Characterization of cellulose acetate based on empty fruit bunches and dried jackfruit leaves as replacement candidates for microbeads

Dewi Tristantini[1*], and *Andersen Yunan*[1].

[1]Department of Chemical Engineering, Faculty of Engineering, University of Indonesia, Depok, 16424, Indonesia.

Abstract. Scrubs used in other skin care and beauty products usually contain tiny fine grains of synthetic polymer called microbeads that usually pose threats to marine environment. Empty Fruit Bunches (EFB) and Dried Jackfruit Leaves (DJL) as organic and environmentally friendly can be alternative sources for polymer microbeads. Cellulose acetate is prepared by acetylation reaction between cellulose and acetic acid anhydride. Cellulose from EFB and DJL was extracted through a process of delignification with 12% NaOH treatment for EFB and 10% for DJL to obtain maximum yields of 38.964% and 14.449% respectively, followed by bleaching using peroxide 10 %. The formed cellulose acetate with 88.5% and 79.7% yield respectively is then filtered using a sieve mash 60 and 80 to obtain particle sizes ranging that are in the microbeads size range. The density test resulting in 0.73 g/cm^3 and 0.52 g/cm^3 respectively for EFB and DJL. Then, physical characteristic test was done by water and oil absorption test with variation at 25^{o}C and 40^{o}C. EFB at 25^{o}C and 40^{o}C shows water absorption at 23.39% and 26.09% and oil absorption at 7.59% and 13.95%. DJL at 25^{o}C and 40^{o}C shows water absorption at 22.56% and 27.32% and oil absorption at 13.09% and 15.36%.

1.Introduction

Cleaning products usually contain abrasive polymer scrubs that are highly developed. Usually, when one begin to apply it to skin, the mechanical exfoliation start to remove the outer skin surface and soften the skin [1]. According to Mills (1979), an abrasive scrub consists of natural and synthetic materials such as polyethylene granules, aluminum oxide, fruits grown in soil, and sodium tetraborate decahydrate grains made with varying degrees of exfoliation. However, the presence of polymer microbeads as a scrub material that is widely used in cosmetics and personal care becomes a new problem in the environment. Lighter-than-water properties [2] and small size particles cause microbeads to be unprocessed in wastewater treatment plants and overflow into waters and end up at sea. Microbeads are highly hydrophobic, so it is easier to absorb toxic pollutants [3] eaten by marine animals and distributed through the food chain. In addition, contaminated microbeads in the oceans can also damage coral reefs due to microbeads clogging up the digestive tract. Polymers used as microbeads are also very persistent and require a very long time to be degraded naturally in nature. Characteristics of white and stable, hard, and raw cellulose acetate are widely available in nature [4] making it an alternative to microbeads. Cellulose acetate is applied as body scrub with formulations comprising microbeads of cellulose acetate, sugars, acids, vitamins [5], emollient, dye, a little NaOH and fragrance.

According to National Oceanic Atmosphere Association, the amount of pollutants that accumulate in microbeads such as PCBs (Polychlorinated biphenyls) reaches 100.000-1.000.000 times the amount detected in seawater. Average the content of microbeads found in the five waters of the north Atlantic, southern Atlantic, southern india, northern and southern fasific is 120 particles / liter [6]. Based on several criteria, cellulose acetate meets the substitute criteria of microbeads. Cellulose is a biopolymer whose material is available in large quantities in the world, and many studies that prove its application on a wide scope. Various types of biomass can be used as a source of cellulose to produce cellulose acetate such as cotton waste, recycled paper, agricultural waste, and wood [7]. Empty fruit bunches (EFB) and dried jackfruit leaves (DJL) can be found commonly in indonesia in large quantity. These raw material also contain high percentage of cellulose that can potentially replace microbeads. However, there are still many aspects that need to be

* Corresponding author: detris@che.ui.ac.id, andersen.yunan@gmail.com

considered when it comes to replacement, for instance characteristics.

Therefore, the main purpose of this study is to give characteristics of both raw materials in terms of potential replacement to microbeads, such as cellulose and cellulose acetate yield, density, oil and water absorption and size of cellulose acetate by both materials.

2.Experimental

2.1. Materials

The raw materials used in this study were empty fruit bunches obtained from puspitek complex, BSD city, Indonesia and dried jackfruit leaves from Faculty of Engineering, University of Indonesia, Depok, Indonesia.

