



RAMM 2018

# Structural and morphological studies on alkaline pre-treatment of oil palm empty fruit bunch (OPEFB) fiber for composite production

N.A. Latip<sup>a</sup>, A.H. Sofian<sup>a,\*</sup>, M.F. Ali<sup>a</sup>, S.N. Ismail<sup>a</sup>, D.M.N.D. Idris<sup>a</sup>

<sup>a</sup>*Faculty of Chemical and Natural Resources, Universiti Malaysia Pahang, 26300 Kuantan, Pahang, Malaysia*

---

## Abstract

Empty fruit bunch from the palm oil industry can be classified as a popular source among various waste streams in Malaysia as one of recyclable raw material. It offered broad useful applications especially in bio-composite production. However, one of the major weakness of oil palm empty fruit bunch (OPEFB) is their hydrophilic characteristic that will cause the weak binding between the interaction of fiber and polymer matrix during the composite production. Thus, the pre-treatment need to be done in order to improve their compatibility. In this work, the effect of alkali pre-treatment by using different alkaline solution (NaOH, KOH, Al(OH)<sub>3</sub>) with fiber to solution ratio at 1:20 have been investigated. Their physicochemical and structural behavior were studied in details by several analysis. The experimental result showed that the decreasing in ester linkage stretching, aromatic groups and also lignin for Fourier Transform Infrared (FTIR) analysis by NaOH and KOH treated OPEFB fiber. Scanning Electron Microscopy (SEM) observation also contributed to highlight these changes by exposing their structure and morphology of treated fiber. Meanwhile X-ray Diffraction (XRD) analysis clearly observed that the highest crystallinity index was 60.8% by KOH solution just slightly different from the NaOH solution by 0.5% compared to Al(OH)<sub>3</sub> solution by 22.9%. From this finding, the modification of OPEFB fiber through alkaline pretreatment by three different alkali solution gave some changes to the nature of OPEFB fiber and can be seen clearly that both NaOH and KOH gave better perspective in term of the hydrophilicity reduction and surface effectiveness as well as cellulose structure improvement.

© 2018 Elsevier Ltd. All rights reserved.

Selection and peer-review under responsibility of the scientific committee of the 6th International Conference on Recent Advances in Materials, Minerals & Environment (RAMM) 2018.

**Keywords:** Alkaline solution; pre-treatment; oil palm empty fruit bunch (OPEFB); physicochemical; structural; composite

---

\* Corresponding author. Tel.: +609-549 2866  
E-mail address: [azizulh@ump.edu.my](mailto:azizulh@ump.edu.my)

## 1. Introduction

The growing ecological and environmental consciousness globally has probably triggering the world of material design and engineering. This has driven effort towards the evolution of advance innovation of materials and design that must be properly ascertained to fulfill human needs as well as the environment protection entirely. Reinforcement of natural fiber with polymer matrix are seems to be significance in enhancement the thermal and mechanical performance in composites production which is in demand for several industry like automotive, agriculture, construction and many more [1-3]. Nowadays, exploration on bio-composites industry has become significant in Malaysia. This is because its raw material which called as natural fiber usually came from various source of waste that abundantly available and currently underutilized. The idea of reuse is quite economically so that the cost of processing or composite production at least can be reduced. Besides they give low environmental impact compare to the usage of non-natural fiber [4,5]. In composite production, the application of all sorts of natural fibers as alternative to replace the ‘non-easy’ degradable synthetic fiber is not only poses a good potential to minimize our dependence on non-renewable materials but also may have great contribution in promoting recycling activities since this also can be as one of the best option instead of just to dispose the residues without being utilize to the maximum [6].

One of the natural fiber that has received much attention from Malaysia’s researchers was oil palm empty fruit bunch (OPEFB) fiber. OPEFB other than oil palm frond (OPF) and oil palm trunk (OPT) that consist in total 40 million tons of biomass from palm oil industry alone in Malaysia are abundantly produced after oil extraction but apparently not being fully utilized [7,8]. Previously, OPEFB was involved in steam generation through incineration process as a fuel but later on this activity got criticism due to the bad impact towards surrounding and environment because of the emission of white smoke excessively [9]. At present, OPEFB has become the starting material for the production of bio-products like bio-compost, biofuels such as bioethanol and biobutanol, lignophenol and others due to its availability and low cost [10,11].

