

# Mechanical Reinforcements Of Composites Made From Fiber Of Fruit Bunch Palm Oil By Adding Carbon Nanotube

Praswasti PDK Wulan, Asep Handaya Saputra, Widodo Wahyu Purwanto

**Abstract:** Composite materials (also called composition materials or shortened to composites) are materials made from two or more constituent materials with significantly different physical or chemical properties, that when combined, produce a material with characteristics different from the individual components. Fruit bunch palm oil is a palm oil plantation wastes containing cellulose fibers can be used as the building blocks of the composite. Natural fiber composites with epoxy matrix is known to have good chemical resistance. The addition of carbon nanotubes (CNT) in composites is known by many studies can improve the mechanical properties. In this study, the addition of carbon nanotubes in the composite fiber of fruit bunch palm oil with epoxy matrix as much as 0.1%, 0.5%, and 1% of the weight matrix is used. Fruit bunch palm oil fiber obtained by chemical retting methods. To improve compatibility, and functionalization of CNT and fruit bunch palm oil fiber conducted using mild acid oxidation and silane coupling agent and proven not to damage the structure and size of the CNT. The addition of CNT increases the tensile strength of fruit bunch palm oil fiber with epoxy matrix of 10.03%, 4.75%, and 7.75%. The increase in buckling strength occurs at 51.64%, 65.8%, and 105.9% respectively.

**Keywords:** carbon nanotubes, mechanical strength, epoxy matrix, fruit bunch palm oil fiber

## 1 INTRODUCTION

Indonesia is one of the biggest palm oil product producers. Approximately, Indonesia has 8.04 ha palm oil cultivation that can produce 19.76 million tonnage of crude palm oil on 2010. Along with it, it also produce around 155.22 million tonnage waste in form of empty palm oil fruit bunch, trunk, and empty shell. These waste contain cellulose based fiber which can be separated from the empty fruit bunch through several process and can be used as reinforcement filler in composite material. The utilization of cellulose-based fiber composite has broadly known in furniture and home industry. It is also interesting to be used in automotive and aeronautical industry because of its low density. Although cellulose-based fiber composite has many advantages such as low density, high yield, low cost of production, and biodegradable, this still cannot be implemented in automotive and aeronautical industry because it has not appropriate mechanical properties for the purpose. On the other side, nanotechnology has rapidly grown in the past several years, providing us understanding of how nanostructure material can enhance some properties of material such as mechanical and electrical properties. nanostructure materials are known have a good mechanical properties so that it can be used to enhance mechanical properties of composite materials [1]. One of nanostructure materials that has been studied is carbon nanotube (CNT).

CNT is basically carbon allotrope with nanometer diameter tubular shape and know to have extraordinary mechanical and electrical properties [2]. Several studies has shown that CNT can be reinforcement filler in polymer [3], ceramics [4], and metal [5] matrix. Addition of single walled CNT as much as 0.1%-0.2% wt PVC matrix and multi walled CNT as much as 5%-20% wt PVC matrix can improve the composite electrical conductivity and mechanical properties [6]. Addition of CNT on epoxy matrix of carbon fiber or fiber glass multiscale composite also known to have significant effect on its interlaminare strength and crack strength [7-9]. Utilization of CNT in natural fiber (hemp fiber) reinforced composite also has shown improvement in mechanical properties with epoxy matrix [10]. In this experiment, Fruit bunch palm oil fiber/epoxy composite will be reinforced by addition of CNT. The fiber is collected by atmospheric chemical retting process from empty palm oil fruit bunch. The CNT used is multi walled CNT, functionalized by mild acid oxidation process. Surface treatment of the natural fiber and CNT performed by silane coupling agent to improve compatibility between the materials. FTIR (Fourier transform infrared spectroscopy) performed in order to make sure the functionalization and surface treatment are succeed. FE-SEM (field emission scanning electron microscope) performed to make sure the treatment of CNT (oxidation and surface treatment) did not change or damage the nanostructure and size of CNT. Composites were fabricated by hand lay-up method. Tensile and 3-point flexural test was performed according to ASTM D638 and ASTM D790 in order to study the effect of CNT to the mechanical properties of multiscale composite.