2.2. Preparation of Raw Materials

Preparation for both raw materials is done simultaneously in the same way. EFB and DJL are cleaned from the remains of the still-sticking fruit and other impurities. Then EFB and DJL was washed with water and dried in the sun to dry. EFB and DJL fibers are separated and cut to a size of 1-2 cm then stored at room temperature before proceeding for the research phase

2.3. Cellulose Extraction

Cellulose extraction is a pure cellulose removal step from EFB and DJL by removing other constituent parts such as lignin, hemicellulose, protein, and fat by using alkali treatment method. Cellulose extraction from EFB and DJL has the same stages. Cellulose extraction consists of 2 stages, such as:

2.3.1. Delignification with sodium hydroxide

The prepared raw materials, according to previous study that produces maximum yield of cellulose incorporated in a 12% EFB mixture and DJL 10% with a volume of 30 times the weight of the raw material and heated for 3 hours at a temperature of 90°C - 100°C. The result of heating is then filtered and washed until the filtrate is neutral.

2.3.2. Bleaching with peroxide

The samples were then bleached with 10% H_2O_2 with 20 times by weight of raw material for 2 hours. After that the sample was filtered and washed again until neutral and heated at 105^{o}C temperature for 6 hours before stored.

2.4. Cellulose Acetate Synthesis

At this stage, the reactants used are cellulose, glacial acetic acid, and anhydrous acetic acid. The preparation of cellulose acetate from EFB and DJL has the same stages, such as :

2.4.1. Activation

The obtained cellulose was added with glacial acetic acid with a volume ratio of 1:10, and heated with hot plate strirer at 38^{o}C for 60 minutes before 98% sulfuric acid catalyst was added with a ratio of 1 gram of cellulose using 0.4 ml and reheated at a fixed temperature for 45 minutes.

2.4.2. Acetylation

The result of the activation process was added with anhydrous and glacial acetic acid with a ratio of 3:2. The volume ratio between cellulose and glacial acetic acid was made for EFB 1:10 and DJL 1: 5 (w/v). The solution was then heated at 38°C for 30 minutes.

2.4.3. Hydrolisis

The process of hydrolysis is done by stopping the acetylation process first, then added aquades and glacial acetic acid with a ratio of 1:2 and heated at a temperature of 50^{o}C for 30 minutes.

2.4.4. Drying

The drying was carried out in an oven at 105^{o}C for 6 hours after the resulting cellulose acetate washed until neutral pH and acetate odor were gone. After drying is complete then we get the dry cellulose acetate in the form of crude fiber. The result of cellulose acetate drying will then be tested for its physical characteristics.

2.4.5. Calculation of results

The calculation of cellulose and cellulose acetate yield in this experiment is as follows:

$$\% \text{ yield} = (\text{cellulose/raw material}) \times 100\% \quad (1)$$

2.5. Characteristic Tests

Characteristic tests for this study are done by conducting density, size, water and oil absorption test as follows :

2.5.1. *Test particle sized*

The cellulose acetate particle size test was carried out by grinding EFB and DJL cellulose acetate fibers that had been dried in the oven for 6 hours at 105°C by using sieve mash 60 and 80 which were placed parallel to the upper and lower borders so that the particle size tested resembled the size range of microbeads.

2.5.2. *Density Test (Rabek, 1983)*

Calculation of cellulose acetate cell density of EFB and DJL is done by calculating the mass of each with ratio to the sample volume. Mass measurements were made by weighing the samples on analytical scales and volumes by multiplying the length, width and thickness of the sample, by the following formula.

$$\rho = m/v \quad (2)$$

2.5.3. *Water and Oil Absorption Test*

The samples were then dried for 24 hours in the oven at 50°C, then cooled in the desiccator after weighing them first. Data from water and oil absorption were then obtained by immersing the sample into water and oil for 24 hours at variable temperature of 25°C and 40°C. Then the sample is dried by wiping it with a cloth and then weighed again. The weight gain is calculated as percentage for materials that has lost the solute during immersion, such as a cellulose-containing material, the sample should be dried back and recalculated for later to be reported as percent of the lost solute. Calculations of percent water absorption can be calculated by the following formula.

$$\text{Absorption (\%)} = [W_a\,(\%) + M_s\,(\%)] \quad (3)$$

$$W_a = [(W_1 - W_0)/W_0] \times 100\% \quad (4)$$

$$M_s\,(\%) = [(W_0 - W_2)/W_0] \times 100\% \quad (5)$$

Where W_a is added weight with component W_0 as initial weight of material and W_1 as weight after sample has been immersed under oil or water and W_s is missing solute with component W_2 as weight after sample has been dried in oven.

