Alkaline Treatment of Oil Palm Frond Fibers by Using Extract of Oil Palm EFB Ash for Better Adhesion toward Polymeric Matrix

Warman Fatra[1], Randi Sanjaya[2], Zulfansyah[2], Hari Rionaldo[2] & Zuchra Helwani[2]

[1]Department of Mechanical Engineering, University of Riau
[2]Department of Chemical Engineering, University of Riau
Jl. HR Subantas KM 12,5, Kampus Bina Widya, Simpang Baru,
Pekanbaru, Riau 28293, Indonesia
Email: warman_fatra@unri.ac.id

Abstract. In Indonesia, 187 million tons of biomass were produced from 8.11 million ha of oil palm plantation in 2009. This massive amount of biomass mainly consists of oil palm fronds (OPF) and oil palm empty fruit bunches (EFB), which are normally categorized as waste. The properties of OPF fibers compared to those of synthetic fibers, such as low density, low cost, less abrasion of equipment, and safer production, makes them an attractive reinforcement for composite materials. In this work, the utilization of oil palm empty fruit bunch ash for OPF fiber-polyester resin composite and the effect of process conditions were studied. Water absorption, tensile and flexural strength were used to characterize the effects of alkaline treatment on modified OPF fibers in polyester resin. The investigation focused on the effect of alkaline treatment time. Treatment temperature and liquid to solid ratio were analyzed using Response Surface Method-Central Composite Design (RSM-CCD). The highest tensile strength (44.87 MPa) was achieved at 12 hours soaking time, at 40°C treatment temperature and 5:1 water to ash ratio. The highest flexural strength (120.50 MPa) was obtained at 1.3 hours soaking time, 4 dissolving ratio and 35°C treatment temperature. The lowest water absorption of composite (3.00%) was achieved at the longest soaking time (14.7 hours), 4 dissolving ratio and 35°C treatment temperature. Variance of soaking time, dissolving ratio and temperature in the alkaline treatment process using extract of oil palm empty fruit bunch ash significantly affected the mechanical and physical properties of the oil palm frond fibers reinforced composite.

Keywords: *alkaline treatment; composite; oil palm; empty fruit bunch ash; oil palm frond.*

1 Introduction

The utilization of natural fibers for composite reinforcement has been a research topic of interest in the last few decades due to their availability in large amounts and their renewable and biodegradable properties. Advantages in processing

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such as low cost of processing, less equipment abrasion, less skin and respiratory irritation, make natural fibers an interesting alternative for synthetic fibers [1,2]. Natural fibers produce a composite with lower density compared to synthetic fibers, suitable for interior applications such as furniture and automotive elements.

In 2009, approximately 8.11 million ha were planted with oil palm trees in Indonesia and 1.65 million ha in Riau Province, as stated by the Central Bureau of Statistics (BPS). Each oil palm produces 40-50 fronds/year on every hectare planted with 100-120 oil palm trees. This shows that oil palm fronds are abundantly available as a natural fiber.

Natural fiber's challenges include poor compatibility with hydrophobic polymer matrices, the tendency to form aggregates, and low resistance to moisture resulting in poor mechanical properties of the composite [1]. Chemical modification of the fibers such as alkaline treatment can increase compatibility [3]. The alkaline solution can be obtained from oil palm empty fruit bunch (OPEFB) ash, which is disposed of in large quantities. OPEFB ash majorly contains potassium, which dissociates in water to form potassium hydroxide.

2 Material and Method

2.1 Material and Apparatus

The materials used for manufacturing composite in this study were oil palm frond fibers, oil palm empty fruit bunch ash and unsaturated polyester resin (UPR) Yukalac 157 BQTN-EX obtained from Justus Kimia Raya Ltd. OPF and OPEFB ash obtained from Experimental Plantation University of Riau and the National Plantation V palm oil mill in Sei Galuh, respectively. The universal testing machine at the Mechanical Engineering university laboratory of Riau was used to conduct the tensile and flexural test.

2.2 Fiber Preparation

Fibers were extracted by water-ret process for a day and cut at a length of 16.7 cm. The fibers were dried for 3 hour at 60°C before treatment with alkaline solution. The OPEFB was dissolved in water with different water to ash ratios (varying from 3-5 weight basis) for 48 hours. Alkaline treatment was conducted at temperature 30-40°C for 4-12 hours soaking time. After treatment, the fibers were stored in a desiccator before composite molding.