## 2 EXPERIMENTAL

### 2.1 Materials

CNT used in this experiment was commercial multi walled CNT produced by chemical vapor deposition with 10 nm average outer diameter, 1-5  $\mu\text{m}$  long, 500 m<sup>2</sup>/gr surface area, and purity higher than 95% (Chengdu Organic Chemicals Co. Ltd., China). The epoxy matrix used is DGBA (Diglycidylether Bisphenol A) with TETA (triethylenetetraamine) as the curing agent. Fruit bunch palm oilare waste from palm oil cultivation in Bangka Belitung Province, Indonesia. Functionalization of

- *Praswasti PDK Wulan is currently lecturer in Chemical Engineering Department in Universitas Indonesia, Indonesia, PH-622178885335. E-mail: [wulan@che.ui.ac.id](mailto:wulan@che.ui.ac.id)*
- *Asep Handaya Saputra and Widodo Wahyu Purwanto is currently lecturer in Chemical Engineering Department in Universitas Indonesia, Indonesia, PH-622178885335. E-mail: [saeep@che.ui.ac.id](mailto:saeep@che.ui.ac.id) & [widodo@che.ui.ac.id](mailto:widodo@che.ui.ac.id)*

CNT were performed by HNO<sub>3</sub> 3M and H<sub>2</sub>O<sub>2</sub> 30% v/v (Sigma Aldrich, U.S.A). surface treatment of natural fiber and CNT performed with  $\gamma$ -Glycidoxypropyltrimethoxysilane (GPTMS) (Silquest A-187, Momentive, U.S.A).

## 2.2 Fruit Bunch Palm Oil Preparation

Approximately 300 gr of Fruit bunch palm oil was chopped in to 10 cm in size in order to ease the penetration of chemical retting liquor. Sodium hydroxide (10 % wt of empty palm oil fruit bunch) was dilute in 1.7 liter of distilled water then the chopped Fruit bunch palm oil was added and mixed in 100°C for 3 hours. Black liquor produced separated from the fiber and the fiber washed with tapped water to dilute remaining NaOH. The fiber collected then dried in 110°C oven for 3 hours. GPTMS silane coupling agent added to 95% ethanol to produce 10% vol GPTMS solution then mixed for 5-10 minutes to form silanol compound. The dry natural fiber then mixed with 2 liters GPTMS solution for 24 hours to make sure the silane-coupling agent modify the surface of the fiber. The fiber then dried in room temperature for 24 hours followed by oven drying in 110°C for 2 hours to make sure the curing of silane group. FTIR analysis with Perkin Elmer FT-IR Spectrum was performed prior and after the surface treatment with GPTMS to observe addition of epoxy group in fiber surface.

## 2.3 CNT Preparation

Approximately 2 gr of CNT was added in 200 ml of HNO<sub>3</sub> 3M. The solution then mixed in 60°C with hot plate magnetic stirrer for 15 minutes then followed by sonication in water bath sonicator for 2 hours. The solution then thoroughly washed with H<sub>2</sub>O<sub>2</sub> 30% v/v and the functionalization continued with H<sub>2</sub>O<sub>2</sub> 30% in precisely the same way with HNO<sub>3</sub>. After sonication, the solution was washed with distilled water and then filtered. The corresponding CNT was then oven dried in 110°C. FTIR analysis with Perkin Elmer FT-IR Spectrum was performed prior and after the functionalization to observe the formation of -OH group on the surface of CNT. The functionalized CNT mixed with the similar GPTMS solution used in natural fiber surface treatment. Prior to the mixing, the GPTMS solution was mixed for 5-10 minutes to form silanol group. The CNT was mixed with the GPTMS solution for 24 hours then filtered and oven dried in 110°C for 2 hours. FTIR analysis was performed before and after treatment with GPTMS. FE-SEM analysis was performed before functionalization and after surface treatment to make sure those processes did not damage and reduce nanostructure of CNT.

