

Properties of Bio-Phenol Formaldehyde Composites Filled with Empty Fruit Bunch Fiber

Sharifah Nabihah Syed Jaafar, Umar Adli Amran, Rasidi Roslan, Chia Chin Hua, Sarani Zakaria

Abstract—Bio-composites derived from plant fiber and/or bio-derived polymer, are likely more ecofriendly and demonstrate competitive performance with petroleum based composites. In this research, the bio phenol-formaldehyde (bio-PF) was used as a matrix and oil palm empty fruit bunch fiber (EFB) as reinforcement. The matrix was synthesized via liquefaction and condensation to enhance the combination of phenol and formaldehyde, during the process. Then, the bio-PF was mixed with different percentage of EFB (5%, 10%, 15% and 20%) and molded at 180°C. The samples that viewed under scanning electron microscopy (SEM) showed an excellent wettability and interaction between EFB and matrix. Samples of 10% EFB gave the optimum properties of impact and hardness meanwhile sample 15% of EFB gave the highest reading of flexural modulus (MOE) and flexural strength (MOR). For thermal stability analysis, it was found that the weight loss and the activation energy (Ea) of the bio-composites samples were decreased as the filler content increased.

Keywords—EFB, liquefaction, phenol formaldehyde, lignin.

I. INTRODUCTION

NOWADAYS, demand of sustainable and renewable resources materials is increasing and demanding [1]. The utilization of biomass and wastes in making composites has become more important and feasible. In addition, bio-composites offered several advantages such as low cost, lightweight structures, and tailored properties. Bio-composite is taking place mainly in automotive and packaging materials [2]. The unique properties of the combination natural fiber as reinforcements and bio-based polymer as matrix in producing composite materials will not found in the single material [3].

Bio-phenol formaldehyde (bio-PF) is used in many applications such as a binder, adhesives, household appliances and others. It can be synthesized via thermochemical method with low temperature, low pressure and the addition of acid catalyst such as hydrochloric and sulfuric acid. Liquefaction is an excellent method to convert lignocellulose material (LS) into liquid using phenol as a solvent and continue with condensation of phenolated LS with formaldehyde. The pathway of bio-PF process is decomposition of LS to the

certain point and thus reacted with the specific solvent to produce various value added chemicals. Introducing the aromatic structure in LS into phenol can enhance the PF resin properties and performances. One example of LS that rich with aromatic structure is lignin. It consists of highly branched structure of phenyl propane units. Lignin is a byproduct from pulp and paper industry. The existence of lignin caused the paper properties incredibly reduced.

Empty Fruit Bunch (EFB), acts as reinforcement was blended into the bio-PF to improve the stiffness and strength properties of the matrix. Awareness of using EFB fibers has been popular and chosen in this research due to its availability, non-abrasive and biodegradable material. The addition of EFB in the matrix should give high impact strength and better water resistivity, good dispersion and great wettability. The purpose of this work is to study the effect of EFB percentage into the bio-PF which has been synthesized from lignin on their morphology, mechanical, physical and thermal properties.

II. EXPERIMENTAL AND PROCEDURE

A. Preparation of Bio-PF

For bio-PF synthesize, there were two steps to be undergone. First was liquefaction of lignin into phenol with acid catalyst and followed with condensation of liquefied lignin in 37% formaldehyde.

Dried lignin and phenol with ratio 1:3 and 5% of hydrochloric acid were added into three necked flask and heated at 130°C, in a reflux condenser, equipped with thermometer and stirrer. The liquefaction process was continuously stirred at for 90 minutes, to obtain a homogenous mixture. Then, the liquefied sample was added with formaldehyde for 60 minutes at 100°C by completing the condensation reaction of synthesized PF.

After that, the resulting reaction mixture was diluted using 500 ml methanol and filtered to separate the soluble and insoluble products. The soluble part was continued with neutralization with magnesium oxide (MgO) and filtered. The filtered solution was recovered by evaporations at temperature 70°C and 180°C to remove the methanol and unreacted phenol, respectively.