2.3 Composite Molding

The composites were molded by six pieces of squared glass that were arranged in a certain direction with dimensions of 105 x 175 x 5 mm^3. The fibers were lain in continuous-aligned orientation using hand-layout. Each molded composite was cut into three samples for the tensile strength test, three samples for the flexural strength test, and two samples for the water absorption test.

2.4 Mechanical and Physical Properties

Tensile strength, flexural strength, and water absorption tests were carried out using methods developed by the American Society for Testing and Materials (ASTM). Tensile strength was tested in accordance with the ASTM D 638-03 Standard Test Method for Tensile Properties of Plastics with specimen dimension type I (165 x 19 x 5 mm^3). Flexural strength was tested using a universal testing machine in accordance with the ASTM D 790-03 Standard Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials. Water absorption was tested in accordance with the ASTM A 570 Standard Test Method for Water Absorption of Plastics. The test specimens were immersed in distilled water for 24 hours at room temperature. After immersion, the specimens were removed from the water and weighed immediately after all the surface water was wiped off with a dry cloth.

2.5 Data Tabulation

A mathematical model of variables and responses can be obtained from the design of the experiment, the central composite design [4]. A second order regression model (Eq. (1)) was generated to relate the variables and responses.

$$Y = \beta_o + \beta_o X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X \quad (1)$$

Y = response
$\beta_o, \beta_i, \beta_{ij}$ = model coefficient
X_i = coded variables

The analysis of variance model was calculated using Design-Expert® 7.0.0 to check the lack of fit of the current model based on F-value and P-value.

3 Results and Discussion

Fiber is a lignocellulose material that has bonds in the amorphous matrix of lignin and hemicellulose. The fibers are embedded in the hemicellulose and bound by pectin. In the water-ret process, skinned-chopped oil palm fronds were soaked and biological decomposition occurred because a pectinolytic

bacterial community developed and attacked the pectin [5]. Pectin is the major component of hemicellulose that binds the fibers together. The water-ret process took 10-15 days to extract the fibers completely. A change in water physical properties could be observed, such as an increase in viscosity and a darker color. The presence of residue after the process was observable. The product of this process was whitish-continuous oil palm frond fibers.

After the soaking time reached its set time, the fibers were removed from the solution and washed with tap water. While washing, a slippery surface on the fibers could be felt. This is caused by the nature of the alkaline solution, which is slick. The fibers were washed until the pH of the wash solution was neutral, which was tested by universal pH paper in order to ensure the complete removal of the alkaline solution from the fiber's surface. After washing, the fibers were dried in an oven for 3 hours to reduce the moisture content. This treatment was carried out to minimize the risk of the fibers decomposing. The weight after treatment should be reduced, which was confirmed by weighing the fibers before and after treatment.

Table 1 shows the experimental design obtained in each response for tensile strength, flexural strength and water absorption under process conditions of soaking time (X_1), water to ash dissolving ratio (X_2), and treatment temperature (X_3).

Table 1 Experimental Design and Results of Properties.

Run	Natural variables			Tensile strength (MPa)	Flexural strength (MPa)	Water absorption (%wt)
	X_1 (hour)	X_2	X_3 (°C)			
1	4	3	30	36.55	111.60	4.24
2	12	3	30	39.53	100.92	3.47
3	4	5	30	32.95	119.32	4.95
4	12	5	30	40.8	89.61	4.74
5	4	3	40	32.01	114.26	3.47
6	12	3	40	39.08	121.91	3.83
7	4	5	40	38.70	94.25	4.66
8	12	5	40	44.87	98.82	3.80
9	1.3	4	35	39.08	120.5	3.82
10	14.7	4	35	31.89	98.45	3.00
11	8	2.32	35	38.89	98.57	4.57
12	8	5.68	35	35.85	89.30	4.86
13	8	4	27	40.79	97.97	6.37
14	8	4	43	44.31	75.73	3.79
15	8	4	35	33.95	85.51	4.24
16	8	4	35	35.28	103.86	4.14
17	8	4	35	35.54	88.99	4.20
18	8	4	35	36.73	84.89	3.86
19	8	4	35	36.87	80.55	4.54
20	8	4	35	34.90	89.22	4.53

3.1 Analysis of Tensile Strength

The tensile strength of the oil palm frond fiber reinforced composite ranged from 31.89-44.87 MPa. The highest tensile strength of the composite resulted from 12 hours soaking time, 40 °C treatment temperature, and 5:1 water to ash ratio.