## 2.4 Composite Fabrication

The treated CNT was suspended in acetone using water bath sonicator for 30 minutes then the suspension was added to preheated epoxy resin (70°C) and mixed with hot plate magnetic stirrer in the same temperature for 3 hours or until all acetone evaporated. Curing agent and treated natural fiber was added and mixed after evaporation of acetone. The mixture then poured on aluminum open molding that had been coated with wax as releasing agent. The mixture then cured for 48 hours in room temperature. Since the purpose of this research is to know the effect of CNT addition on composite with empty palm oil fruit bunch/epoxy composite, the amount of CNT mixed was varied in 0.1%, 0.5%, and 1% of epoxy matrix. The composite without addition of CNT also fabricated as the controlled variable. The Fruit bunch palm oil fiber used is 10% wt of composite, the utilization of the natural fiber more

than this composition was hard to performed because of the low density of the fiber. The composite fabricated was then tested by ASTM D638 (Tensile Properties of Plastics) and ASTM D790 (Flexural properties of plastics and electrical insulating materials) with SHIMADZU AG-Xplus Material Universal Tester.

## 3 RESULTS AND DISCUSSIONS

### 3.1 Fruit Bunch Palm Oil Preparation

The Fruit bunch palm oil was chopped and cut into smaller size as shown by Figure 1 in order to maximize NaOH solution penetration during chemical retting. After chemical retting, most of the Fruit bunch palm oil were separated into fiber and the liquor was darkened because dilute most of the pectin and lignin contained as shown by Figure 2. This chemical retting process was based on different solubility between lignin and pectin (compound that glue fiber into bundle) which is highly soluble in hot NaOH solution and cellulose (natural fiber) [11]. The weight of dry natural fiber produced was 243 gr or 81% weight of dry empty palm oil fruit bunch. The 19% weight loss indicates that most of the lignin has been diluted in NaOH solution since the Fruit bunch palm oil contains 22.12% lignin [12]. GPTMS is an organo-functional silane with epoxy organic functional group and hydrolyzable alkoxy group [13]. This

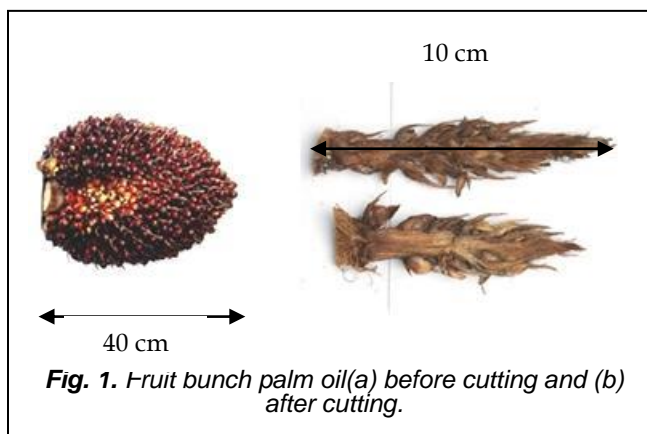


Fig. 1. Fruit bunch palm oil (a) before cutting and (b) after cutting.

