Effect of oil palm empty fruit bunches fibers reinforced polymer recycled

B Hermawan[1], S Nikmatin[1], Sudaryanto[2], H Alatas[1] and S G Sukaryo[2]

[1]Applied Physic Division, Department of Physics, Bogor Agricultural University,
Jl. Meranti, Kampus IPB Darmaga, Bogor,16680, Jawa Barat, Indonesia.
[2]Centre for Science and Advanced Materials Technology, National Nuclear Energy Agency of Indonesia, South Tangerang, Indonesia

E-mail : sitinikmatin@yahoo.co.id

Abstract. The aim of this research is to process the OPEFB to become fiber with various sizes which will be used as a filler of polymer matrix recycled acrylonitrile butadiene styrene (ABS). Molecular analysis and mechanical test have been done to understand the influence of fiber size toward material capability to receive outer deformation. Single screw extruder formed a biocomposites granular continued with injection moulding to shaped test pieces. Maleic anhydride was added as coupling agent between filler and matrix. Filler concentration were 10 and 20% in fiber size respectively with constant additif. Two kind of fiber glass (10%) were used as comparator. In order to analyze the results of the mechanical test Fisher least significant difference (LSD) in ANOVA method was performed (-with α=0,05-).

1. Introduction

Nowadays a lot of special interest in environmental friendly material developing especially wasted natural products processing with a touch of technology. Oil palm empty fruit bunches (OPEFB) were one of the solid waste produced from crude palm oil (CPO) manufacturing and its biomass were totally plentiful [1]. Concern increase in polymer waste is a starting point to reduce and reuse it. The Acrylonitrile Butadiene Styrene (ABS) plastics are found in numerous items, such as household items (appliances, piping, luggage, etc), automobile parts, and aircraft interior structure [2].

In term of reinforcement material two fiber categories has been defined, first are fibers from natural on the other hand is sintetic material [3]. Several study has explored the using of natural fiber as a reinforcement agent in biocomposites, the material of wich include rattan [4], banana [5], nut-shells [6], almond shells [7].

In this research a mechanical milling without chemicals assistance has been processed OPEFB to become a various fiber [8]. It is a great challenge in order to screening the composition that have a good mechanical properties, and a statistical model was performed to make a clear difference among all of the treatments. Because of the abundant of the OPEFB and its sustainability, it would be efficient to utilize them as a biocomposites application to reinforced matrix recycled polymer ABS. Other than that, the use of of this natural fiber can replace the need of synthetic fiber as a

reinforcement agent. Thus, the aim of this research is to process the OPEFB to become fiber with various sizes which will be used as a filler of polymer matrix acrylonitrile butadiene styrene (ABS) and also can replace the used of fiberglass as a synthetic filler.

2. Materials and Method

OPEFB was taken from PKS-PTPN VIII Cikasungka, Bogor, West Java. The research was held at laboratory of physics department Bogor Agricultural University (IPB), National Nuclear Energy Agency of Indonesia (BATAN) Serpong and PT MUB Jaya Cibinong.

In this research the OPEFB immediately taken from the conveyor before it entered the dump truck then brought it to the laboratory to be cleaned in a container full of tap water. All cleaned OPEFB has been chopped to form a chip afterward dried under the sun about 2 days and continued by oven (YENACO tipe YNC-OV) at $100^{o}C$ about 6 h, m= 2 kg. Into a mechanical milling (FOMAC type FCT-Z2000) a dried chips milled about 10 min, v= 25000 rpm, m= 0.5 kg. A score of times sieve-shaker was done to obtained a various fiber size using a 20 mesh and 100 mesh sieve.

For the matrix recycled ABS supplied by PT MUB Jaya, Bogor was then used. The additives used in this study were maleic anhydride from Germany. A prepared mixture stirred up by a mixer machine afterward get it into the single screw extruder (SSE) machine hopper, m= 25 kg to form a biocomposites granular. In the barrel samples blended with a gradient temperature of 195–215–220–220–220–225–225–225°C. Biocomposites granular entered the moulding machine (Hwa Chin, HC-250, China), m= 5 kg with a gradient temperature of 170-185- 200°C to shaped a test pieces.

