

Processing of oil palm empty fruit bunch as filler material of polymer recycles

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Abstract. Oil palm empty fruit bunches (OPEFB) is waste from crude palm oil (CPO) processing plants. This research aims to process OPEFB to be a reinforcement polymer recycle with the mechanical milling method and identify each establishment molecular with the orbital hybridization theory. OPEFB fibers were synthesized using a mechanical milling until the size shortfiber and microfiber. Then do the biocomposite granular synthesis with single screw extruder. TAPPI chemical test shows levels of α -cellulose fibers amounted 41.68%. Based on density, the most optimum composition contained in the filler amounted 15% with the size is the microfiber. The test results of morphology with SEM showed deployment of filler OPEFB fiber is fairly equitable distributed. Regarding the molecular interaction between matrix with OPEFB fiber, described by the theory of orbital hybridization. But the explanation establishment of the bond for more complex molecules likes this from the side of the molecular orbital theory is necessary complete information of the hybrid levels.

1. Introduction

Palm oil is the source of the state's non-oil and gas foreign exchange, the working field procurement, the source of state's income, and the national economy driver. Currently, Indonesia has become the biggest palm oil's producer in the world, where Indonesia contributes 48% of the total volume of palm oil production in the world. Palm oil production in Indonesia in 2014 reached 31,5 million ton, where the quantity has shown a stable increase for the last 20 years which is 11% every year. In 2020, Indonesia's Crude Palm Oil (CPO) is estimated will reach 40 million ton [1].

The high productivity of palm oil is accompanied with the overflowing production of waste as the side product. Every ton of oil palm fresh fruit brunches (OPFFB) that has been processed, produced about 50% of the total waste, while the oil palm empty fruit brunch (OPEFB) produced about 23% of the total waste. If not processed well, it will be hazardeous to the environment [2].

OPEFB is solid waste that is produced by the CPO factory or industry. At the factory, OPEFB was only burned and now is prohibited due to the recent concern of the environment defilement or is dumped therefore caused complaines and problems because it can decrease soil's ability to absorb water. One of the solution to solve the problem is by reusing or reproducing OPEFB's waste into other usable materials [3].



OPEFB is widely known to contains lot of fiber and cellulose that are useful as recycle polymer reinforcer in biocomposite application [4]. OPEFB's fiber is bind-able with *Acrylonitril Butadiene Styrene*/ABS ((C₈H₈·C₄H₆·C₃H₃N)_x) polymer through chemical binding in a composite structure. The bind between OPEFB's fiber dan ABS polymer can be explained by the molecular orbital theory [5].

The molecular orbital theory sees that the bonds between the molecules occurred due to the hybridisation between the orbitals of each molecules. When the OPEFB's fiber molecules placed near with the ABS molecules, the wave function of each molecules will be supepositioned liniery, forming hybrid binding that has the hibrid energy levels characteristics, which principally can be found by solving the multiatomic Schrodinger equation. Even so, the solving of the equation for complex molecule such as lignocellulose or ABS polymer required mathematical approachment and computed modelling which are quite complicated and is outside this research's field. In this research, in addition to process the OPEFB's waste to be a filler, there will also qualitative analysis on how the hybridisation bonds between the cellulose and ABS polymer were formed [5].

Molecular Orbital is the result of a linear superposition of the orbital wave functions and the marges of atomic orbitals on molecule. Approach the wave function can be formed as a linear combination of

$$\psi = \sum_i^n c_i \phi_i \quad (1)$$

Where the coefficient optimal uses variation principle. So that the expectation value of the energy is minimum. The function is called molecular orbital. From basis functions n, the n that differs in their orthogonal molecular orbital can be constructed according to the rules of atomic orbitals combination, amount of molecular marges equal to the atomic orbital marges. When two atoms are marges, each atom give an atomic orbitals then produced two molecular orbitals, one of which is a combination of the sum the atomic orbital is a superposition constructive associated with energy levels of bonding and the rest is a superposition of destructive associated with energy levels antibonding. The strength of the bond depends on the degree of superposition (overlap) of orbital.