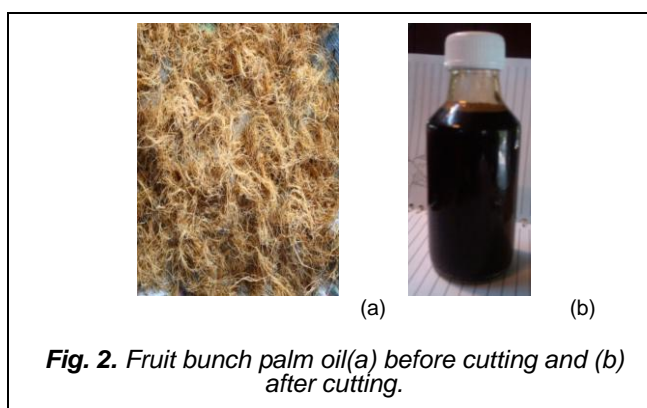
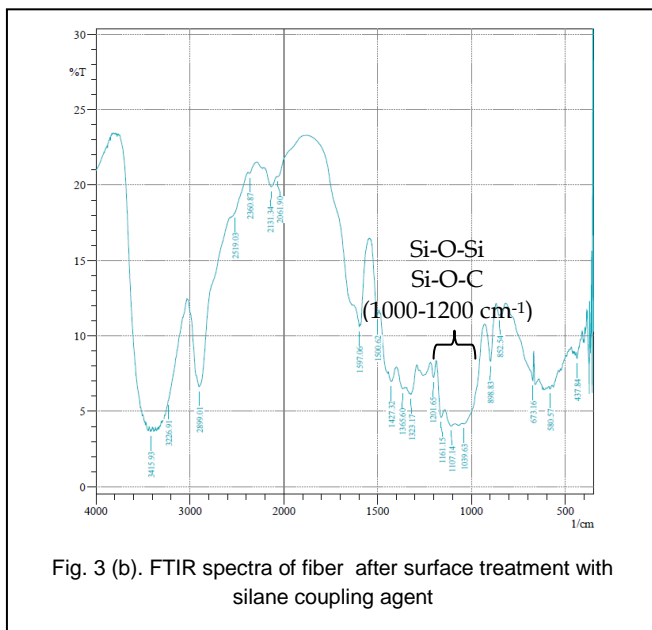
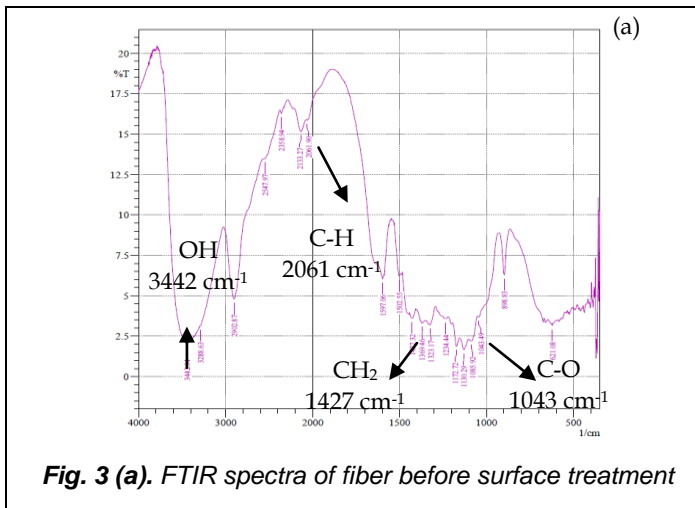


Fig. 2. Fruit bunch palm oil (a) before cutting and (b) after cutting.

alkoxy group is highly reactive with water in 95% ethanol to form silanol Si-OH groups [13]. This silanol will form Si-O-Si covalent bonding with -OH group on the surface of substrate, in this case natural fiber, forming stable covalent bonds [14].