B. Blending Bio-PF with EFB

The synthesized PF was then diluted in acetone. Zinc stearate (accelerating agent), calcium hydroxide (lubricating agent), hexamine (curing agent) and different percentage of EFB (5%, 10%, 15% and 20%) were premixed in the mortar and mixed with bio-PF until homogenous. The resulting

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Syed Jaafar. Sharifah Nabihah is with Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia (corresponding author to provide phone: 603-89214983; fax: 603-89213777; e-mail: nabihah@ukm.edu.my).

Amran. Umar Adli and Roslan. Rasidi are postgraduate students in School of Applied Physics, Universiti Kebangsaan Malaysia (email: adliamani90@gmail.com & rasidiroslan2006@gmail.com).

Chin Hua. Chia and Zakaria. Sarani are with Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia (e-mail: chia@ukm.edu.my, szakaria@ukm.edu.my).

mixture was reground in electric grinder after it has been dried in an oven at 70°C for 1 hour.

About 45 g of the mixture were molded into test specimens of 50mm x 130mm x 3mm. The molded sample was undergone a preheating treatment for 1 minute and followed by 10 minutes molding at 185°C. The molded sample was cooled under room temperature before it was cut to a certain dimensions. The molded bio-composite were analyzed and tested for morphology, mechanical, physical and thermal behavior. Sample without any filler could not be formed due to poor wet ability between resin and EFB hence the addition of filler has encountered to this problem.

III. CHARACTERIZATIONS

A. Morphology Analysis

Morphology of the fractured samples were coated with gold and observed with a scanning electron microscope (Philips, XL-30) at 20 kV.

B. Mechanical Testing

Impact strength of the samples was determined by using Universal Impact Pendulum Tester Ceast Code 6545/000 by following ASTM D256. The un-notched samples was cut with dimensions 60mm x 15mm x 3mm. Value of the impact strength obtained represented the mean of five samples.

The modulus of rupture and (MOR) and modulus of elasticity (MOE) was conducted according to ASTM D790, three point bending system by using Testometric machine with a crosshead speed 10mm/min. The size specimen for this testing was 13 mm x 130 mm x 3.4 mm. Five samples were tested for each composition and the average values were reported.

For the hardness testing (ASTM D2240), the samples were tested by using durometer hardness shore D (Zwick Model). The value of the hardness was measured just after the pressure foot is contact with the specimen.

C. Physical Testing

Determination for the density of composite samples was undergone according to ASTM D1037. The density of the composite samples (60mm x 15mm x 3mm) was measured by a Mirage electrical densitometer MD-200S with 0.001 resolution.

For the water absorption test, the samples were immersed in the distilled water. After the required period, the samples were taken out, wiped to remove the excess water and the width of the samples was measured by using the digital calliper. At least five samples were used to obtain the accurate readings. The test condition was followed by ASTM D570.

D. Thermal Analysis

Thermogravimetry was carried out to investigate the thermal performance of EFB content in the samples. The analyses were performed by using TGA Mettler Toledo 220, between temperature 30°C until 700°C at a heating rate of 10°C/min and under a nitrogen atmosphere. The Broido

equation, as shown in (1) was used to determine the activation energy (Ea) of the samples.

$$\ln\left(\ln\frac{1}{y}\right) = -\frac{Ea}{R} \frac{1}{T} + \ln\left(\frac{R}{Ea} \frac{Z}{R_H} T_m^2\right) \quad (1)$$

IV. RESULTS AND DISCUSSION

A. SEM Morphology

From SEM studies, it shows that the EFB is successfully embedded in the bio-PF even after been undergone high speed load testing. This is due to a good interaction between bio-PF and EFB. No fibers have been pulled out and they are fully covered by the resin. The position of EFB in the bio-PF is different in every specimens. However, increasing the EFB content would eliminate the interactions between bio-PF and EFB [4].