The strength of the bond between the two molecular orbitals are influenced by molecular symmetry and type of bonding orbitals hybridize. Two types of bonding that occurs is a σ bond and π . σ bond is a bond where the lines symmetrical electron density is concentrated along the line connecting the two atoms. For example, Figure 1 shows the formation of σ bonds between two molecules [5].

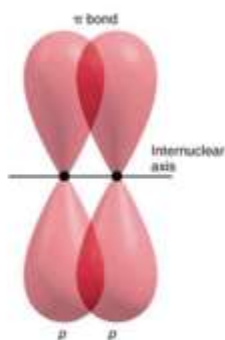


Figure 1. π Bonding

While the π bond is a bond where there superposition area above and below the internuclear axis (the line of nodes located along the internuclear axis). Examples of π bond can be seen in Figure 2.

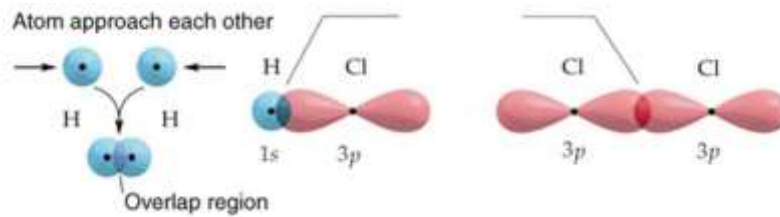


Figure 2. σ Bonding

The amount of the bond that forms is determined by the number of valence electrons in bonding and antibonding levels and can be calculated using the equation.

$$N_{\text{bonding}} = \frac{1}{2} (N_{e^- \text{ orbital bonding}} - N_{e^- \text{ orbital antibonding}}) \quad (2)$$

2. Methods

2.1 Sample Preparation

OPEFB as the main materials of research were obtained from PT Perkebunan Nusantara VIII Cikasungka- Bogor, while the matrix ABS recycle obtained from PT MUB Jaya Cibinong. In addition, there are additives used for the manufacture of granules, antioxidants, Scavenger Acid and Maleic Acid.

The initial stage of this research is the preparation of palm bunches to be cleaned of impurities and enumeration manually to get OPEFB in chip size. Then warmed by drying and oven at 100 °C for 8m hours to reduce the water content OPEFB. Furthermore, the initial testing includes testing the chemical composition, density test, and FTIR (Fourier Transform Infrared Spectroscopy).

2.2 Filler Production

Chopped OPEFB was gradually milled using miller at the speed of 25.000 rpm. Milling for 5x1 minutes. The results of the first milling sieved to 20 mesh sieve to separate the fibers are too large in size with a tiny fibers. Fiber large size (retained 20 mesh) be milled back until the size is able to pass through a sieve. While for the fibers that pass 20 mesh sieving will be continued with a 60-mesh sieve. Just like before, for a fiber that can pass through 60 mesh sieve will be continued with 100 mesh sieve. While the fiber cannot pass through the sieve are reprocessed until smooth. Fibers used in this research is a fiber that can pass through 60 mesh sieve size which is 250 μm fiber can be referred to as the short fiber and fiber that can pass through a 100 mesh sieve size which is 150 μm fiber can be referred to as micro fiber.

2.3 Manufacture of composite granules

The next phase is to make granular biocomposite by combining components of biocomposites are fillers, polymer recycle (matrix) and additive materials on an industrial scale machine single screw extruder. The composition of each buffer material shown in Table 1.

Tabel 1. Biocomposites Composition

Identity	Composition (gram)					
	OPEFB Fibers	ABS			Additives	
		Recycle	Antioxidants		Scavenger	Coupling
					Acid	Agent
1a	Short fiber	10%	87%	1%	0.3%	2%
1b		15%	82%	1%	0.3%	2%
1c		20%	77%	1%	0.3%	2%
2a	Micro fiber	10%	87%	1%	0.3%	2%
2b		15%	82%	1%	0.3%	2%
2c		20%	77%	1%	0.3%	2%

3. Result and Discussion

3.1 Chemical analysis composition of OPEFB fiber with TAPPI method

Tabel 2. Chemical composition with TAPPI method

OPEFB	Chemical composition (%)			
	α -cellulose	Hemicellulose	Lignin	Holocellulose
Without treatment	35.63	32.10	16.38	67.73
Treatment 100 °C, 8 Hours	41.68	20.35	16.78	62.03

The chemical composition of the OPEFB can be identified by standard methods of the Technical Association of the Pulp and Paper Industry (TAPPI). TAPPI T222 om-88 (1988) is a method for determining the composition of lignin, TAPPI T203 OS-61 (1961) method is used for determination of α -cellulose and TAPPI T9m-54 (1988) for the determination of holocellulose.