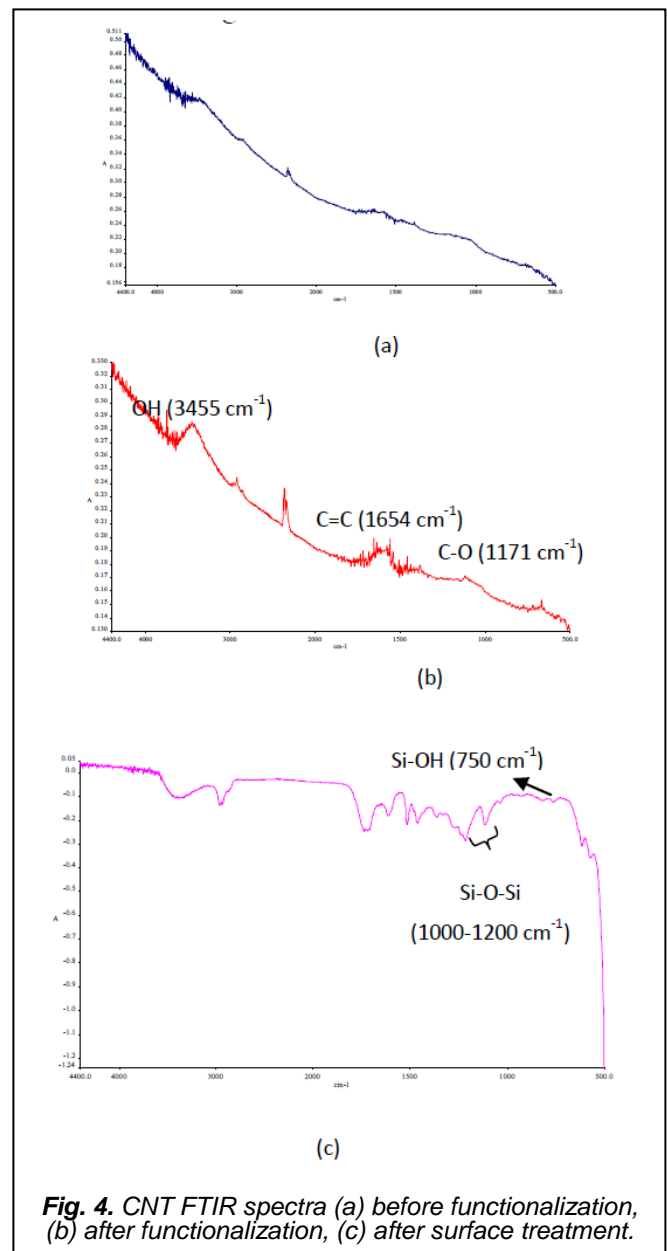


The FTIR spectra of natural fiber before and after surface treatment with GPTMS silane coupling agent shown by Figure 3 (a) and (b). Figure 3 (a) show several peak character of cellulose which are peak at 3442  $\text{cm}^{-1}$  wavelength (stretching of -OH group), 2061  $\text{cm}^{-1}$  (stretching of C-H bond-ing), 1427  $\text{cm}^{-1}$  (bending of  $\text{CH}_2$ ), 1379  $\text{cm}^{-1}$  (C-H bending), and 1043  $\text{cm}^{-1}$  (C-O stretching). FTIR spectra of treated natural fiber show quite similar peaks with untreated natural fiber as shown by Figure 3 (b). However, it also show increasing intensity of peak at 1000-1200  $\text{cm}^{-1}$  wave length (Si-O-Si and Si-O-C stretching which the evidence of silane coupling agent presence on the natural fiber [15].

### 3.2 CNT Preparation

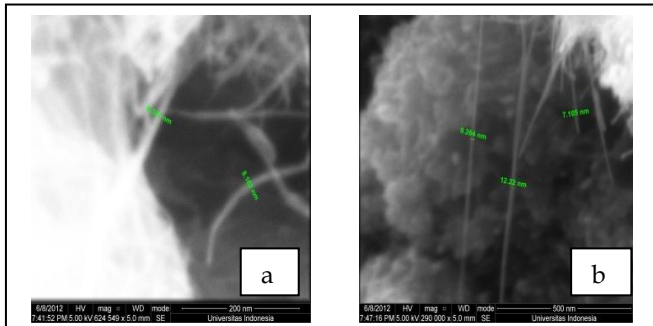
Carbon nanotube tends to form agglomerate if it is dispersed in a liquid phase. This agglomeration can cause some of CNT surface do not have con-tact with  $\text{HNO}_3$  and further cannot be functional-ized. The water bath sonicator was used to break and prevent further agglomeration of CNT. FTIR spectra of CNT before and after functionalization shown by Figure 4 (a) and (b). The figure show that there are some new peaks after