Samples with 10% and 15% of EFB show very strong interaction between PF resin and EFB. Fig. 1 shows that after the impact test, the bio-PF has been removed from the fiber surfaces but the EFB fiber remained in their positions. It is obviously can be seen that there is resin adhering on the surface of the EFB from (Figs. 1 (b) and (c)). This result indicates strong interaction between the matrix and EFB. On the other hand, the fiber and matrix in 5% EFB and 20% EFB sample were broken and cracked. The result indicates that absorption of the impact energy has been successfully transferred from the bio-PF to fibers.

The bio-PF composites produced voids and bubbles in the sample. Both can be found on the matrix surface. However, the number and size of voids reduce as the EFB content increase. The existence of the voids and bubbles are due to temperature and pressure during molding.

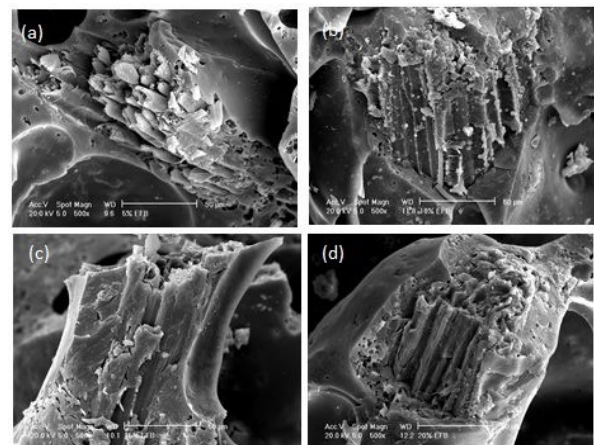


Fig. 1 SEM micrographs of the fractured surface for composite samples (a) 5% EFB (b) 10% EFB (c) 15% EFB (d) 20% EFB

B. Mechanical Testing

Fig. 2 shows the trend in impact strength of the composite samples. Generally, the impact strength decrease as the EFB content increased. The highest impact is observed at 10% EFB followed by 15%, 20% and 5% at the strength of 1805, 1733, 1086 and 1067 J/m² respectively. The greater addition of EFB

eliminates the interaction capability between bio-PF and EFB. According to Rozman et al. [5], the weak interaction between matrix-fiber, can reduce the efficiency of the load transfer during the testing. High content of filler might interrupt the interaction between matrix and fibre.

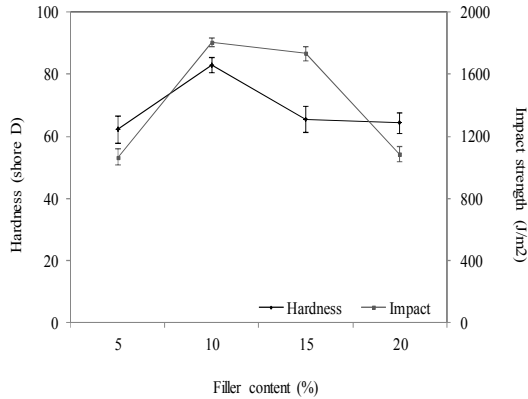


Fig. 2 Effect of filler content on the impact strength and hardness

Results of hardness (Fig. 2) shows the same trend as the impact strength, where the hardness decreases as the EFB content increase. Sample with 20% EFB shows the lowest hardness at the scale of 64.4. The amount of bio-PF is not enough to encapsulate the EFB and in addition, the matrix-fiber has a weak interfacial adhesion.

Fig. 3 presents the variation of the flexural strength (MOR) and flexural modulus (MOE) of the composite samples. The MOR and MOE have similar trends which the value increases as the EFB increase linearly but drop after an optimum content of EFB. Maximum value of MOR and MOE are encountered at 15% of EFB with 17.9 MPa and 3110 MPa respectively. However, with 20% fiber content, MOR and MOE decrease to 17.05 MPa and 2770 MPa, by about 4.8% and 10.9% respectively.