Nevertheless, natural fiber like oil palm empty fruit bunch are not a problem-free material as it has its own major drawback which is their lack in dimensional stability and also the hydrophilic behavior. These shortfalls in properties has led to poor bonding with polymer matrix that affected throughout the interface of composite with the inefficient of stress transfer [12]. This can be solved by surface treatment. Some modification on the surface of natural fiber are certainly necessary by using chemical treatments so that the moisture absorption of fiber can be minimize. Hence the bonding strength can be amplified as well as the stress transferability in the composite, not to be neglected is the thermal stability that also shows some improvement [3,13,14]. In dealing with natural fibers, treatment can be the most significant element that need to be contemplated thoroughly by researchers. Kabir and his friends [15] discovered that hydrophilic behavior of fiber will be reduced after chemical treatment due to the detachment of hydroxyl groups. This process eventually will improve dimensional stability along with enhancement in the mechanical strength of natural fiber reinforced polymer matrix composites.

Scientifically, uppermost layer of fiber cell wall consist of few unwanted components such as natural oil, pectin, lignin, hemicellulose and waxy substances. These undesirable components basically will be evacuated through the chemical treatment so that the existence of fibrils will be disclosed. This process caused the irregular in the arrangement of physical features at the surface of fiber. Alkaline pretreatment has been recognized as one of the best chemical treatment and modification on the natural fiber [16,17]. This process involve the application of alkali solution with certain concentration and other condition towards the natural fiber to eliminate lignin and a part of hemicellulose as well as enhance the comprehensibility of enzyme to the cellulose.

The purpose of this study was to investigate the structural and morphological properties on the treated OPEFB by using different alkali solution. All the solution such as sodium hydroxide (NaOH), potassium hydroxide (KOH) and aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ) will go through the same condition for treated fibers preparation and will be undergo some characterization process like scanning electron microscopy (SEM) to provide quantitative compositional details and elemental identification of the treated fibers meanwhile X-ray diffraction (XRD) to identify the presence of crystalline material like cellulose inside the treated fibers. The chemical structures of treated and untreated fibers also will be analyze by using Fourier transform infrared (FTIR) spectrophotometer.

## 2. Materials and methods

### 2.1. Materials

Oil palm empty fruit bunch (OPEFB) fiber was supplied by local palm oil, Lepar Hilir Mill Palm Oil. Sodium hydroxide (NaOH), potassium hydroxide (KOH), aluminum hydroxide  $\text{Al}(\text{OH})_3$  and acetic acid were purchased at Sigma Aldrich.

### 2.2. Methods

- Preparation of untreated fiber:-

The OPEFB fiber had been dried under sunlight for three days, chopped by using crusher machine (TST plastic crusher SC7514 series SCB 3140/14 Hp) and then a sieve was used on OPEFB fiber to obtain a uniform size and length of fiber within range 2 to 4 mm. The diameters of the fibers were found 0.06 to 0.08 mm. These chopped fibers were immersed in hot distilled water at  $70^\circ\text{C}$  for 6 hours to eliminate any impurities from the surface and then dried again to provide the sample of untreated OPEFB fibers.

- Preparation of treated fiber:-

The untreated OPEFB fiber were treated with alkali solution by immersing about 25g fibers in 500 ml of distilled water containing 15% (w/v) of sodium hydroxide (NaOH) solution at  $130^\circ\text{C}$  and for 40 minutes with fiber to solution ratio at 1:20. After these treatments, the fibers were washed thoroughly with water flow and then got engaged by few drops of acetic acid to counteract the existence of excess alkali content in the fiber. This activity was conducted at room temperature for several minutes. A pH meter was used to confirm the neutralization process after the treated fiber frequently washed until the excess acetic acid were fully removed. Lastly the fibers were dried in an oven at  $70^\circ\text{C}$  for 15 hours to obtain treated OPEFB fibers. The treatment had been repeated by using two other alkali solutions which are Potassium Hydroxide (KOH) and Aluminum Hydroxide ( $\text{Al}(\text{OH})_3$ ).