CNT functionalization which are peak at 3455  $\text{cm}^{-1}$  (OH stretching), 1654  $\text{cm}^{-1}$  (C=C stretching), and 1171  $\text{cm}^{-1}$  (C-O stretching) so it can be confirmed that the functionalized CNT has OH group. As mentioned before, the GPTMS will react readily with water, forming silanol groups. This groups react readily with OH groups at the sur-face of oxidized CNT to form polymeric bond Si-O-Si [16]. The presence of Si-O-Si bonding was confirmed by FTIR analysis as shown by Figure 4 (c) where there are new peaks at 1000-1200  $\text{cm}^{-1}$  wavelength (Si-O-Si stretching). There is also peak at 750  $\text{cm}^{-1}$  which is Si-OH stretching from unreacted silanol. Figure 4 (c) also shown lower intensity of 3400  $\text{cm}^{-1}$  peak (OH stretching) that means some OH had reacted with Si from GPTMS. FE-SEM analysis of CNT before and after func-tionalization and surface treatment also shown that the treatments did not damage or reduce the structure and the size of CNT.



From comparison between Figure 6a and Figure 6b, it can be said that the structure and size of CNT did not change after

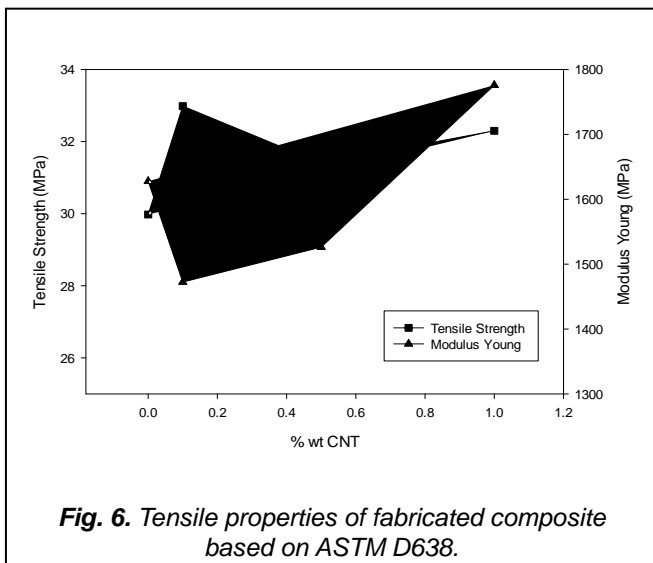
functionalization and surface treatment because there are no significant differences in outer diameter size and length.



**Fig. 5** FE SEM of CNT (a) before surface treatment (b) after surface treatment

### 3.3 Composite Fabrication

In this research, there is variation of CNT composition in order to learn the effect of CNT addition and its composition to the mechanical properties of composite. The CNT composition variation was 0.1%, 0.5%, and 1% based on weight of matrix used. The Fruit bunch palm oilseed was 10% of composite weight. Utilization of fiber higher than this could make the mixing and molding of composite difficult because of its low density. The fabricated composite with 0%, 0.1%, 0.5%, and 1% wt addition of CNT shows that addition of CNT affects the color of the composite formed, the higher the CNT content, the darker the composite will be. The composite fabricated was multiscale composite, means that the composite are fabricated from several compound that have relatively high difference in size. In this case macro size of natural fiber and nano size of CNT. In this multiscale composite both natural fiber and CNT act as reinforcement filler.



