Effects of Corn Husk and LLDPE Ratio on the Properties by Thermo-pressing

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Abstract. The corn production in Indonesia, based on the data from *Badan Pusat Statistik* in 2011, amounted to 17.6 million tons, the corn husk from the corn crop is about 38.38%. The utilization of corn husk itself has not been maximized yet, so the research to maximize the utilization of corn husk is required. In this research, the biocomposite of the corn and Linear Low Density Polyethylene (LLDPE) with thermo-pressing method has been made. Biocomposites is made of corn husk variations: LLDPE are 30:70, 40:60, 50:50, 60:40, 70:30, and characterized the mechanical properties (tensile and tear) with a universal testing machine (UTM), biodegradation qualitatively and morphology by scanning electron microscopy (SEM). The thermal properties of corn husk is also analyzed by using differential scanning calorimetry (DSC). Mechanical analysis indicates the increasing of the mechanical properties with the addition of LLDPE concentration in biocomposites, with a concentration 30:70 has supreme mechanical properties with 24.77 Mpa of tensile strength, 19.10% elongation, and tear strength of 53.94 N/mm, while the highest elasticity of modulus is owned by the biocomposite with the concentration of 50:50. This result contrasts to the biodegradable analysis, where the greater concentration of the corn husk the higher biodegradability level. Mechanical analysis results are also supported by the results of biocomposites morphological analysis and LLDPE.

Keywords: Biocomposites; biodegradability; corn husk; mechanical properties

Introduction

Corn is a popular crop commodity in Indonesia. This commodity can also easily be found in every region in Indonesia. The corn production in the world according to Agriculture Organization of the United Nations in 2010 amounted to 844 million tons, while in Indonesia according to the data of Statistics Indonesia (BPS), it amounted to 18.33 million tons in 2010 and is predicted to keep increasing.

Large corn production impacts on the amount of corn waste. From the corn harvest, corn husks amounted to 38.38%. To date, corn husks in Indonesia are often used as animal feed, traditional food wrapper, and traditional crafts. The utilization of corn husks as mentioned above effectively maximizes the potential of corn husks, so further research is required to maximize the utilization of corn husks.

Corn husk development as bioplastics is often used as a solution to maximize the potential of corn husks. This is because corn husks have high fiber contents of about 38%-50% and carbohydrate contents of about 38%-55% [1]. Bioplastic development itself is often conducted. One of its benefits is bioplastics' ability to degrade more quickly than synthetic plastics. Another thing which supports bioplastic development is that synthetic plastics are made from petroleum byproducts, such as polyethylene. With petroleum as the basis, synthetic plastics have limited materials and cannot be renewed. Biodegradable plastics or bioplastics are one of the innovations created to reduce the amount of pollution caused by plastic waste. Bioplastics are made from a mix of synthetic polymer and natural materials such as starch or cellulose [2,3].

Previous research uses starch or tapioca as the material for making bioplastics [3]. However, the starch is obtained from tubers commonly used for food, so further research investigating bioplastic materials which do not compete with crop is necessary.

This research investigate~~s~~d the potential of corn husks as bioplastics using the analysis of Fourier Transform Infra-Red (FTIR) and Scanning Electron Microscopy (SEM). In this study, biocomposites made from corn husks and polyethylene polymer type Linear Low Density Polyethylene (LLDPE) were also made. LLDPE was used since this type of polymer is a low density polyethylene that is easily manufactured and commonly used for thin sheets so that it has a higher elasticity than other types of polyethylenes. The use of LLDPE also aim~~s~~ed to improve the mechanical properties of biocomposites. Corn husk biocomposites and LLDPE were printed using a thermo pressing method. This method was selected since it suits the standards for manufacturing biocomposites in which the temperature and the pressure can be adjusted according to the need. These biocomposites were then characterized mechanically by biodegradable and SEM tests.

This research was expected to serve as a study to initiate the role of corn husk as a bioplastic. The results of the study suggest the properties of corn husks that are expected to be a reference for the development of corn husks as a bioplastic. The biocomposite properties of corn husks are expected to be a reference for the direction of the application of bioplastics made from corn husks.

Experimental

Material

The materials used in this study were the 5th to 13th segments of corn husks obtained from markets in Bogor, LLDPE with technical quality from PT. Chandra Asri Petrochemical Tbk, and Oleic acid with technical quality from PD. Cipta Bangun Nauli. The technical quality was selected due to the majority of industrial needs for the application of plastic ores uses ores with technical quality.

Corn Husk Preparation

Corn husks obtained from markets in Bogor were sorted and cleaned. The parts of the corn husks taken were the middle and inner parts of the 5th to 13th segments. Corn husks were then dried in an oven at 60^{o}C for 8 hours. After drying, the corn husks were milled until they reached a size of 60 mesh (0.25 mm).