3.Results and Discussion

3.1. Cellulose extraction yield

The results of cellulose extracted from the delignification and bleaching process were of the type α-cellulose with average yield of oil palm empty bunches reaching 38.964% (w/v) and dried leaves of 14.449% (w/v). This extraction results close to the maximum cellulose content of EFB of 38.76% [7] and DNK of 21.45% [8].

In EFB, high yields are caused by strong bonding structures between EFB molecules so that there is still a lignin content remaining on the fiber whereas in small DJL yields indicates cellulose purity. The small yield on the DJL is due to the amorphous DJL structure so that the intercellular molecule is weaker than the crystal structure of the EFB making it more likely that many dissolved cellulose in sodium peroxide [9]. Different yields between EFB and DJL are mainly due to the initial content of plant species used in cellulose extraction processes. Figure 1. Shows the average of cellulose extraction yield.

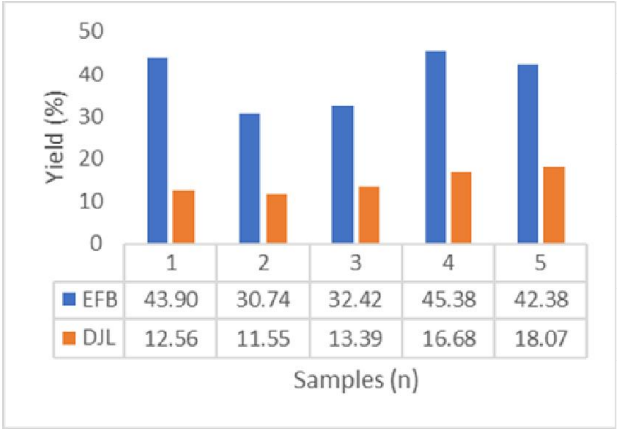

Fig. 1. Cellulose yield of EFB & DJL

3.2. Cellulose acetate synthesis yield

Calculations of the yield of cellulose acetate EFB and DJL can be seen in Figure 2. The yield yields are based on the weight ratio of cellulose acetate obtained by the weight of cellulose used in the acetylation process [7]. In this research, the ratio of acetate and anhydride ratio of EFB is 1:10 and DJL is 1:5. This is due to an increase in the amount of reactants increasing the likelihood of inter-collision reactants resulting in greater yield. However, if the amount is too large, the faster reaction speed causes the absence of product taking that produces cellulose acetate so that the product can be degraded and produce a lower yield [9].

In this study, the synthesis of EFB cellulose acetate at a ratio of 1:10 yielded a yield with an average of 88.5% and DJL at a ratio of 1:5 with an average of 79.7%. The yield produced in this study is much higher than the previous study because cellulose acetate synthesis in this study used the same cellulose sample with repeating it after failed several times to produce cellulose acetate. In the process of repetition with the same sample causes the weight of cellulose samples are wasted so that the synthesis process produced in this study produces higher percentage of cellulose acetate because it had been done repeatedly.

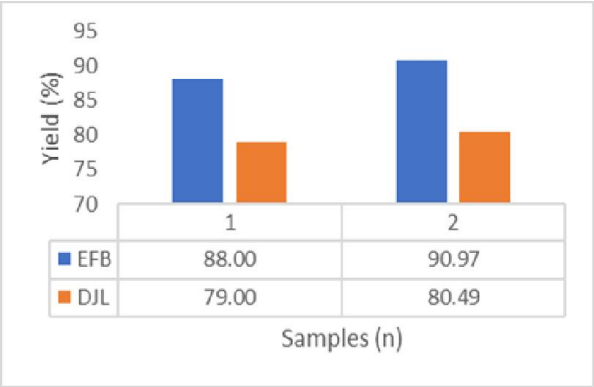

Fig. 2. Cellulose acetate yield of EFB & DJL

3.3. Particle test results

The particle size test is carried out after the density test and the water and oil absorption test where in the cellulose acetate that has been produced is crushed on the mortar and then the result of scouring in the form of EFB and DJL cellulose acetate powder is filtered on sieve mash 60 and 80 which is placed parallel so that the size particles are homogeneous and between the two sieve mash, which are 0.250 mm and 0.180 mm. The remaining unfiltered particles in the sieve mash due to larger size are then crushed back to mortar to the appropriate size. The size of microbeads generally ranges from 4 µm to 1 mm hence the produced cellulose acetate are within the range of common microbeads known.