- Structural and morphological characterization of the fiber:-

The treated and untreated fiber were analyzed with an analytical technique of Fourier Transform Infrared (FTIR) by a spectroscopy analyzer (SHIMADZU, series 8300) where the transmittance was discovered over a range from 4000 to  $500\text{ cm}^{-1}$ . Then the morphology of treated and untreated fiber were observed by the Cambridge S200 microscope for Scanning Electron Microscopy (SEM) analysis. To check the crystallinity, XRD analysis will be used by X'Pert High Score PW3050/60 diffractometer using  $\text{Cu-K}\alpha$  radiation at 45KV and 40Ma with the equatorial diffraction patterns ( $2\theta$ ) were recorded from 10 to  $40^\circ$ . Segal empirical method will be used to calculate the Crystallinity indices (CI):

$$CI(\%) = \left[ \frac{I_{002} - I_{am}}{I_{002}} \right] \times 100 \quad [18]$$

Where  $I_{002}$  indicate the maximum intensity of the 002 lattice reflection of the cellulose crystallographic and  $I_{am}$  is the intensity of the amorphous diffraction.

## 3. Result and discussion

In this work, the effects related to FTIR, SEM and XRD analysis for different alkali solution (NaOH, KOH and  $\text{Al}(\text{OH})_3$ ) on the treated and untreated OPEFB fiber were studied and presented in details. Fig. 1 showed the FTIR spectra of untreated and alkali treated OPEFB fibers by three different alkali solution to detect the loses of functional group for several compound. The broad absorption band related to hydroxyl (O-H) stretching vibration can be seen around 3329.89 for all the samples that shows the exposure of cellulose structure [19]. It appeared weaker in intensity of the spectrum for  $\text{Al}(\text{OH})_3$  solution and slightly averted from the untreated sample that might be related to the hydrogen bonding between different functional group. While there is the presence of C-H stretching that can be seen at the absorption peak around 2900 in the spectrum of all the treated OPEFB [20].

