Molecular analysis on the utilization of oil palm empty fruit bunches fiber as reinforcement for acrylonitrile butadiene styrene biocomposites

B Hermawan¹, S Nikmatin¹, H Alatas¹, Sudaryanto² and S G Sukaryo²

¹ Department of Physics, Bogor Agricultural University, Bogor, Indonesia
² National Nuclear Energy Agency of Indonesia, South Tangerang, Indonesia

Email : eyosganteng@gmail.com

Abstract. Oil palm empty fruit bunches (OPEFB) was one of the solid waste produced by the palm oil factory and were totally plentiful in biomass. OPEFB fiber used as reinforcement of polymer matrix acrylonitrile butadiene styrene (ABS). The use of FTIR is to see that there is no changes in the molecules of the constituent biocomposite ABS and OPEFB. The reactivity of butadiene and styrene through the double bond- π conjugated system, contributed to the bond reaction with the maleic acid as compatibilizer which is grafted to the system. It is concluded that the possible grafting reaction occurs by the addition of the MAH to the double bond of the butadiene and styrene. The hydroxyl group of cellulose can interact with this maleic acid to form a bond through the carboxyl group.

1. Introduction

Utilization of oil palm fruits as raw material to produce CPO leaves a problem associated with the processing of solid and liquid waste, one of which is oil palm empty fruit bunches (OPEFB). The development of environmentally-friendly materials derived from natural materials, especially waste with a touch of technology becomes very important and need special attention. OPEFB processed by physical method of heating and mechanical milling techniques without chemicals to form fiber[1]. OPEFB fiber is then added as filler ABS polymer matrix to be processed into biocomposite. Heat received by the composites reinforced with natural filler (rattan 5%) has a much higher melting point[2].

Molecular vibration analysis on biocomposite ABS will be carried out to see whether or not changes to a particular functional group, which will then be used to ensure the bond between ABS and OPEFB. Molecular vibrations can range from the simple coupled motion of the two atoms of a diatomic molecule to the much more complex motion of every atom in a large polyatomic molecule. In order to begin with a basic model, a molecule can be looked upon as a system of masses joined by bonds with properties like spring. Stretching or compressing a spring produces potential energy. When the spring is released, this energy is translated into a restoring forces which results in vibration about the
equilibrium length of the spring. For a diatomic molecule, only one vibration that corresponds to the stretching and compression of the bond is possible. It is no longer obvious how many modes of vibration they have when we consider polyatomic molecules containing more than three atoms[3,4].

Molecular vibration spectrum is a unique nature and a molecular characteristics. Natural vibrations of molecules is a marker for the identification of molecules contained on the materials. Each molecule has a specific natural vibration depending on the type of molecules and molecular bonds. Vibration is presented through FTIR measurements in the form of peaks. Infra Red spectrum can be used as a fingerprint for identification by comparing the sample spectrum with "reference" spectrum. Characterize molecular structures, either "backbone" of the molecule or functional groups attached to the molecule will produce the absorption spectrum. This information can indicate backbone on the structure and specific functional groups of aromatic rings and show backbone on a straight chain or branched chain[5]. Therefore, we wanted to get information whether there is a reaction between components of a mixture of biocomposites through FTIR spectra.

2. Material and Method
OPEFB was taken from PKS-PTPN VIII Cikasungka, Bogor, Jawa Barat. The research was held at laboratory of physics department Bogor Agricultural University (IPB) and PT MUB Jaya Cibinong.

Materials used in this research is the oil palm empty fruit bunches obtained from palm oil mill PTPN VIII, Cikasungka Bogor, West Java, Indonesia. OPEFB is a complete waste which has been separated from the seeds. OPEFB were cleaned and cut into chips and dried for 2 days then put into oven at 100^0C for 6 hours, m = 2 Kg. Into a mechanical milling (FOMAC, type FCT-Z2000, China) a dried chips milled about 10 minutes, v = 25000 rpm, m = 0,5 Kg. To obtained OPEFB micro fiber a score of times milling and sieving (100 mesh) were done.

The fabrication of biocomposites granules- MF20 performed by mixing the OPEFB micro fibers with the ABS polymers (2:8) using Single Screw Extruder (SSE), in the barrel samples blended with a gradient temperature of 195 ^0C – 215 ^0C – 220 ^0C – 220 ^0C – 225 ^0C – 225 ^0C – 225 ^0C – 225 ^0C.

OPEFB chips, OPEFB micro 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 micro fiber powder made into pellets with KBr method, while granular ABS and MF20 is made into a thin film (± 1 micron).

3. Results and Discussion
An infrared (IR) spectrum provides a rapid and simple method for obtaining preliminary information on the identity or structure of a molecule. The spectrum is a plot of the amount of IR radiation that passes through the sample (transmittance T) versus the wavelength, λ (or wavenumber, ν) of the radiation. The sample absorbs IR radiation at various wavelengths (or wavenumbers) and the positions of the absorptions give clues to the structure of the molecule, as indicated in figure 1. The spectra may also be exhibited in absorbance (A=log10 1/T) versus wavenumber units. Absorption maxima (or transmission minima) are referred to as peaks, bands, or absorptions[6].