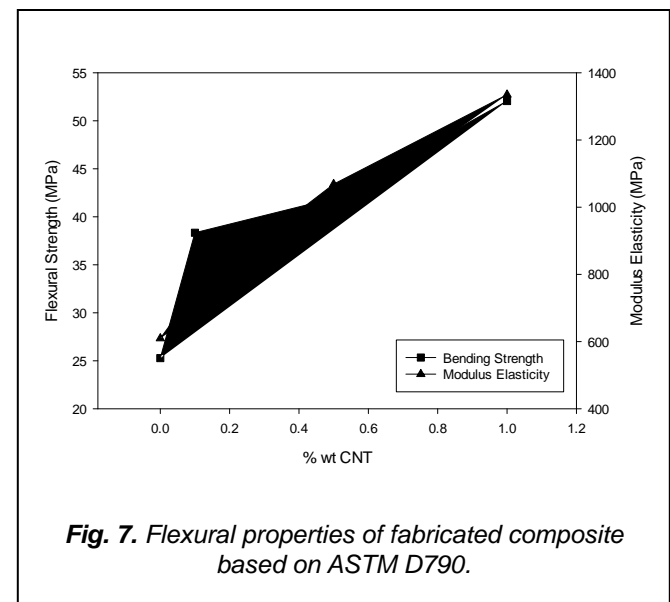
**Fig. 6.** Tensile properties of fabricated composite based on ASTM D638.

The addition of CNT as much as 0.1%, 0.5%, and 1% weight of matrix has increased the tensile strength as shown as Figure 6 by 10.03%, 4.75%, and 7.75%. This also shows that addition of CNT can cause the composite to be able to hold bigger loading on in-plane direction before failure. Commonly failure happened in tensile test caused by crack opening mechanism. Addition of CNT did not significantly increase the tensile strength because

this is fiber controlled properties while CNT modify the resin rich area. The slight improvement of the tensile strength could be caused by larger surface area between fiber surface and epoxy matrix in presence of CNT. However the composite fabricated has higher tensile strength compare to commercial car bumper from polypropylene produced by Shanghai/Beijing Expert in the Developing of New Material Co. Ltd which is 25 MPa [17]. Young's modulus shows a comparison between stress experienced by the material. Effect of CNT in the fabricated composite Young's modulus cannot be determined from this study since the Young's modulus decreased 9% and 6% respectively by CNT addition of 0.1% and 0.5%. However, the composite Young's modulus increased by 9% with the addition of CNT as much as 1% by weight of the epoxy matrix.