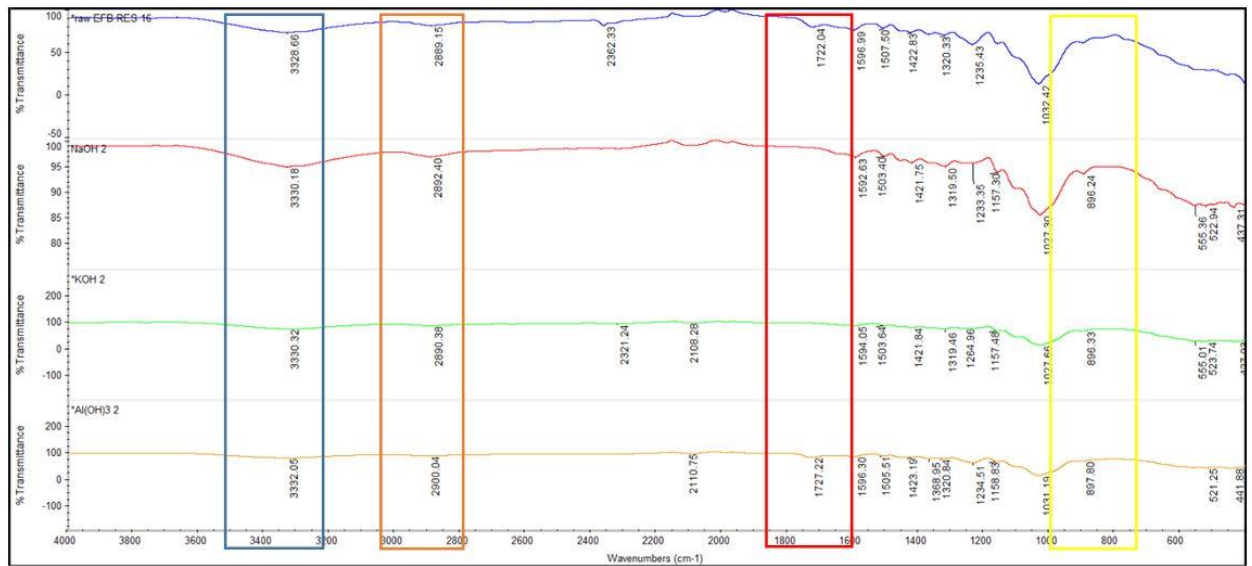


Fig. 1. FTIR Spectra untreated (pure) and treated OPEFB fiber by NaOH, KOH and Al(OH)<sub>3</sub> solution.

It is also noticeable that the band around 1729.74 were disappeared for NaOH and KOH treated fiber suggesting the removal of non-cellulose component such as lignin, pectin and hemicellulose due to the linkage between functional group of carbonyl ester of coumeric lignin or C=O acetyl group of hemicelluloses ester that probably exist at this peak [18,21,22]. An absorption band can be seen round 897 indicated to C-O-C stretching in cellulose at the linkage of (1,4) glycosidic [20].

The physical change and structural modification of treated and untreated OPEFB were elaborated by using SEM analysis as shown in Fig. 2. The scanning electron micrograph of OPEFB fiber for untreated or raw and treated by three different alkaline solution such as NaOH, KOH and Al(OH)<sub>3</sub> can be seen in the Fig. 2 (a), Fig. 2 (b), Fig. 2 (c) and Fig. 2 (d). There were significant differences in the fiber surface morphology for both treated and untreated OPEFB. As shown in Fig. 2(a), untreated OPEFB fiber relatively had a smooth surface that was covered with a layer of substances consist of wax, lignin and hemicellulose which prevent the rupture activity to the fiber [15,23]. Significant alteration of the surface fiber was happened after the pretreatment as some interfiber material were removed. Rough surface that quite same can be seen in the treated fiber for NaOH (Fig. 2b) and KOH (Fig. 2c) alkaline solution. This is due to the orientation changing of highly packed crystalline cellulose order to form an amorphous region that allowed O-H group from alkaline solution broken down in order to react with water molecules and then leave the fiber structure. Other than reducing the hydrophilicity of fiber, this reaction also remove the lignin, wax, hemicellulose and also oil that has coating the fiber surface [15]. The removal of certain portion of these binding and sizing structure has resulted in increasing porosity of the fiber as well as make surface area became more effective [24]. But NaOH treated fiber slightly better in term of structure. This finding is in line with the study reported by Fairouz Jahaan and his friends [10] that they claimed due to the silica removal and partial lignin decomposition cause the surface of OPEFB treated with NaOH covered with craters. As been shown at Fig. 2(d) there were deposited not only on the surface of fiber but also interiors of the fiber due to the insoluble compound in the Al(OH)<sub>3</sub> solution which minimized the porosity of the fiber [25].

