Effect of ball-milling time on chemical property of coconut shell powder

I Ismail1, Arliyani1, S Fathmiyah1, Mursal1, Z Jalil1 and H P S A Khalil2

1Department of Physics, Universitas Syiah Kuala, Banda Aceh 23111, Indonesia
2School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia

* ismailab@unsyiah.ac.id

Abstract. Coconut is one of the abundant agricultural products in Indonesia. Coconut shell is one of the wastes from coconut products that can be used as biocomposite material. The purpose of this study was to find out the effect of ball milling time on the chemical properties of coconut shell powder. X-ray diffraction (XRD) and X-ray fluorescent (XRF) have been used in this study. Coconut shell powder 200 mesh was milled using mechanical ball milling for various milling times (20, 30, and 40 hours) at 350 rpm constant speed. The results of our study using XRD showed that the coconut shell powder contains SiO$_2$, C, Fe$_2$O$_3$, CaO, K$_2$O, and Al$_2$O$_3$. The intensity of the diffraction pattern from our sample increased when the ball-milling time was increased. This implies that the crystallinity of the sample was influenced by the ball-milling time. By using XRF, it was found that the coconut shell powder contains 13.6% of Fe$_2$O$_3$, 25.7% of CaO, 46.1% of K$_2$O, 2.8% of CuO, and 8.2% of P$_2$O$_5$. The percentage composition of Fe$_2$O$_3$ increased from 13.6% for 0 hours milling time to 30.2% after the sample was milled for 20 hours. The percentage composition of Fe$_2$O$_3$ rose to 32.2% for the milling time of 40 hours. However, the percentage compositions of CaO and K$_2$O decrease as the milling time is increased. The percentage composition of P$_2$O$_5$ is independent of milling time. Our results show that the chemical properties of coconut shell powder are influenced by the ball-milling time or particle size of coconut shell powder.

1. Introduction

Data from the Food and Agriculture Organization (FAO) shows that there are around 12 million hectares of coconut plants planted in 86 countries [1]. Indonesia is a country that has the largest coconut plantations with an area of 3.88 million hectares, which produces coconut 3.2 million tons copra [2]. So, Indonesia produces a lot of waste from coconut production; one of them is coconut shell. However, until now, the use of coconut shells has not been optimal. Generally, coconut shells are only used as charcoal and raw material for insect repellent. On the other hand, the results of previous studies found that coconut shells contained 29.4% lignin, 26.6% cellulose, and 27.7% pentosans [3]. Besides, coconut shell also contains carbon [4]. Vasu et al. argued that coconut shell has a potential for a biocomposite material that can be applied to aircraft and automotive parts [3].

A recent study found that the physical and mechanical properties of the composite were influenced by the particle size of filler [5-8]. Bello et al. studied the physical properties of coconut shell nanoparticles. The nanoparticle of coconut shell was produced by using the mechanical ball milling,
after milling for 16 hours. They found that the optical properties of coconut shells were significantly influenced by the ball-milling time [9]. Toozandehjani et al. found that the time of ball milling had a large contribution to the density, hardness, and Young's modulus of Al-5Al₂O₃ nanocomposites. The hardness value of composite increased by 46% after milling the sample for 12 hours [10]. Thus, it is very interesting to study the ball-milling time effect on the physical, mechanical, and chemical properties of the composite.

As discussed previously above, coconut shell powder has great potential for composite. To our knowledge, there is no study found in the literature so far about the particle size effect on the chemical property of coconut shell powder. In connection with that matter, we have investigated the effect of ball-milling time on chemical property of coconut shell powder. The results are reported in this paper.

2. Material and Method
The 200 mesh coconut shell powder was purchased from PT Indratma Sahitaguna Indonesia. The coconut shell powder was milled by using a planetary ball mill manufactured by Fritsch. The ball-milling time was varied from 0, 20, 30 and 40 hours. The milling speed was constant at 350 rpm for all samples. The ratio of ball to powder was 10:1 gram. X-ray diffraction (XRD) manufactured by Shimadzu serial D6000 was utilized to determine the composition of phases contained in the coconut shell powder. X-ray fluorescent (XRF) manufactured by PANalytical MiniPal Type 4 was used to determine the percentage of chemical compositions contained in the coconut shell powder samples.