2.1. Fiber Size Measurement

In order to make a measurement of the real fiber size samples were put under a light microscope (OLYMPUS BX-51) connected to a computer installed with DP2-BSW software to help carry out the measurements. The t-student distribution was performed to make the 95% confidence interval of the fiber size using Minitab 17 software.

2.2. Molecular Analysis

OPEFB fibers, ABS polymers, and biocomposites granular then analyzed further related to functional groups of constituent materials using Spectrophotometer Fourier Transform Infra Red (ABB, model MB300, Canada). OPEFB short fiber powder made into pellets with KBr method, while granular ABS and biocomposites is made into a thin film ($\pm$ 1 µm).

2.3. Mechanical Test

Rockwell test method has been done according to ASTM D-785 using Jinan hensgrand instrument, model XHRD-150 from China to test the sample hardness. Whereas izod impact test also has been done according to ASTM D-256A using Jinan hensgrand instrument, model XJU-22 from China to determined the samples ability to received outer impact. Both of the test performed in five repetition. All of the results were analyzed by Fisher least significant difference (LSD) test in ANOVA one way method (with $\alpha=0.05$) using Minitab 17 software.

3. Results and Discussions

3.1. Fiber size

Prior to analyzed both of outlier test and normality test was performed. Outlier test use to identify a single outlier in a sample, Dixon ratio help to detect outlier in the presence of other suspected outlier. Dixon noted that larger samples from normal population are more likely to include extreme values. Whereas Normality test used to determine wether the data follow a normal distribution, because tests that require normally distributed data could produce misleading results if used with non normal data.

Kolmogorov-Smirnov (K-S) test can be used for detecting differences of any kind between the population from wich samples have been drawn [9]. The distribution size of fiber obtained from the microscope observation (Figure 1) were shown in Table 1. In terms of size the mention of medium and short fiber based on the fiber separation using a sieve.

Table 1. t-student distribution of fiber size from microscope observation.

Sieve	Fiber Size		Class
	Length (µm)*	Diameter (µm)*	
Passed through 20 mesh	339 - 1746	104.6 - 191.0	Medium
Passed through 100 mesh	161.9 - 298.3	42.05-75.02	Short

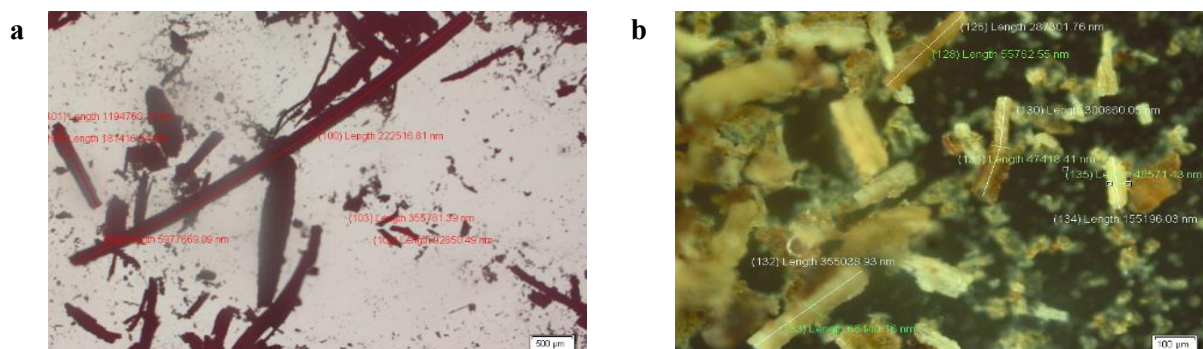***** 95% confidence interval

Figure 1. OPEFB fiber image (a) medium (b) short

Table 2 shows the wide variety of treatments based on the size of the fibers to produce biocomposites. Fiberglass composites used as comparison because it is used by companies to supply the demand for raw materials for making other products. Concentrations of 10 and 20% used to be able to see the extent to which the composition OPEFB as natural fibers can replace the use of fiberglass as synthetic fibers. Coupling agent were added in a fixed amount in order to see the effects of fiber size and fiber concentration.

Table 2 Various biocomposites treatment.