3.4. Density test results

In general, density also relates to the physical properties of a material, either from the absorption of the material to other substances. Testing of density values in cellulose acetate is important because density can show the structure of cellulose acetate in general. Density affects a material's ability to protect products from substances such as water, oxygen and carbon dioxide. In addition, the known density values can also compare it with the density of polyethylene microbeads which are generally lower than that of 0.91 - 0.96 g/cm^3. The density value of cellulose acetate is obtained from the ratio of mass weight to water volume. This parameter aims to determine the density value of EFB and DJL cellulose acetate. The repetition of the density test in figure 3 was performed three times with EFB and DJL cellulose acetate samples still in the form of fibers soaked in the measuring glass with different volumes to obtain the average density for TKKS of 0.73 g/cm^3 and the average density for DNK of 0.52 g/cm^3. The obtained density value proved to be lower than that of water such as polyethylene microbeads density. In a study conducted by Bahmid (2014), the density value obtained was also close to the density of the study, ie 0.79 g/cm^3.

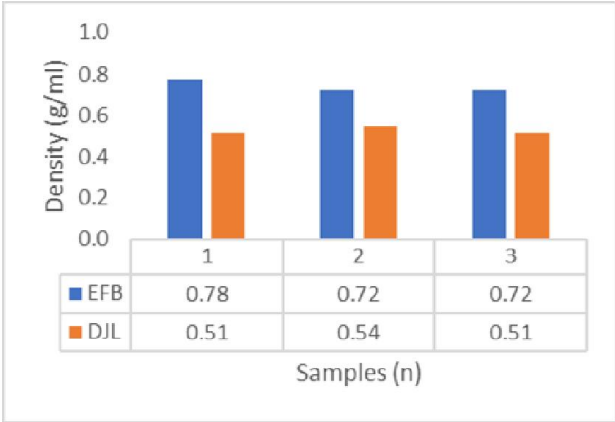

Fig. 3. Density test of EFB & DJL

3.5. Water and Oil Absorption results

Testing of water and oil absorption parameters is done to provide information on the dimensions of stability of cellulose acetate EFB and DJL. This is because the materials that are susceptible to water and oil can cause significant mechanical properties [7]. Material resistance is required during storage of cellulose acetate on the packaging. In addition, water and oil absorption is needed to find out whether the resulting cellulose acetate can be applied to human skin which is generally moist and there is oil in the pores of the skin.

The absorption rate of cellulose acetate water, both EFB and DJL, is higher than oil absorption. This is because in cellulose acetate there are still unsubstituted -OH groups which still allow for greater water absorption. The high absorption of water is also caused by the structure of the cellulose acetate-forming components of both materials. The absorption value of water and oil tends to increase at higher temperatures. Water and oil absorption experiments were performed twice and the scores taken were the average of both experiments. In figure 4, it can be seen that the value of EFB water absorption at temperature 25^{o}C is 23.39% and temperature 40^{o}C is 26.09% while the value of EFB oil absorption at 25^{o}C is 7.59% and temperature of 40^{o}C is 13.95%. For DJL, the value of water absorption at 25^{o}C is 22.56% and temperature 40^{o}C is 27.32% while the value of DJL oil absorption at 25^{o}C is 13.09% and the temperature of 40^{o}C is 15.36%.

The value of water and oil absorption in cellulose acetate shows a linear increase with an increase in temperature. Overall, the water absorption value of cellulose acetate EFB and DJL has the same value, similar value was also obtained by Bahmid (2014) when experimenting the absorption of EFB cellulose acetate water at a temperature of 23^{o}C with a water absorption rate of 19%. As for oil absorption, DJL

has higher absorption value than EFB. This can be due to structural differences between EFB and DJL, where the EFB structure is more crystalline and DJL is more likely to be amorphous. In addition, the high absorption of oil in DJL can also be caused by the chemical and structural properties of the compound.