3. Results and Discussion
Figure 1 shows our X-ray diffraction data of coconut shell powder for several ball-milling times. By using JCPDS (Joint Committee on Powder Diffraction Standards), the kind of compound in the sample can be determined. The highest broad peak was observed at the Bragg angle (2θ) of 21.7 degrees, which is amorphous carbon. The coconut shell powder contains the amorphous SiO₂ which was observed at 15.4 degrees of Bragg angle. The coconut shell powder also contains some other compounds that are K₂O, CaO, Fe₂O₃, and Al₂O₃ (see figure 1).

![Figure 1. X-ray diffraction patterns of coconut shell powder.](image-url)
The chemical compositions of coconut shell powder for various ball-milling times have also been measured by using X-ray fluorescent (XRF). Our results are shown in table 1 (chemical elements) and figure 2 (chemical compounds). The coconut shell powder contains K, Ca, Fe, P, Cu, and Ni. The oxide compounds contained in the coconut shell powder are Fe$_2$O$_3$, CaO, K$_2$O, CuO, and P$_2$O$_5$. Unfortunately, there was no carbon observed using XRF because carbon is a light element which is difficult to be detected by XRF. The oxide compounds of SiO$_2$ and Al$_2$O$_3$ were also not observed in the XRF measurement, which could be due to the small amount of these compounds contained in the coconut shell powder.

Leman et al. studied the coconut shell powder by using XRF. They found that the coconut shell powder contains 10% of carbon, 1.21% of K$_2$O, 0.98% of SiO$_2$, 0.35% of Fe$_2$O$_3$, and 0.23% of CaO [11]. All of these elements or compounds were observed in our study discussed above. Ting et al. studied coconut shell ash by using XRF. They found that the coconut shell ash consists of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, CaO, K$_2$O, and MgO [12]. All of these compounds were observed in this study except MgO. By using the atomic absorption spectrophotometer, Liyanage et al. argued that the coconut shell powder ash contains Na, K, Mg, Ca, Fe, Zn, and Cu [13]. However, some elements Na, Mg, and Zn were not observed in our samples. This discrepancy could be related to the sensitivity of the instrument.

Table 1. Chemical composition of coconut shell powder.

| Element | Composition (%) |
|---------|----------------|
|         | 0 hours | 20 hours | 30 hours | 40 hours |
| K       | 49.6    | 38.8    | 38.7     | 38.0     |
| Ca      | 24.4    | 18.2    | 18.5     | 17.4     |
| Fe      | 13.3    | 30.0    | 30.0     | 32.2     |
| P       | 4.2     | 4.0     | 3.8      | 4.2      |
| Cu      | 3.2     | 3.8     | 3.7      | 3.6      |
| Ni      | 0.7     | 2.0     | 2.0      | 1.9      |

The composition of K is 49.6% in the coconut shell powder before milling (0 hours milling time). When the coconut shell powder was milled for 20 hours, the composition of K decreases to 38.8%. The composition of K decreases to 38.0% for 40 hours of milling time. This trend is the same for Ca. However, the composition of Fe increases from 13.3% for 0 hours milling time to 30.0% after the sample was milled for 20 hours. After milling for 40 hours, the composition of Fe increases to 32.2%. However, the composition of P, Cu, and Ni are independent of the ball-milling time.