The F-value of the model was 3.28, which is greater than $F_{0.05,9,29}$. In this case, the model was significant to the responses, which means that the model could be used to predict the response. The P-value of the model also supported the significance of the model, which value was at 0.0071. Tensile strength can be modeled to:

$$Y = 35.56 + 0.88X_1 + 0.37X_2 + 0.79X_3 - 0.14X_1^2 + 0.52X_2^2 + 2.35X_3^2 + 0.49X_1X_2 + 0.39X_1X_3 + 1.85X_2X_3 \quad (2)$$

Table 2 ANOVA Summary of Each Response.

Source	Tensile Strength		Flexural Strength		Water absorption	
	F-value	P-value	F-value	P-value	F-value	P-value
Model	3.284	0.007	6.400	< 0.0001	5.87	0.000
X_1	2.312	0.139	6.901	0.014	4.30	0.047
X_2	0.410	0.527	6.292	0.018	6.85	0.014
X_3	1.859	0.183	1.423	0.243	18.60	0.000
X_1X_2	0.431	0.517	1.352	0.254	0.40	0.534
X_1X_3	0.158	0.694	7.660	0.010	0.20	0.661
X_2X_3	6.043	0.020	4.318	0.047	0.58	0.452
X_1^2	0.066	0.798	27.117	< 0.0001	12.79	0.001
X_2^2	0.867	0.359	4.424	0.044	1.20	0.283
X_3^2	17.551	0.000	0.473	0.497	5.73	0.023
Lack of Fit	6.056	0.003	0.679	0.776	3.41	0.026

Note: X_1=soaking time; X_2=dissolving ratio; X_3=temperature

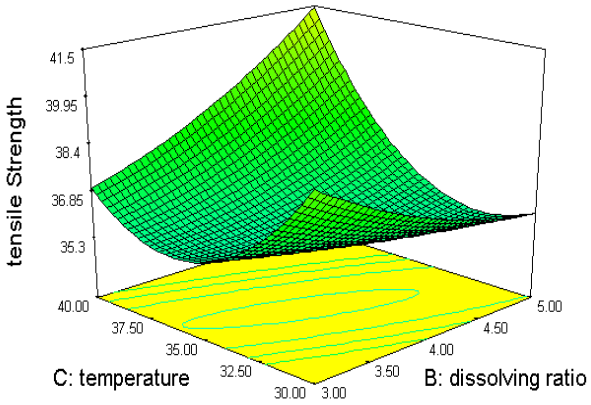


Figure 1 Tensile strength as a function of treatment temperature and dissolving ratio.

Eq. (2) was modeled on the codec variable to see the significant terms of response. Analysis of variance of the tensile strength model gave a P-value of the terms X_2X_3 and $X_3^2 < 0.05$, which means the interaction of water to ash ratio with temperature and temperature square had significant effect on the model (see Table 2).

In Figure 1, the tensile strength increased with the increase of soaking time at low and high temperature. The longer the soaking time, the more impurities such as lignin and hemicellulose were removed from the fiber's surface. This result is different from that of previous research [6].

3.2 Analysis of Flexural Strength

The flexural strength is the parameter of maximum stress or load of material when its bends. The flexural strength results showed good statistical parameters for influenced variables. The flexural strength of the OPF fiber reinforced composite ranged from 75.73-120.50 MPa. The highest flexural strength was obtained at 1.3 hours soaking time, 4 dissolving ratio and 35°C treatment temperature.

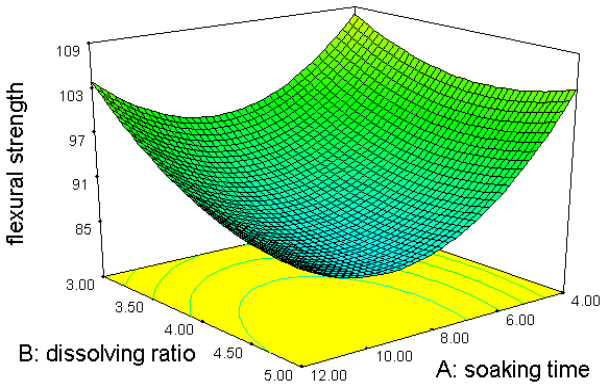


Figure 2 Flexural strength as a function of soaking time and dissolving ratio.