Treatments	Fiber conc (%)	Coupling agent (%)	ABS recycled (%)
Fiber glass 1 (FG1)*	10	-	-
Fiber glass 2 (FG2)**	10	-	-
Medium Fiber 10% (MF10)	10	2	88
Medium Fiber 20% (MF20)	20	2	78
Short Fiber 10% (SF10)	10	2	88
Short Fiber 20% (SF20)	20	2	78

 * Fiberglass-ABS composites from factory 1
**Fiberglass-ABS composites from factory 2

3.2. Molecular Analysis

A common way of polymer blends is adding a coupling agent to reduce the interfacial tension, increase the adhesion, and obtain better properties. We shall be concerned mainly with organic molecules, both of butadiene and styrene in ABS matrix and maleic anhydride. This three molecules, because of the C=C (Carbon double bond) were extremely reactive (**Figure 2**). Methacrylic acid, acrylic acid, maleic anhydride (MAH), and long chain unsaturated monomers are among the monomers most commonly grafted onto polymers containing butadiene [10-11].
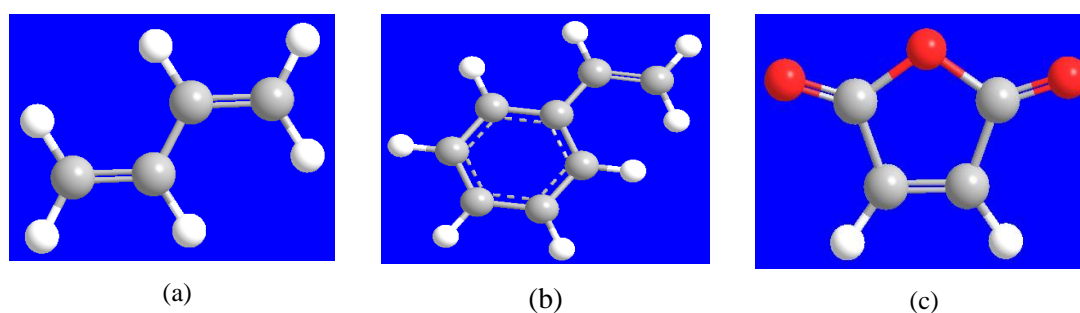

(a)   (b)   (c)

Figure 2. Double bond conjugated system (a) butadiene (b) styrene (c) Maleic anhydride ; grey = Carbon; red = Oxygen; white = Hydrogen

In this case, the two double bonds are separated by one σ bond. Due to the close proximity of the two π bonds, they can conjugate with one another, for which we shall develop the Hückel molecular-orbital theory. A molecular orbital (MO) may be considered to be built up from a combination of atomic orbitals (AOs), and to extend over the whole molecule. The σ frame- work

(using the 2s, $2p_x$ and $2p_y$ orbitals on carbon with the 1s orbitals on hydrogen) separated completely from the π system made up from the $2p_z$ orbitals.

Since this conjugated double bond consists of 4 2p orbitals of carbon to house 4 electron delocalized, by appropriately constructing LCAO-MO (linear combination atomic orbital-molecular orbital) wave functions from 2pz AOs and subjecting these to the secular determinant [12]. Through the Hückel theory, two p orbitals are described as being conjugated with each other in making the π bond. Electrons are delocalized in conjugated systems. This generally lowers the overall energy of the molecule and increase the stability and are subject to the symmetry of the molecule, its point group. Conjugated bonds are stabilizing because they increase the number of resonance stabilized structure that can form. Highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the most important orbitals with respect to reactivity [13-16].
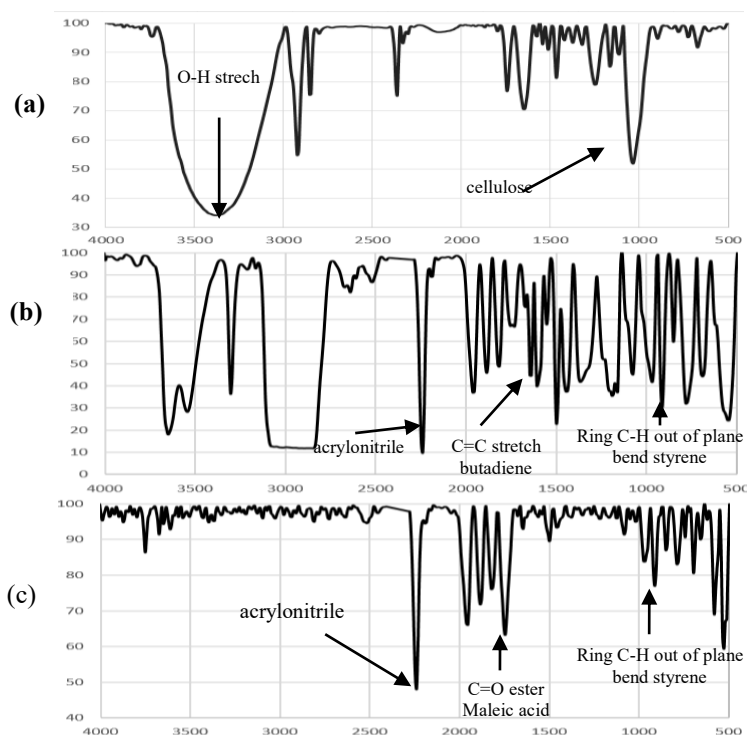