From the data presented, the composition of the cellulose is 41.68% in the treatment of 100 ° C for 8 hours, while it OPEFB without heat treatment had a composition of 35.63% cellulose. Based on this, it can be seen that an increase in cellulose after heat-treated so that the crystallization and decomposition of cellulose. On the other hand, the amount of hemicellulose decreased from 32.10% to 20.35% and holocellulose decreased from 67.73% to 62.03%. Meanwhile lignin, are relatively fixed in the range of 16%, because lignin will be decompose at a temperature 280-500 °C [6]. A decrease in the presence of hemicellulose and holocellulose caused by heat and it is adequate to make hemicellulose and holocellulosa degraded. The composition cellulose of the OPEFB, has sufficient minimum levels to be used as a polymer filler. Because in previous research of composite-based cellulose, cellulose content in the range of 40% [7]. In addition, OPEFB has a density of 770 kg / m³, high tensile strength and elastic making the OPEFB as filler composites can improve the mechanical properties of a material polymer [8].

3.2 Density analysis of OPEFB fiber

Density testing can be done based on the principle of Archimedes. That is explain the objects that are partially or wholly in the fluid will receive upward lift force equal to the weight of the displaced fluid. The fiber density is measured chip sized fibers with a length of 2-3 cm, short fiber and micro fiber. Each fiber density will be measured and compared. From the graph above it can be seen that the fiber-

sized chip has the least density of 770 kg/m^3 , for short fiber sized have density of 938.363 kg/m^3 while the microfiber sized have a density of 1350.073 kg/m^3 . The difference in the density of fibers because the size is different. When the particle is smaller, the surface area will be greater so that the volume constant number of particles that occupy more and more space. Therefore, the smaller the particle size will make greater density. With this will certainly affect the density of biocomposite after the fiber is inserted into the matrix.

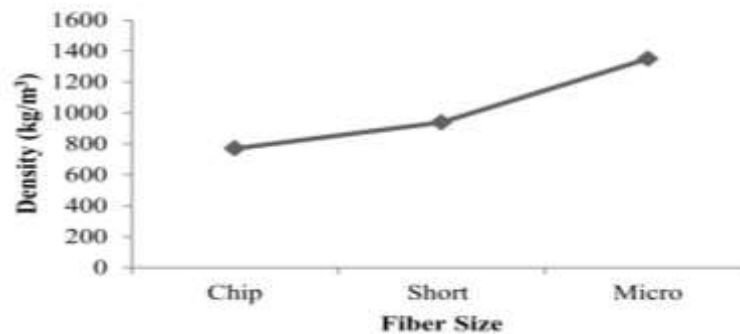


Figure 3. Graph relationship the particle size with density

3.3 Result of Granular Biocomposit Syntesis with Exstrusion Method

OPEFB fibers, recycled polymer and additives were weighed according to Table 4. Then the materials inserted into the mixing machine to do the mixing until the materials mixed with average. Mixing is done in order to bind the material that forms the optimum between the filler, the matrix and additives as well as the homogeneity of all three constituent can be achieved.

The use of additives in this research are useful to maintain the condition of the plastic / polymer used. The addition of the antioxidant additive serves to prevent the oxidation reaction by oxygen that can cause polymer degradation [9]. Acid scavenger while the addition of serves to neutralize the acid formed during the extrusion process so that the polymer chains are not degradation [10]. While the coupling agent serves to increase the degree of dispersion, where the coupling agent serves as the interface that affect the interfacial adhesion and interfacial tension. Interfacial adhesion will be greater and the interfacial tension will drop with the addition of coupling agent [11].