The F-value of the model was 6.40, which is greater than $F_{0.05,9,29}$. In this case, the second order regression model was significant to the responses, which means the model could be used to predict the response. The P-value of the model also supported the significance of the model with a value at < 0.0001. From the experimental data above, the flexural strength could be modeled to:

$$Y = 88.54 - 4.78X_1 - 4.56X_2 - 2.17X_3 + 9.22X_1^2 + 3.72X_2^2 + 1.22X_3^2 - 2.76X_1X_2 + 6.58X_1X_3 - 4.94X_2X_3 \quad (3)$$

Eq. (3) was modeled on the codec variable to see the significant terms of response. Analysis of variance of the flexural strength model gave a P-value of the terms X_1, X_2, X_1X_3, X_2X_3, X_1^2 and $X_2^2 < 0.05$, which means that each mentioned term had a significant effect on the model, with X_1^2 having the largest effect.

From the significance of each term, the soaking time and dissolving ratio had a significant effect on the flexural strength, as shown in Figure 2. At a longer soaking time, the flexural strength showed a significant increase by reducing the dissolving ratio. A shorter soaking time and lower dissolving ratio showed the highest prediction of flexural strength. This result is in contrast with the tensile strength. The difference may be due to the different direction of the load, which greatly affects anisotropic materials. An anisotropic material is a material that has different properties in different directions. A matrix is considered an isotropic material. When reinforced with fibers, the material becomes anisotropic so that it should be classified as an orthotropic material. Orthotropic materials have properties that are different in three mutually perpendicular directions [7].

Flexural strength increased with the decrease of soaking time and temperature. The longer the soaking time and the higher the treatment temperature, the more impurities such as lignin and hemicellulose were removed from the fiber's surface. This suggests that the OPF fibers become relatively ductile after the removal of some hemi-cellulose and lignin [8]. The dissolving ratio had a weaker effect on the flexural strength compared to temperature as can be seen from the gradient. At higher temperature, the dissolving ratio showed a more significant effect on flexural strength.

3.3 Analysis of Water Absorption

Water absorption was determined to measure the effect of the process variables of the treatment. High water absorption will result in less dimensional stability, matrix and fiber adhesion, biological degradation, mechanical and electrical properties. The main factor that affects water absorption in natural fiber reinforced composites is the hydrophilicity of the natural fiber. The water absorption of OPF fiber reinforced composite ranged from 3.00-6.37%. The lowest water absorption of the composite was achieved at the longest soaking time (14.7 hours), 4 dissolving ratio and 35°C treatment temperature. From the experimental data above, the water absorption could be modeled to:

$$Y = 4.26 - 0.21X_1 + 0.27X_2 - 0.44X_3 - 0.35X_1^2 + 0.11X_2^2 + 0.24X_3^2 - 0.084X_1X_2 + 0.059X_1X_3 - 0.10X_2X_3 \quad (4)$$

Eq. (4) was modeled on the codec variable to see the significant terms. The significance of each term in the equation can be seen from its P-value. Analysis of variance of the tensile strength model gave P-values of the terms X_1, X_2, X_3, X_1^2 and $X_3^2 < 0.05$, which means that the terms had a significant effect on the model. The F-value of the model was 5.87, which is greater than $F_{0.05,9,29}$. In this case, the model is significant to the responses, which means the model could be used to predict the response. The P-value of the model also supported the significance of the model, with a value of 0.0001.

Figure 3 shows a graphical representation of the water absorption model being most significantly affected by the dissolving ratio and treatment temperature. The trend of water absorption is in agreement with the trend of tensile strength, which are desirable properties achieved at higher soaking time and higher temperature. The result can be related to the removal of hydrophilic components from the fiber's surface. The reduction of the hydrophilic character of the fibers also contributes to lowering the water absorption of the composite [9]. Alkaline treatment promotes ionization, which substitutes the hydrogen ions in the hydroxyl groups of cellulose and lignin with alkoxide and changes the hydrophilicity of the fiber [2]. Alkaline treatment removes a certain amount of the amorphous waxy layer on the surface that normally holds water molecules and lowers the water absorption rate.