IR spectra of a large number of compounds containing a particular functional group such as carbonyl, phenyl, amino, nitro, and so on are found to have certain features that appear at more or less the same frequency for every compound containing the group. Then, it is reasonable to associate these spectral features with the functional group, provided a sufficiently large number of different compounds containing the group have been studied.
Upon analysis of the spectrum in figure 1a we see that there is several peaks associated with the functional groups of cellulose at peak 1034 cm$^{-1}$, whereas the peak at 1730 cm$^{-1}$ as a hint of functional group associated with lignin[4,7]. Figure 1b shows the peak at 2237 cm$^{-1}$ was associated with acrylonitrile, while peak 910 cm$^{-1}$ related to butadiene. The aromatic band at 1605 cm$^{-1}$ is free from interference, and is utilized as marker of styrene[8].

![Figure 1. FTIR peaks of (a) micro fiber (b) ABS (c) MF20.](image)

There is a sharp difference between ABS before and after the addition of filler (OPEFB micro fiber) as we can see in figure 1b, 1c. The peaks of styrene and butadiene either change its shape and size, on the contrary the peak of acrylonitrile unchanged. Likewise if figure 1a and 1c compared, will be seen a dramatic difference, such as the loss or alteration of the peaks of the filler. This is could be linked to the reactivity of the two monomer molecules due to π bond the C = C, and single torsional bond[9]. Both of butadiene and styrene have a double bond. There is therefore bonding between C-1 and C-2 and between C-3 and C-4, but not between C-2 and C-3 (figure 2). 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.

![Figure 2. Double bond conjugated system (a) butadiene (b) styrene](image)
We shall be concerned mainly with organic molecules, for which we shall develop the Huckel 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. Through the Huckel 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. The most important orbitals with respect to reactivity are highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [10,11,12,13].

We continue to separate completely the σ frame-work (using the 2s, 2px and 2py orbitals on carbon with the 1s orbitals on hydrogen) from the π system made up from the 2pz orbitals. Since this conjugated double bond consists of 4 2p orbitals of carbon to house 4 electron delocalized. After setting up the secular problem by appropriately constructing LCAO-MO (linear combination atomic orbital-molecular orbital) wave functions from 2pz AOs and subjecting these to the secular determinant, it is solved after making the following approximations (equation (1)). The linear combination of these orbitals takes the form of equation (1)[14].

\[
x^4 - 3x^2 + 1 = 0
\]

\[
x^4 - 3x^2 + 1 = (x^2)^2 - 3x^2 + 1 = 0
\]

\[
x = \pm \left( \frac{1}{2} (1 + \sqrt{5}) \right), \pm \left( \frac{1}{2} (\sqrt{5} - 1) \right)
\]

\[
x = \pm 1.618, \pm 0.618
\]

With energy put one by one into secular equations and evaluate determinant there are four level of molecular orbital energy each described in equation (2). therefore we construct the wave function as described in figure 3.

A common way of polymer blends is adding a compatibilizer to reduce the interfacial tension, increase the adhesion, and obtain better properties. The double bond in maleic anhydride is also extremely reactive. Methacrylic acid, acrylic acid, maleic anhydride (MAH), and long chain unsaturated monomers are among the monomers most commonly grafted onto polymers containing butadiene[15,16].

\[
\psi_1 = 0.372p_1 + 0.602p_2 + 0.602p_3 + 0.372p_4
\]

\[
\psi_2 = 0.602p_1 + 0.372p_2 - 0.372p_3 - 0.602p_4
\]

\[
\psi_3 = 0.602p_1 - 0.372p_2 - 0.372p_3 + 0.602p_4
\]

\[
\psi_4 = 0.372p_1 - 0.602p_2 + 0.602p_3 - 0.372p_4
\]
Figure 3. $\pi$ molecular orbital of conjugated double bond.

Figure 4 shows the possible grafting reaction occurs by the addition of the MAH to the ABS, however we still can not convince the bond between MAH and cyclic of the styrene. The hydroxyl groups at C-2, C-3 and C-6 of cellulose are reactive and can react with anhydride. The intensity of the peak at 3379 cm$^{-1}$ in the reduced obviously, indicating that more intermolecular hydrogen bond is destructed compared to the intramolecular hydrogen bond[17]. The reaction mechanisms for cellulose with MAH described in figure 5.

Figure 4. Possible reaction of ABS and maleic anhydride.

Figure 5. The mechanism reaction for cellulose with maleic anhydride.

4. Conclusions
The reactivity of butadiene and styrene through the double bond- $\pi$ conjugated system, contributed to the bond reaction with the maleic acid as compatibilizer witch is grafted to the system. It is concluded that the possible grafting reaction occurs by the addition of the MAH to the double bond of the butadiene and styrene. The hydroxyl group of cellulose can interact with this maleic acid to form a bond through the carboxyl group.
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