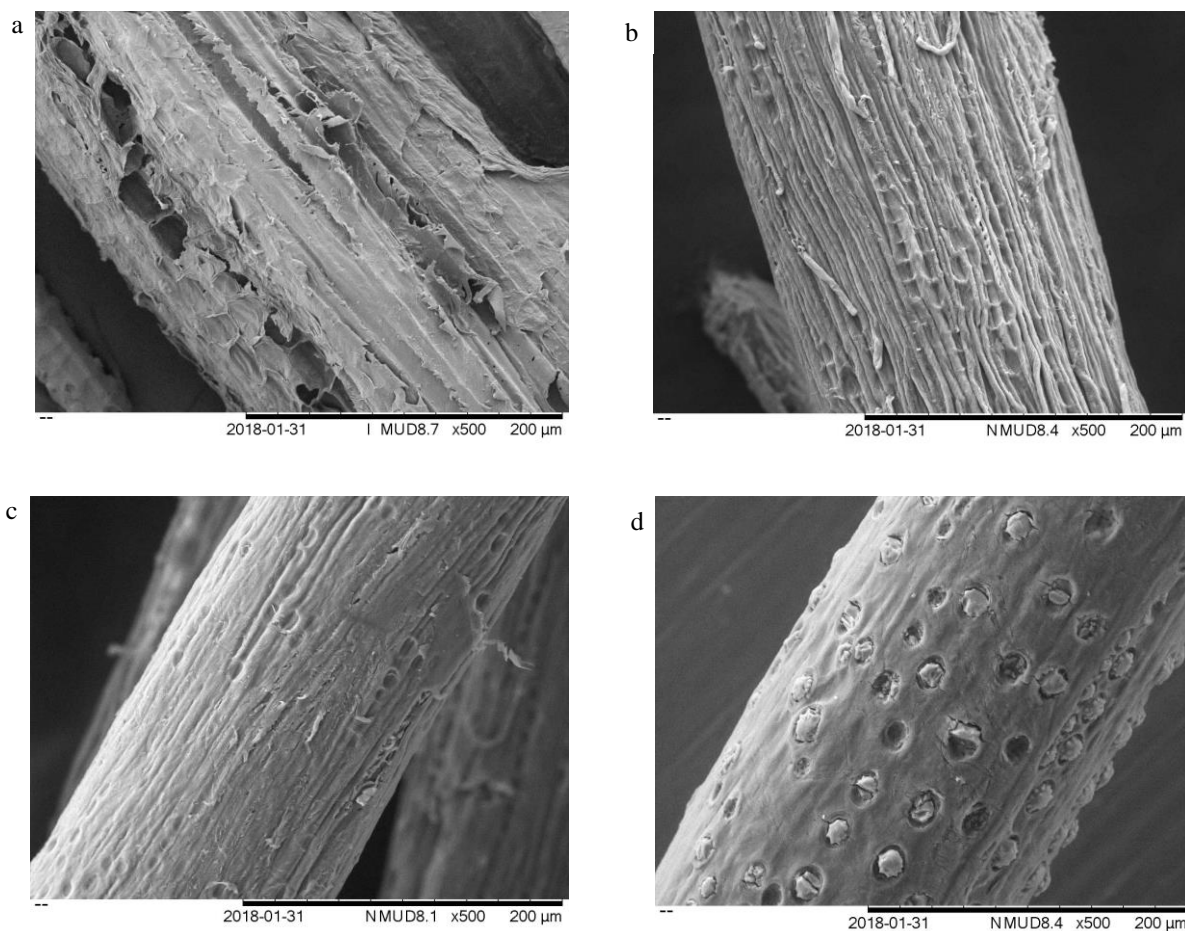


Fig. 2. SEM micrograph of (a) pure/raw (b) NaOH pretreatment (c) KOH pretreatment (d)  $\text{Al}(\text{OH})_3$  pretreatment of OPEFB fiber

The XRD analysis of the treated and untreated fiber were performed to investigate the crystalline structure and the results are shown in Fig. 3. The significant peaks of interest were at  $2\theta \approx 15.8^\circ$  and  $2\theta \approx 22.9^\circ$  represented as crystalline and amorphous portions of cellulose respectively. It can be seen clearly that OPEFB fiber exhibit a typical cellulose I pattern and the reflection peak at  $2\theta = 22.5^\circ$  correlate with the 002 crystallographic plane of cellulose. Crystallinity index (CI) were calculated based on Segal Empirical Method detailed in experimental section and the result are presented in Table 1. The crystallinity value of pure OPEFB fiber and after pretreatment by NaOH, KOH and  $\text{Al}(\text{OH})_3$  solution were 41.3%, 60.5%, 60.8% and 46.9% respectively. The increasing crystallinity of the treated fiber compared to the raw one perhaps due to the possible trancrystallinity and formation of new chains by hydrogen bonding that cause realignment in the cellulose molecules as resulted from the removal of lignin and hemicellulose through alkaline solution pretreatment on OPEFB fiber [24]. Some researchers also have been proven by their observation that alkali solution has cause the growing in amorphous cellulose content at the expense of crystalline cellulose which also indicated the improvement in cellulose structure and can increase the rigidity of cellulose. Hence contributed to the higher tensile strength of fiber [26].