The extrusion is a polymer material process establishment by pressing the polymer material through a mold cavity arranged magnitude. On the machine there is a screw extruder that rotates so that the material can lead to the extrusion machine parts ranging from the feed zone, melting zone to the melt-pumping zone which has the function of each. Machines used in this study is single screw extruder who only had one screw is placed in the barrel will move toward the exit [12]. Polymer which will be shaped like an elongated "noodles", then pulled through the water for cooling and hardening towards the mower. Inside this machine composite cut into small pellet shaped as shown in.

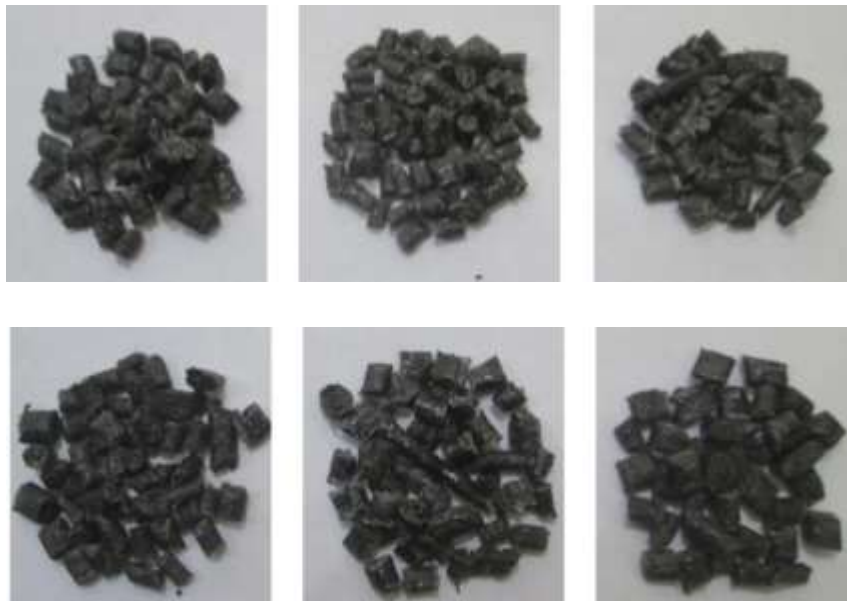


Figure 4. Granular with different compositions (Table 1)

Figure 4 is a granular result of mixing and extrusion. In the visible shape and size is not much different because it has the same basic ingredients. Only differ in the composition. To know the differences of each granular necessary to test the more that will be discussed in further discussion.

3.4 Density analysis of Granular

Tests a granular density did not differ by testing the density of the fiber by using archimedes principle. The sample being measured is granular which is a blend of ABS with OPEFB fibers with different fiber composition. From the picture above can be seen that with the granular filler has a density microfiber TKKS size or greater density in each composition. This is because the density of the filler matrix polymer recycle OPEFB microfiber which is greater than the OPEFB shortfiber as described previously. However, the addition of fiber composition actually makes the density of the shrinking. It is caused by a number of empty spaces in granular compositions along with increase fiber. Empty spaces were caused air trapped in the biocomposite extrusion process in which air is trapped as a result of fiber agglomerated [13].

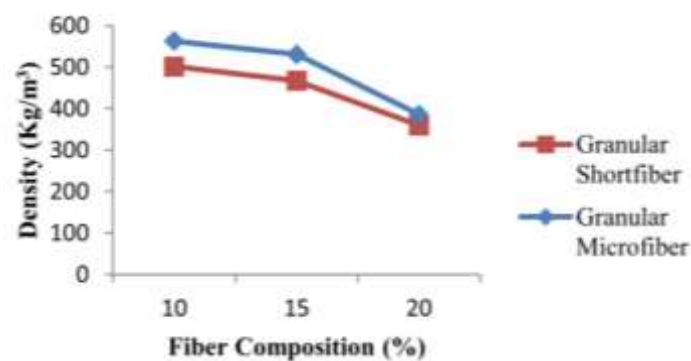


Figure 5. Test result of granular composite density

3.5 Molecular analysis from FTIR data

Results of FTIR spectra (Figure 6) can be known about the compound structure of the fiber OPEFB (filler), ABS polymer recycle (matrix) and biocomposites mixture of both. FTIR spectra can be seen in biocomposites dominated by the peaks of the matrix that is the wave number 2237 cm^{-1} ($\text{N}\equiv\text{C}$), 30, 1600-1900 cm^{-1} which is the carbon bonds ($\text{C}=\text{O}$) of the polymer ABS and in the range of 670-1000 cm^{-1} identified a bond and $\text{CH}=\text{CH}_2$ Benzene, which is part of the ABS polymer matrix as well. While the peak that appears at wave number 2360 cm^{-1} and 1627 cm^{-1} are both derived from the peak OPEFB fiber. Their dominance of matrices ABS recycle is because the composition of its own biocomposite mostly ABS polymers recycle. While fiber OPEFB only ranged from 10-20% of the