Samples with low MOR cause poor properties and ductility. This phenomenon has been approved with deflection testing (Fig. 4) where the deflection for sample 15% EFB gives the highest value compare to other samples. This is due to the poor compatibility between resin and EFB and increment in EFB-EFB interactions [6] and also the existence of voids in the samples. The mechanical properties of the composite samples are strongly affected by the voids [7].

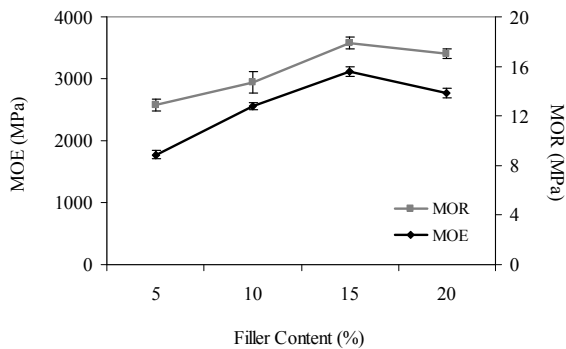


Fig. 3 Effect of filler content on the MOR and MOE

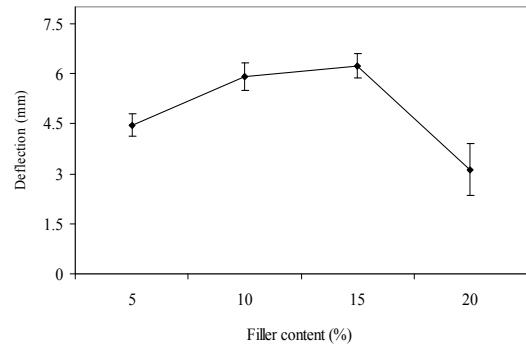


Fig. 4 Deflection versus filler content

C. Physical Properties

Fig. 5 shows the density of the composite samples increase as the EFB fiber increase. The addition of EFB gives a significant effect to the density of the composite samples. Moreover, the addition of the EFB fiber would reduce the existence of voids in the samples. The figure indicates that the addition of 20% EFB caused the density increases up to 34.09%.

Poor mechanical properties due to weak adhesion between bio-PF and EFB increase the tendency of the composite samples to absorb water [8]. As discussed before, sample 10% and 15% of EFB show the best mechanical properties compare to 5% and 20% of EFB. From Fig. 6, it shows clearly that sample with 10% and 15% of EFB just absorb 2.0% and 2.4% respectively compare to sample 5% and 20% which absorb 2.6% and 5.1% respectively for 72 hours immersion. Samples with high content of EFB tend to absorb more water [9].

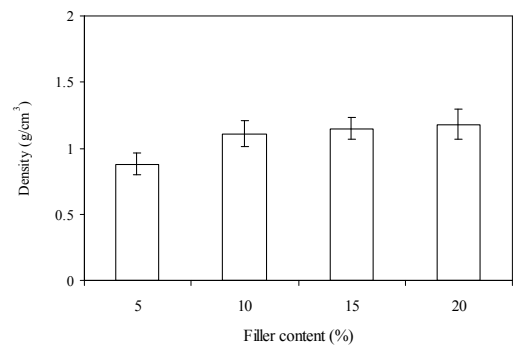


Fig. 5 Effect of filler content on the density of the samples

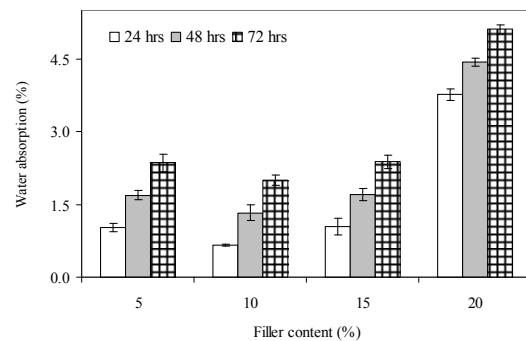


Fig. 6 Influence of filler content on water absorption of the samples at different time