It was observed that from Table 1 the crystallinity index for both treated fiber by NaOH and KOH solution was not far from each other as the difference was about 0.5% compared to untreated or treated by  $\text{Al}(\text{OH})_3$  solution. This

was due to the characteristic of both NaOH and KOH as basic compound that had made them more reactive than  $\text{Al}(\text{OH})_3$  as amphoteric compound. However the KOH pretreatment is slightly highest than NaOH pretreatment and this finding was contradict and not in the line with the study reported by most of the researchers [10,27] perhaps due to the difference in ion where potassium ion is larger than sodium ion thus the dissociation process can be done easily.

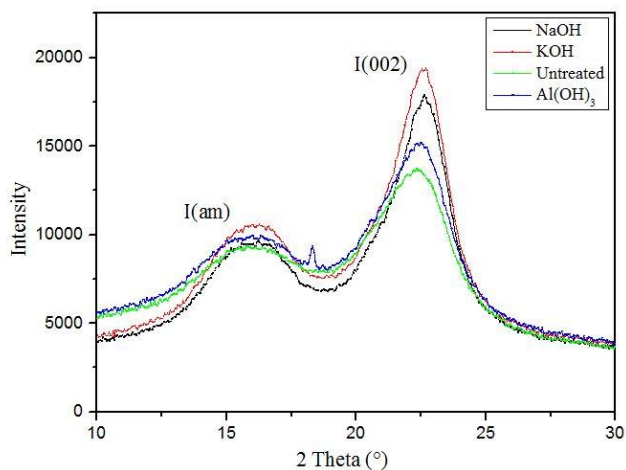


Fig. 3. X-Ray diffraction (XRD) patterns of untreated (pure) and treated OPEFB fiber by NaOH, KOH and  $\text{Al}(\text{OH})_3$  solution.

Table 1. Crystallinity index of untreated OPEFB fiber (pure/raw) and treated OPEFB fiber by NaOH, KOH and  $\text{Al}(\text{OH})_3$  solution.

Sample	Crystallinity Index (%)
Pure/raw OPEFB fiber	41.3
NaOH pretreatment OPEFB fiber	60.5
KOH pretreatment OPEFB fiber	60.8
$\text{Al}(\text{OH})_3$ pretreatment OPEFB fiber	46.9

#### 4. Conclusion

In this study, the removal of unwanted component such as lignin, pectin and hemicellulose that also responsible for flame degradation properties [14] can be seen clearly at the peak around  $1729.74 \text{ cm}^{-1}$  for FTIR analysis by using NaOH and KOH alkaline pretreatment with the support in morphology modification in SEM analysis. The split of hemicellulose and lignin that cause the fiber more porous can be observed significantly compared to the treatment by  $\text{Al}(\text{OH})_3$  solution and untreated fiber. The XRD analysis revealed that KOH treatment shows the highest crystallinity index by 60.8% yet only slightly different from NaOH treatment which is 60.5% which both contributed to increasing in tensile strength due to improvement in cellulose structure [26]. Even though there were only few difference between NaOH and KOH pretreatment for all the analysis, it can be concluded that both can be used as the best solution of alkaline pretreatment for natural fiber as from the result there can be seen some enhancement in term of fiber properties that showed the treated OPEFB fibers are suitable as eco-friendly reinforcement material in composite production. Hence these transformation literally affected and contributed to the improvement in bonding strength with thermal stability that can be applied generally for advanced polymer composite production.

## Acknowledgements

This research was financially supported by internal grant vot number RDU1803122 entitled Potential utilization of OPEFB fiber and recycle PP reinforce fly ash for manufacturing fire resistant composite pallet under Universiti Malaysia Pahang.