Figure 2 shows the oxide compounds contained in the coconut shell powder for 0, 20, 30, and 40 hours of milling time. The coconut shell powder contains 13.6% Fe$_2$O$_3$, 25.7% of CaO, 46.1% of K$_2$O, 2.8% of CuO, and 8.2% of P$_2$O$_5$. As the coconut shell powder was milled for 20 hours, the composition of Fe$_2$O$_3$ significantly increases to 30.2%. After milling for 40 hours, the composition of
Fe$_2$O$_3$ in the coconut shell powder increases to 32.2%. The composition of K$_2$O decreases from 46.1% (0 hours milling time) to 35.7% after milling time for 20 hours. After milling time for 40 hours, the composition of K$_2$O is 34.8%. The composition of CaO decreases to 18.4% after milling time for 20 hours. The composition of CaO decreases to 17.5% after milling time for 40 hours. Thus, the compositions of Fe$_2$O$_3$, K$_2$O, and CaO are affected significantly by the ball-milling time. Meanwhile, the compositions of CuO and P$_2$O$_5$ are independent of milling time, as shown in figure 2.

![Figure 2](image)

**Figure 2.** Composition of oxides in coconut shell powder for various milling times.

As the ball-milling time is increased, the intensity of diffraction increases (see figure 1). Figure 3 shows the intensity of the carbon peak for several milling times. Before the coconut shell powder was milled (0 hours), the intensity of diffraction for carbon is 906. When the sample was milled for 20 hours, the intensity of the carbon peak increases to 1049. The intensity of carbon peak continues to increase to 1132 for 30 hours milling time. The intensity of carbon peak for 40 hours is about the same as that for 30 hours milling time. The increasing intensity of diffraction is related to the crystallinity of the sample. As the sample was milled, then particle size of coconut shell powder is reduced, which affects the crystallinity of the biocomposite sample.
4. Conclusions
By using XRD and XRF, we have determined the chemical property of coconut shell powder for various ball-milling time. Our results showed that the coconut shell powder contains 13.6% of Fe₂O₃, 25.7% of CaO, 46.1% of K₂O, 2.8% of CuO, and 8.2% of P₂O₅. The percentage composition of Fe₂O₃ increased significantly after the sample was milled for 20 hours. Meanwhile, the percentage compositions of CaO and K₂O decrease significantly after milling time for 20 hours. Our results indicated that the chemical property of coconut shell powder is significantly affected by the ball milling time. This finding suggests that the particle size can drive the property of coconut shell powder.

5. References
[1] FAO, http://www.fao.org/docs/eims/upload/216252/Infosheet_Coconut.pdf
[2] Kementerian Perindustrian, 2009, https://kelapaindonesia2020.wordpress.com/kebijakan-pengembangan-kelapa/departemen-perindustrian/
[3] Vasu A T, Reddy C, Danaboyina S, Manchala G K and Chavali M 2017 J.Polym Sci Appl 12
[4] Bledzki A K, Mamun A A, Volk J 2010 Journal Composites Science and Technology 70 840–846
[5] Cezarygozdecki, Zajchowski S, Kociszewski M, Wilczyński A and Mirowski J 2011 POLIMERY 5 375 – 380
[6] Jaya H, Omar M F, Akil H M, Ahmad Z A and Zulkepli N K 2016 BioResources 11 6489 – 6504
[7] Fu S Y, Feng X Q, Lauke B, Mai Y W2008Composites: Part B 39 933–961
[8] Martin Y, Permata D, Ulya A, Despa D, Marwansyah M, Rahmat A 2020 Ufer Grounding System to Minimize Risk of Lightning Strike using Concrete Mixed with Bentonite and Coconut Fiber J. Ilm. Pendidik. Fis. Al-Biruni. 9 1 133-140
[9] Bello S A, Agunsoye J O, Adeebi J A, Kolawole F O, Hassan S B 2016 Journal of Science, Engineering and Technology 12 63-79
[10] Toozandehjani M, Matori K A, Ostovan F, Aziz S A and Mamat M S 2017 Materials 10 1232
[11] Leman A S, Shahidan S, Senin M S, Hannan N I R R 2016 IOP Conf. Series: Materials Science and Engineering 160 012059
[12] Ting T L, Jaya R P, Hassan N A, Yaacob H, Jayanti D S, Ariffin M A M 2016 JurnalTeknologi
Acknowledgments
This work was funded by the Ministry of Research, Technology and Higher Education Indonesia under the WCR grant in 2019.

[13] Liyanage C D and Pieris M 2015 *Procedia Chemistry* **16** 222-228