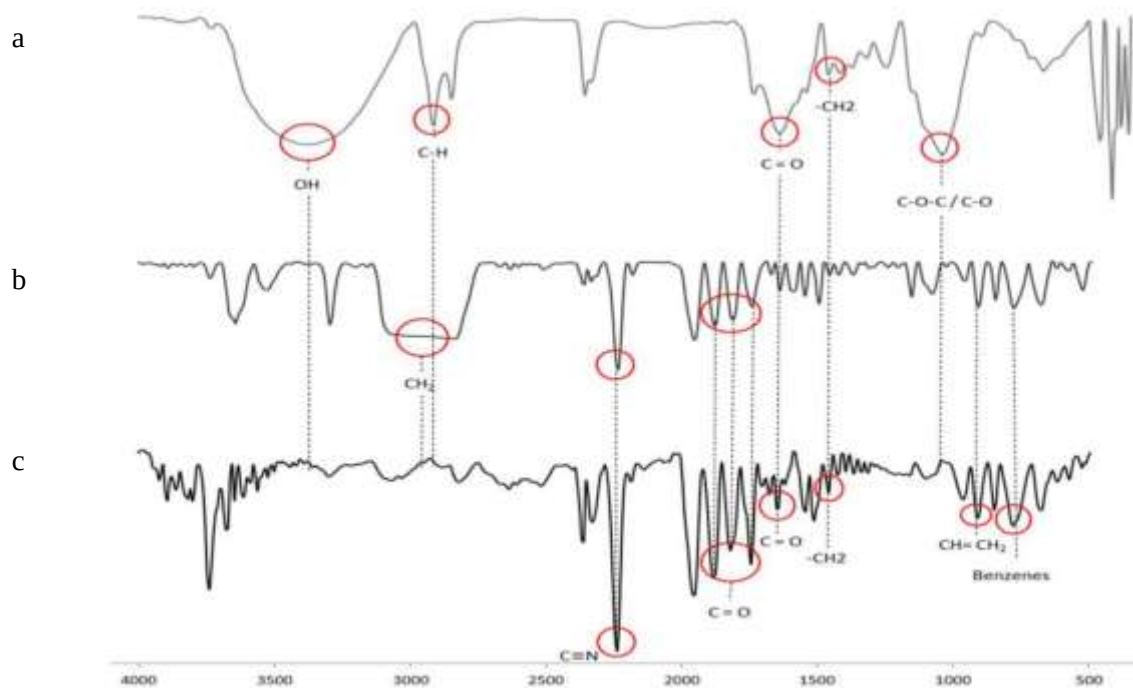


Figure 6. Test Result of FTIR (a) OPEFB fiber (b) Polymer ABS (c) Granular of Biokomposit

total biocomposites. In addition, it can be seen that an increase in the intensity of absorption at some bonding especially on the $\text{C}=\text{O}$ bond. Where the bond could have come from the fiber and polymer ABS. It can be assumed that the formation of the bond between the filler interface OPEFB fibers with polymer matrices ABS recycle.

Related bond formation cellulose molecules and polymers ABS can be explained by the theory of orbital hybridization. In the figure 6 can be seen there are several kinds of many bonds, ie single bonds, double and triple bonds. This is influenced by the charging of valence electrons in the level of hybridization. If hybridization involves only the s and p orbitals the bond is called hybridization sp . The amount of the bond is determined by the difference between the numbers of valence electrons in the antibonding and bonding level can be calculated using equation (2). The problems that arise for complex molecules such as ABS and lignocellulose is the complexity in determining the levels of hybrid should be done using ab initio quantum calculations that are beyond the discussion of this research. However, in general the type of bond that is formed as bonding π or σ determined from atomic orbitals that contribute to bonding (bonding orbital).