## References

- [1] M. Rivai, A. Gupta, M. R. Islam, and M. D. H. Beg, *Fibers Polym.*, vol. 15, no. 7, pp. 1523–1530, 2014.
- [2] R. Ridzuan, M. D. H. Beg, M. Y. Rosli, M. H. Rohaya, A. A. A. S. Samahani, and I. Zawawi, *Int. J. Chem. Mol. Nucl. Mater. Metall. Eng.*, vol. 7, no. 6, pp. 1961–1969, 2013.
- [3] L. Mohammed, M. N. M. Ansari, G. Pua, M. Jawaid, and M. S. Islam, *Int. J. Polym. Sci.*, vol. 2015, 2015.
- [4] K. L. Pickering, M. G. A. Efendy, and T. M. Le, *Compos. Part A Appl. Sci. Manuf.*, vol. 83, pp. 98–112, 2016.
- [5] M. R. Sanjay, G. R. Arpitha, L. L. Naik, K. Gopalakrishna, and B. Yogesha, pp. 108–114, 2016.
- [6] T. Väisänen, O. Das, and L. Tomppo, *J. Clean. Prod.*, vol. 149, pp. 582–596, 2017.
- [7] N. Abdullah and F. Sulaiman, *Biomass Now – Sustain. Growth Use*, pp. 75–100, 2013.
- [8] A. Keskiäsaari and T. Ka, pp. 1136–1143, 2017.
- [9] S. H. Chang, *Biomass and Bioenergy*, vol. 62, pp. 174–181, 2014.
- [10] F. J. M. Aanifah, P. L. Yee, H. Wasoh, and S. Abd-Aziz, *J. Oil Palm Res.*, vol. 26, no. 4, pp. 321–331, 2014.
- [11] I. Pollution and P. Technology, vol. 3014, pp. 1–5, 2018.
- [12] T. Gurunathan, S. Mohanty, and S. K. Nayak, *Compos. Part A Appl. Sci. Manuf.*, vol. 77, pp. 1–25, 2015.
- [13] M. Abdelmouleh, S. Boufi, M. N. Belgacem, and A. Dufresne, *Compos. Sci. Technol.*, vol. 67, no. 7–8, pp. 1627–1639, 2007.
- [14] M. N. Prabhakar, A. U. R. Shah, and J.-I. Song, *Compos. Res.*, vol. 28, no. 2, pp. 29–39, 2015.
- [15] M. M. Kabir, H. Wang, K. T. Lau, and F. Cardona, *Compos. Part B Eng.*, vol. 43, no. 7, pp. 2883–2892, 2012.
- [16] M. S. Islam, K. L. Pickering, and N. J. Foreman, *Compos. Part A*, vol. 41, no. 5, pp. 596–603, 2010.
- [17] L. Y. Mwaikambo and M. P. Ansell, no. July 2001, pp. 2222–2234, 2002.
- [18] A. Benyahia, A. Merrouche, M. Rokbi, Z. Kouadri, ” pp. 1–6, 2013.
- [19] N. Zulkiple, M. Yusuf, and O. Hassan, vol. 18, no. Mcls 2015, pp. 155–161, 2016.
- [20] N. S. Hassan and K. H. Badri, vol. 438, pp. 433–438, 2014.
- [21] F. Afifah, B. Ahmad, and K. Haji, vol. 456, no. 2014, 2017.
- [22] I. Y. A. Fatah *et al.*, pp. 2611–2624, 2014.
- [23] S. Palamae, P. Dechatiwongse, W. Choorit, Y. Chisti, and P. Prasertsan, *Carbohydr. Polym.*, vol. 155, pp. 491–497, 2017.
- [24] J. O. Akindoyo, S. Ghazali, and H. Beg, no. February, 2015.
- [25] F. Yang, Y. Zhang, and Y. Feng, vol. 12, no. 1, pp. 1826–1834, 2017.
- [26] R. Ramli, N. Junadi, M. D. H. Beg, and R. M. Yunus, vol. 9, no. 1, pp. 8–11, 2015.
- [27] F. Hamzah, A. Idris, and T. K. Shuan, *Biomass and Bioenergy*, vol. 35, no. 3, pp. 1055–1059, 2010.
- [28] T. Sen and H. N. Reddy, *Inter. Journal of Innovation, Management and Technology*, vol. 2, pp. 192–198, 2011.