It can be concluded that DJL cellulose acetate is more suitable to be applied to the face and cellulose acetate of EFB on the body. This is because the faces tend to produce more oil and qualitatively, DJL cellulose acetate is more subtle than cellulose acetate EFB

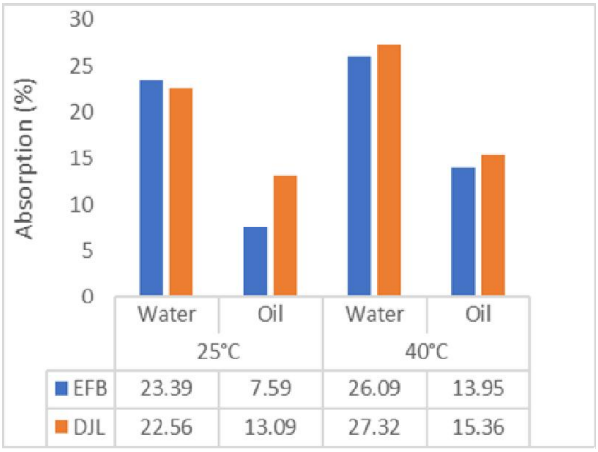

Fig. 4. Water & Oil absorption of EFB & DJL

Table 1 shows the differences between experiment results to commercial microbeads.

Table 1. Microbeads to EFB & DJL comparison

Samples	Size	Density	Absorption (%)	
			Water	Oil
Microbeads A	0,3-5	0,047-0,7	-	-
Microbeads B	0,3-5	0,35	-	-
Microbeads C	0,5-5	0,3	-	-
EFB Research	0,18-0,25	0,73	23,39	7,59
DJL Research	0,18-0,25	0,52	22,56	13,09

4.Conclusion

The cellulose acetate of EFB and DJL gave the similarity to microbeads in term of particle size. Moreover, it also has density lower than water and fully organic material which would not submerge under water and endanger sea animals and also coral reefs. The differences of results between cellulose acetate of EFB and DJL are because the source of cellulose used in the experiment. In addition to absorption properties, it showed linear increase in temperature with highest in oil at 40°C for EFB at 13.95% and DJL at 15.36% and water at 26.09% and 27.32% respectively. It shows that cellulose asetate of both EFB and DJL capable of absorbing oil and water. Therefore, the characteristics of cellulose acetate based on empty fruit bunches and dried jackfruit leaves give suitable traits as replacement candidates for microbeads.

References

1. M. Chang, Reducing microplastics from facial exfoliating cleansers in wastewater through treatment versus consumer product decisions, *Marine Pollution Bulletin*, **101**, 330-333 (2015)
2. Eriksen, M. Microplastics polution in the surface water of Laurentian Great Lakes. **77**, 177-182 (2013)
3. Schneiderman, E. T. Unseen threat: How microbeads harm new york waters, wildlife, health and environment. pp 1-5. (2014)
4. Morice, C. H., Radigue, B., & Winckler, C. Cellulose acetate technology to replace banned PE beads, 10, 1-4. (2015)
5. Thakur S, Shrivastava B, Ingale S, Kuhad RC, dan Gupte A. Degradation and selective ligninolysis of wheat straw and banana stem for an efficient bioethanol production using fungal and chemical pretreatment. *Biotech*, **3** , 365-372 (2012)
6. Nerland, I.L., Halsband, C., Allan, I., Thomas, K.V., Microplatics in marine environments: Occurence, distribution and effects. 23 (2014)
7. Bahmid, N. A., Khaswar S., Akhiruddin M., Pengaruh ukuran serat selulosa asetat dan penambahan dietilen glikol terhadap sifat fisik dan mekanik bioplastik, *Jurnal Teknologi Industri Pertanian*, **3**, 226-234 (2014)
8. D. Tristantini, D.P. Dewanti, and C. Sandra, Isolation and characterization of α-cellulose from blank bunches of palm oil and dry jackfruit leaves with alkaline process NaOH continued with bleaching process of H_2O_2 (2017)
9. Sasongko, W.T., Yusiati, L.M., Bachruddin, Z., & Mugiono. Optimalisasi peningkatan tanin daun nangka dengan protein bovin serum albumin. *Bulletin peternakan*, **34**, 154 (2012)