Figure 3. FTIR peaks of (a) OPEFB fiber (b) ABS recycled (c) SF20

Upon analysis of the FTIR spectrum in Figure 3a we see that there is a peak associated with the functional groups of cellulose at peak 1034 cm^{-1} [17-18]. The spectrum related to ABS (Figure 3b) showing the peak marker associated to acrylonitrile appear at 2237 cm^{-1}. The peak at 1639 cm^{-1} associated to C=C for butadiene and styrene, whereas the C=C at 1590 cm^{-1} is a marker for butadiene.

Determination of the peaks associated with styrene is a bit more difficult, therefore the focused only on the aromatic ring of benzene in styrene. Ring C-H in plane bending appear at the 1157 cm^{-1},

ring C-C stretch at 1083 cm^{-1}, and ring C-H out of plane bend peaks appear at 910 cm^{-1} and 849 cm^{-1}. While a peak 910 cm^{-1} related to butadiene, the aromatic band at 1605 cm^{-1} is free from interference, and is utilized as a marker of styrene [19-21].

There is a sharp difference between ABS recycled before and after the addition of filler as we can see in Figure 3b, 3c. The peaks of styrene and butadiene either change its shape and size, on the contrary the peak of acrylonitrile unchanged. This is could be linked to the reactivity of the two monomer molecules due to π bond the C=C, and single torsional bond [22]. Likewise if figure 3a and 3c compared, will be seen a dramatic difference, such as the loss or alteration of the peaks of the filler. Since intensity of the peak at 3379 cm^{-1} in the figure 1c was reduced obviously, indicating that more intermolecular hydrogen bond is destructed compared to the intramolecular hydrogen bond [23]. The loss in butadiene peaks and increasing of ester peak in the FTIR spectra indicating there is a bond between matrix and filler through the coupling agent. Hence, the short fiber 20% (SF20) has a large surface area and high concentration, we concluded that all of the fiber sizes in all concentration we used in this study could be reacting with the coupling agent.

Figure 4 shows the possible reaction mechanisms for reaction that occurs by the addition of the MAH to the ABS, however we still not convince the bond between MAH and cyclic of the styrene. The hydroxyl group of cellulose can interact with this maleic acid to form a bond through the carboxyl group, therefore hydroxyl groups at C-2, C-3 and C-6 of cellulose are reactive and can react with it.
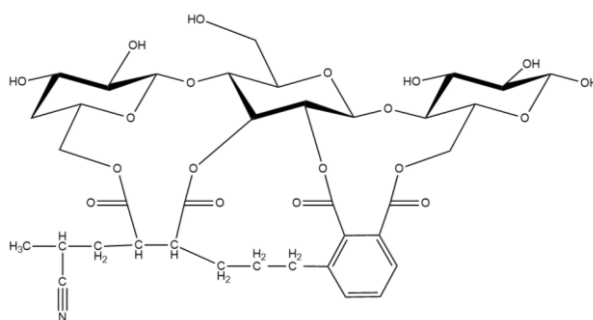

Figure 4. The possible mechanism reaction for cellulose with maleic anhydride and ABS

3.3. Mechanical Test

When several means must be compared we used one-way ANOVA (analysis of Variance), because it is allows us to analyze and interpret observation from several populations. The ANOVA calculation is based on taking the total variation among all observation. This process combines degree to which the confidence intervals overlap into a single measure which, under the null hypothesis of equal population means, has an F-distribution. The level of uncertainty is often expresses as p-value, equivalent to the level of significance at which the null hypothesis would be rejected [9].