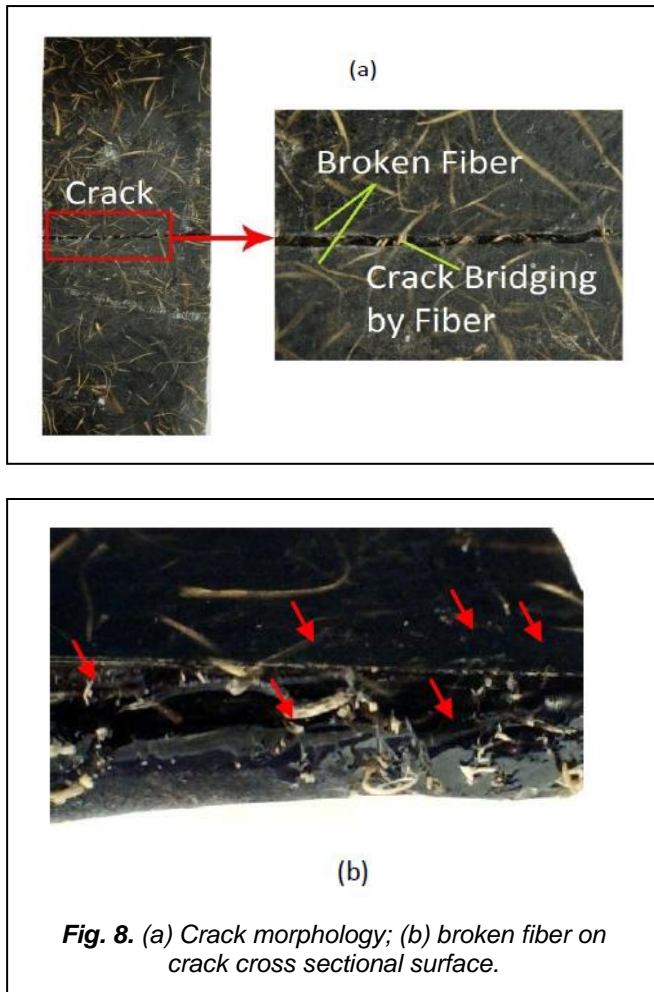
### 3.3 Flexural Properties

The flexural test results in Figure 7 shows that the addition of CNT can improve the flexural strength and modulus of elasticity of the fabricated composites. Flexural strength of composites is increased by 51.64%, 65.8% and 105.9% respectively for the addition of CNT as much as 0.1%, 0.5%, and 1% of the matrix weight. The improvement of flexural strength may be caused by CNT that prevents the propagation of cracks with crack bridging mechanism [18].



**Fig. 7.** Flexural properties of fabricated composite based on ASTM D790.

Unlike the tensile test, the load on the three-point flexural test is a combination of shear stress and tensile stress [19], and the failure mechanism that occurs [20]. At the initiation of cracks caused by shear stress, the CNT help to reduce the propagation of cracks that lead to fracture. In addition, the flexural strength is driven mostly by matrix rich area that is not reinforced by natural fiber because of its size. Carbon nanotube can easily fill the gaps that can be filled by natural fiber because of the size difference. The addition of CNT increases the composite modulus elasticity as much as 23.27%, 75.35%, and 119% respectively by CNT addition of 0.1%, 0.5%, and 1% matrix weight. The presence of CNT, which has good interaction with epoxy matrix, can reduce molecular deformation of the epoxy polymer. In result, the strain can be also reduced [16]. The fabricated composite also has higher flexural strength compare to commercial car bumper made of polypropylene (Shanghai/Beijing Expert in the Developing of New Material Co. Ltd) which is 25 MPa [17].



Different effectiveness of CNT as reinforcement on tensile and flexural properties can be caused by different kind of loading applied in corresponding test. In tensile test, the load applied is in-plane loading where greatly influenced by fiber properties not by the matrix [20]. This cause addition of CNT did not give significant effect on tensile strength. On the other hand, in flexural test, the loading applied is the combination of in-plane and out-plane direction. The out-plane or interlaminar properties if significantly influenced by matrix rich region properties. The addition of CNT modified the properties of epoxy matrix so that can improve the interlaminar properties of composite. The similar result was concluded by Bekyarova et. all where the addition of CNT did not give significant improvement of tensile strength but significantly improved the composite shear strength [21] and by Myungso et. all where addition of CNT in carbon fiber/epoxy composite show significant improvement of flexural strength but not to tensile strength [20].

### 3.3 Composite Morphology

Figure 8 (a) shows that on the crack area the fiber bridge the crack so it can prevent further crack propagation. Move over, Figure 8 (b) shows that the fiber it self was broken, not pulled out. This shows that there is good interaction between fiber and epoxy matrix. The surface treatment caused the fiber to have epoxy group on its surface, similar with the matrix epoxy group. This epoxy group on the surface of the fiber will react with one of amine groups from TETA (curing agent). The other amine groups of TETA can be reacted with epoxy group of the

matrix and so on until the matrix and the fiber surface are highly cross linked, forming polymeric chain..

## 4 Conclusion

From the experiment it can be concluded that the addition of carbon nanotubes increased the tensile strength of Fruit bunch palm oilfiber/epoxy composites of 10.03%, 4.75% and 7.75% respectively for the addition of carbon nanotubes as much as 0.1%, 0.5%, and 1% wt of matrix. The addition of carbon nanotubes also increased the flexural strength of Fruit bunch palm oilfiber/epoxy composite of 51.64%, 65.8%, 105.9% respectively for the addition of carbon nanotubes as much as 0.1%, 0.5%, and 1% wt of the matrix. The strengthening of interlaminar by CNT can enhance the elastic modulus of composite is formed. Besides the addition of CNTs provide a significant increase in buckling strength in the composites due to its presence amplify the matrix-rich regions.

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