1079.95 cm^{-1} was C-O-C group from main carbohydrates of cellulose and lignin. The group peaks at 700 – 900 cm^{-1} were C-H vibration in lignin. The NFH treated with 3-APE found that the IR spectrum significantly reduced of OH group at peak 3330 cm^{-1} to 3399.58 cm^{-1}, remarkably because of the creation of hydrogen bond among NFH and silanol group from 3-APE. The peak at 1083.02 cm^{-1} was credited to stretching of Si-O-Si bonds. Furthermore, band agreeing to Si-O-Si symmetric vibration is placed at 871.26 cm^{-1}. The absorption band for cellulose-O-Si assures condensation response had happened among the cellulose of the NFH and the silanol group, and the band for Si-O-Si is a suggestion of intermolecular condensation having occurred among adjacent silanol groups deposited on the fibers. The presence of 3-APE on the surface of the NFH filler increased the affinity of the filler, thus improving the interaction between NFH and PLA matrix. As a result, the hydrophilic character of the treated NFH decreased significantly.

4. CONCULSION

The optimization and properties of Polylactic Acid (PLA) / Nypa Fruticans Husks (NFH) biocomposite films was successfully investigated via Central Composite Design (CCD) method. From the overall results, the following conclusion can be drawn:

- The design of experiments (DOE) with central composite design (CCD) method confirmed that the optimum value of 3-APE silane coupling agent to improve the tensile strength was 3%. This value did not affect by increased or decreased the NFH content, which has the same efficiency among the range of NFH content used in this study. The ANOVA analysis showed the developed model for tensile strength is significant and it can be used to predict the value of tensile strength in the rage of 3-APE silane coupling agent and NFH content used in this study with same units. This finding was supported by validation with two different sets of values for 3-APE and NFH content
- The incorporation of NFH into PLA matrix tend to decrease of tensile strength and elongation at break of both untreated and treated PLA/NFH biocomposite films with the increasing of NFH content. However, the modulus of elasticity of

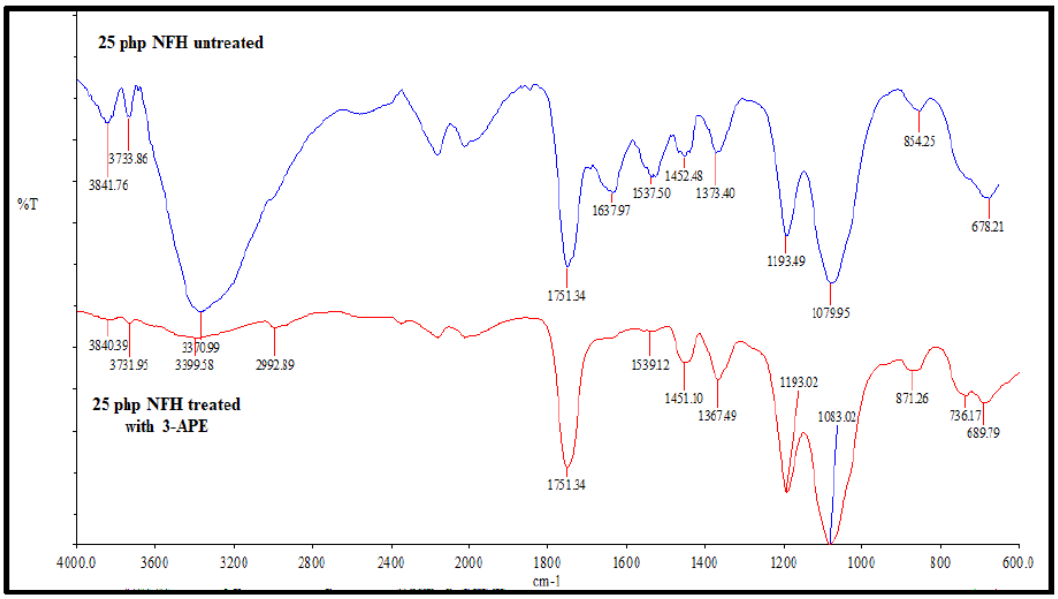

Figure 9: FTIR Spectra of untreated and treated NFH with 3-APE.

untreated and treated PLA/NFH biocomposite films increased with increasing NFH content. This result was supported by SEM micrographs which showed the presence of voids and rough surface on the tensile fractured surface due to poor filler-matrix interaction. Furthermore, the weight loss of PLA/NFH biocomposite films increased with increasing of NFH content and time in enzymatic biodegradation.

- Treated PLA/NFH biocomposite films with 3% 3-APE showed higher tensile strength and modulus of elasticity but lower elongation at break and enzymatic biodegradation rate compared to untreated PLA/NFH biocomposite due to the improved interfacial adhesion between NFH and matrix. The enhancement of interfacial adhesion was supported by the micrographs showing smoother surface, less voids and filler pull out.

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