D. Thermal Analysis

Fig. 8 shows the thermograms of the bio-PF filled with EFB fiber (5%, 10%, 15% and 20%). All samples undergone two stages of weight loss which is at temperature 100°C and ~260°C. It is believe that water was adsorbed at the first stage and continued by degradation of lignocellulosic at the second stage [10]. After 600°C, the residue for every samples of 5%, 10%, 15% and 20% EFB were 59.7%, 53.7%, 53.6% and 52.6% respectively (Table I). The same results also reported by Ruseckaite [11] where sample with the highest content of filler has critical weight loss compared to the sample with the lowest amount of filler [12].

TABLE I
THERMOGRAVIMETRIC RESULTS

Sample	Weight loss (%)	Ea (kJ/mol)	R ²
5% EFB	59.7	17.77	0.999
10% EFB	53.7	17.05	0.999
15% EFB	53.6	16.98	1
20% EFB	52.6	16.09	1

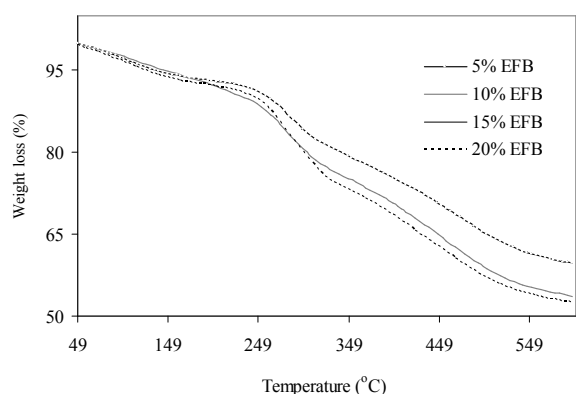


Fig. 7 TGA thermograms of the composite samples with different EFB content

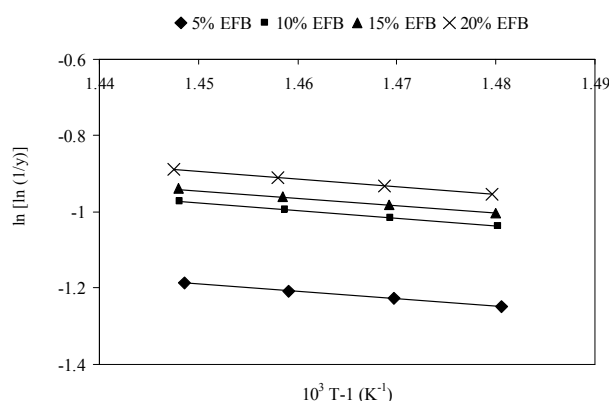


Fig. 8 Plot of $\ln(\ln 1/y)$ vs $1/T$ (kJ/mol) by using Broido equation

The value of activation energy (E_a) decreases as the addition of EFB content increase which is shown in Fig. 8. Sample with 5% EFB has the highest value of E_a with 17.77 kJ/mol meanwhile sample 20% EFB has the lowest value of E_a with just 16.09 kJ/mol. This shows that the content of the

EFB has great effect on the thermal stability of the bio-composite samples. The samples become less stable as the addition of EFB content increase [13] of the samples.

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Syed Jaafar. Sharifah Nabihah was born in February 1st, 1985 in Kuala Lumpur, Malaysia. She started to join Universiti Kebangsaan Malaysia in 2007 as tutor. Hold a bachelor (2004) and master degree (2009) in Material Science from Universiti Kebangsaan Malaysia and doctoral study at University of Natural Resources and Life Sciences (2013), Austria in Renewable Chemistry.