Test of the null hypothesis that the means are equal is performed by comparing the observed F-value with the F-tabulated value. The F test will determine if significant differences exist between

the sample means, if there is really no difference in the mean obtained from the test, the F-value will be close to zero or close to F-tabulated value, and the *p-value* is higher than uncertainty level (in this study we used α=0.05).

Table 3 and 4 shows test of the null hypothesis that the means are equal. Because both of the mechanical test have the observed F-value (18.85 and 23.52) are exceeded from the F-tabulated value (2.64), and the p-value is less than 0.05 (0.000), so we can conclude that there is a significant difference among the population means [24].

Table 3. ANOVA table for impact izod test (KJ/m).

Source	Degree of freedom (df)	Sum of Squares	Mean Square	F-Value	P-Value
Factor	5	1644.1	328.81	18.85	0.000
Error	23	401.1	17.44		
Total	28	2045.2			

Table 4. ANOVA table for hardness test (HRR).

Source	Degree of freedom (df)	Sum of Squares	Mean Square	F-Value	P-Value
Factor	5	3560.7	712.13	23.52	0.000
Error	23	696.4	30.28		
Total	28	4257.1			

ANOVA F-test for equality means is only the initial step in our analysis, our goal should be more than the merely conclude that the treatment differences are indicated by the data. Rather, we must detect likenesses and differences among the treatments. Fisher least significant difference (Fisher LSD) method used in ANOVA to create confidence intervals for all pairwise differences between factor level means while controlling the individual error rate to a level specify [25]. All pairwise were grouped using a letters, if there were a differences or claimed as significantly different it would be shown by a different letters, otherwise if there is a likeness or claimed as significantly not different it would be shown by sharing same letters.

Table 5 shows the impact izod output test that has been performed statistically using Fisher LSD method. MF20 (73.98 kJ/m) was significantly different as a toughest material from all treatments. Both of fiber glass (FG1 and FG2) treatments and MF10 claimed as significantly not different because of sharing same letters. This is due to medium fiber that able to give a good impact because more of the fiber strands inside the test pieces has an effective stress transfer between filler and matrix. An impact strength is defined as how well the material can resist fracturing when force is applied [26-27].

A good bonding between fiber and ABS at high concentration of medium fiber (MF20) has effected the impact strength. Toughness requires strength as well as ductility, which allows a material

to deform before fracturing. The impact strength of the biocomposites are strongly influenced by the nature of the fiber, polymer, fiber–matrix interfacial bonding, and testing condition [28].

Table 5. Fisher LSD (n=15, df=5, α=0.05) for the izod impact test.

Factor	Mean	Grouping*
MF20	73.98	A
FG1	59.63	B
MF10	58.35	BC
FG2	57.74	BC
SF20	53.02	CD
SF10	50.85	D

*Means that do not share a letter are significantly different.

A materials ability to withstand local deformation, essentially abrasion resistance, by an indenter is known as hardness [29]. Fisher LSD for hardness test in Table 6 shows that FG1 and FG2 significantly not different with SF20 as a hardest treatments material. This is due to the surface of short fiber at 20% were bonded well to the matrix through coupling agent, the higher value in the hardness in composites indicating good bonding between filler and matrix [30]. Furthermore, the hardness of composites increases along with the increased of particle loading, since the fillers have much larger modulus than the matrix composites stiffness depends significantly in particle loading not particle/matrix adhesion [31-32].

Table 6. Fisher LSD (N=15, df=14, α=0.05) for the hardness test.

Factor	Mean	Grouping*
FG1	113.76	A
FG2	113.20	A
SF20	107.20	AB
SF10	101.80	BC
MF20	96.50	C
MF10	81.60	D

* Means that do not share a letter are significantly different.

4. Conclusion

OPEFB medium fiber and short fiber can be obtained by the mechanical milling and a score of times sieve shaker using 20 and 100 mesh sieves. ABS and OPEFB fiber can be mixed using MAH as a compatible agent. Possible Grafting reactions of Maleic anhydride molecules occur at the double bond of butadiene and styrene. The hydroxyl group of cellulose molecules can interact with maleic acid molecules through the carboxyl group to form a bond. A better properties of OPEFB fiber could be used to replace fiberglass as a reinforcement agent. Thus the OPEFB waste can be reduced to save the environment.

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