To understand the formation of bonds in complex molecules necessary to understand the process of the formation of a hybrid bond in the molecule is much simpler. For example, carbon monoxide CO molecule. Based on the calculation of molecular orbital theory, the energy levels of CO by Figure 7.

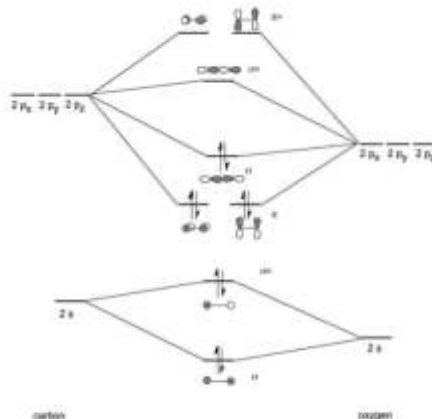


Figure 7. Energy's level diagram of CO molecule

Bonding in CO involving one σ bond and two π bond (Figure 16). C-O bond has a distance of 1.1 Å so consistent with a triple bond. In comparison, a single binding CO has a distance of 1.43 Å and double bond CO within Average 1.23 Å. Based on data from FTIR absorption spectra of CO at wavelength 2143. CO bond formed on the kind of p orbitals serve as bonding orbitals. As for knowing how the process of forming a bond between CO with other molecules such as metal required an understanding of the levels HOMO (Highest Occupied Molecular Orbital) and LUMO (Low Unoccupied Molecular Orbital).

From Figure 8 it can be concluded prior to the hybridization, there are 4 valence electrons in the atom C, two in the 3p level and two at level s with a total molecular orbital amounted 4. As for O there are 6 valence electrons, 4 in 3p level and two at s level with total number of orbital level 4. After hybridization level, the combined energy is $4 + 4 = 8$ by charging the lowest energy level following the first in which only two valence electrons can fill the energy level s in accordance with the rules Pauli. HOMO levels of the CO molecule is filled by two electrons in this case the sigma orbital manifold. From the description of the previous CO can be concluded that the explanation bond formation for more complex molecules of the molecular orbital theory of the necessary information.

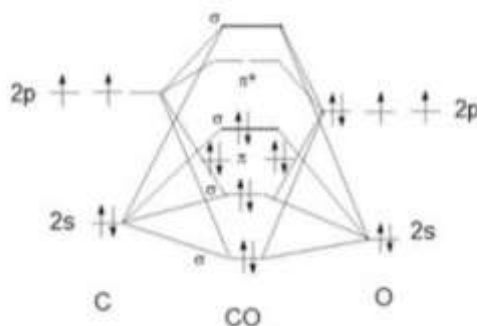


Figure 8. Energy's level diagram of CO molecule

about the levels of the complete hybrid. The number of hybrid orbitals level ABS- OPEFB fiber formed is the summation of the quantities of each molecular orbital ABS and fiber TKKS before bind. The type and amount of the bond that is formed depends on the electron valence electrons fill the

energy level of the HOMO and LUMO levels of availability in ABS or OPEFB fiber. Thus further research is needed to determine the levels of hybridization and the number of valence electrons fill each orbital.

4. Conclusion

Results of the analysis composition showed that the cellulose of OPEFB has ties 41.68% which has a high purity level that can make the better quality materials.

Based on the results of density, particle size capable of affecting the density. The smaller of particle size, the density will be higher as evidenced by the value of the greatest density in the fiber size microfiber. It can also be seen in the granular density testing. Granular premises sized microfiber filler density is higher than the filler-sized granular shortfiber. But with the addition of fiber composition, density will experience deterioration. So the most optimum composition contained in the filler as much as 15% the size of the microfiber because density is quite high and able to absorb quite a lot of waste.

While the results of FTIR can confirm the presence of functional groups contained in granular biocomposites. And it is known that the polymer matrix is seen dominating role as compared to filler. Basically, the molecular interaction between the matrix with fiber filler OPEFB explained by the theory of orbital hybridization. But the explanation bond formation for more complex molecules like this from the side of the molecular orbital theory of the necessary information on the levels of the complete hybrid.

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