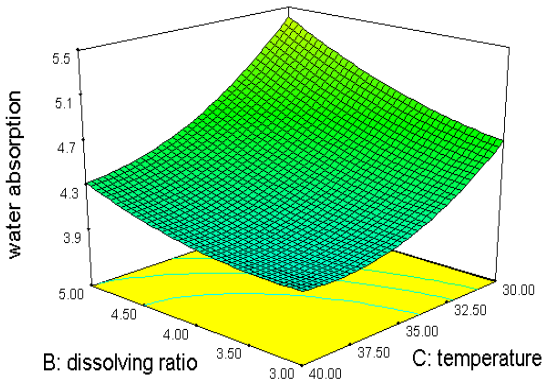


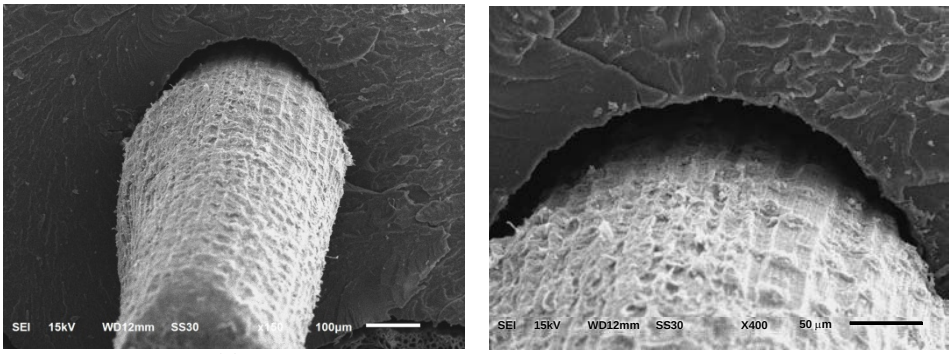
Figure 3 Water absorption as a function of dissolving ratio and temperature.

3.4 SEM Analysis

A morphological analysis of the OPF fibers-polyester composite was carried out using SEM (scanning electron microscopy) at the Mathematics and Science Faculty, Bandung Institute of Technology. The morphological details of a single fiber interaction toward the matrix (unsaturated polyester resin) can be seen in

Figure 4. The highest tensile strength sample was picked and analyzed. Because the fiber loading was relatively low (35% v/v), only a single OPF fiber interaction toward polyester can be observed in these magnifications.

The highest tensile strength was lower than that of the unreinforced polyester, at 5.5 kg/mm^2 (53.94 MPa). The gap between fiber and matrix as can be seen in Figure 4 is the cause of the inferiority. Another cause is the void in the composite that was formed in the molding process. The void was formed because of air trapped in the matrix during processing. Gaps and voids can reduce the mechanical strength of the composite, which lessens the efficiency of the reinforcement. Fiber reinforced composite used for load bearing cannot receive the load because the air that fills the gaps and voids reduce the load transfer [2].



(a) (b)

Figure 4 SEM of fracture surface of OPF fiber composite on (a) 150 x magnification and (b) 400 x magnification.

4 Conclusions and Recommendations

4.1 Conclusions

Variance of soaking time, dissolving ratio and temperature in alkaline treatment using extract of oil palm empty fruit bunch ash significantly affects the mechanical and physical properties of oil palm frond fiber reinforced composite. All models generated from the experimental data could be used to predict the response in the process variable range. The dissolving ratio and temperature have an influence on the tensile strength. An increase in temperature and dissolving ratio increased the tensile strength of the composite. Each variable had a significant effect on flexural strength, but soaking time was the most determining factor. An increase in soaking time lowered the flexural strength of the composite. Each process variable influenced water absorption,

but temperature gave the most significant effect on the response. An increase in treatment temperature lowered the water absorption of the composite.

4.2 Recommendations

Some recommendations for further research are suggested in order to avoid possible mistakes and errors. The recommendations are:

1. To characterize the interaction between fibers and matrix it is better to use less than 10% v/v fiber loading to reduce the risk of void formation.
2. Before the molding process, dry fibers in the oven in order to minimize the water content of the fibers, which will minimize potential void formation.
3. Experiment with anti-bubble layers for resin and other molding techniques to reduce void forming.

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