Composite Preparation

Synthetic polymer (LLDPE) was first mixed with oleic acid as a coupling agent in which the weight of the oleic acid was 2% of the total weight of the composite. The results were mixed with 60 mesh-size corn husks, with 30%, 40%, 50%, 60%, 70% of corn husks variations. They were then extruded at T1=165^{o}C, T2=170^{o}C, T3=170^{o}C, T4=175^{o}C, T5=175^{o}C and T6=180^{o}C with 30 rpm rotational speed. 14 gram of extrusion results were put inside the film printing equipment with a 14 cm diameter, then they were put inside a heat press machine, without pressure at 175^{o}C for 3 min and with 5 bars of pressure at 180^{o}C for 4 min. Then, this process was continued with cooling at 40^{o}C with 1 bar of pressure for 12 min. After the biocomposites had been printed, the samples were conditioned at 23^{o}C for 2 d.

Characterization

FTIR Analysis

The FTIR analysis aims to determine the functional groups of a sample. The sample tested consisted of corn husks which have a mesh size of 60. The test was performed to obtain the functional group contained in the corn husks.

SEM Analysis

SEM analysis aims to look at the morphology of a sample. The sample analyzed consisted of corn husks with a mesh size of 60, extruded results that consisted of 30% corn husks and 70% LLDPE, corn husk biocomposites with 70% LLDPE plus 30% corn husks and 100% sheet-shaped LLDPE. This analysis aims to compare the morphology of each tested sample.

Mechanical Characterization

The mechanical testing that was performed consisted of tensile and tear testing using a Universal Testing Machine (UTM) with the Shimadzu brand type AGS- 10kNG. The tensile test was adjusted to the ASTM D882 standard, the sampling process was done at a speed of 0-5 mm/min until the sample experienced a fracture. The result of this tensile testing was in the form of the stress-strain curve that indicates some resistance of the object or the sample to the tensile load given and the percentage of the increased length when the material fracture occurs (elongation at break). The tear test was adjusted to the ASTM D1004 standard. The tear and tensile tests were performed using the same equipment, the difference was in the preparation of the footage of the machine's tensile speed. In the tensile test, the footage was cut into a rectangular shape while in the tear test, the footage was cut into a V shape at a speed of 0 to 51 mm/min.

Biodegradable Test

The biodegradable test was performed qualitatively with the ASTM G-21-70 standard, where it is the standard for the analysis of biodegradable plastics. Biocomposite samples were cut with a size of 2 x 2 cm^2, placed on the Potato Dextrose Agar (PDA) media and inoculated with *Penicillium sp.* and *Aspergillus niger* mold. *Penicillium sp*. and *Aspergillus niger* mold is a common microorganism that lies in the soil and affects degradation of a certain material. The sample was incubated at 28 ± 1^{o}C for one week. Observations were made by looking at the growth of the mold on the sample, the growth of the mold on the plastic sample followed the ranking presented in Table 1.

Table.1 Biodegradability ranking of the sample.

Ranking	Sample's surface covered by the colony (%)
0	0
1	10
2	10-30
3	30-60
4	60-100

Results and Discussion

FTIR Analysis

The FTIR analysis aims to determine the functional group of a sample. The sample tested consisted of corn husks with a mesh size of 60. Corn husks contain fiber (cellulose, hemicellulose and lignin), proteins, and carbohydrates. Cellulose has a β1,4-glycosidic bond with the chemical formula of $(C_6H_{10}O_5)_n$ where n refers to the degree of polymerization. Structurally, hemicellulose is similar to cellulose that is a polymer of sugarwhat makes them different is that cellulose is made up of glucose while hemicellulose is composed of a variety of sugars. Lignin is a three-dimensional polymer composed of phenyl propane units established through ether bonds (C-O-C) and carbon bonds (C-C). [4] The carbohydrates arranged in plants are glucose units, for long-chain molecules. Proteins are complex organic compounds composed of amino acid monomers that are linked to one another through peptide bonds. Amide bonds consist of C = O and N-H. [5] The analysis results for the functional groups can be seen in Table 2.

Tabel 2. Functional group analysis of corn husk

Wave Number (cm^{-1})	Bond	
3387	streching O-H bonds, H bonds streching N-H bonds	Alcohol, Phenol $1^o,2^o$ Amines, Amides
2993	streching C-H bonds	Alkanes
2291, 2014	streching C-H bonds	Methyne, Saturated Aliphatic
1728	streching C=O bonds	Aldehydes, Saturated Aliphatic
1643	streching C=C bonds	Alkenyl, Olefinic (Alkanes)
1512	asymmetrically streching N-O bonds	Nitro Compounds
1466, 1373	bending C-H bonds	Alkanes
1304	bending C-H bonds	Olefinic (Alkanes)
1257,1065	C-C vibration structure	Alkyl, Saturated Aliphatic
1173	bending C-H bonds, inside the area	Aromatic
671	bending C-H bonds, outside the area bending C-H bonds	Aromatic Acetylenic (Alkyne)

Table 2 above shows that the O-H bond at the wave number 3387 cm^{-1} is cellulose, according to the results of research by Hisikawa (1999) which states the O-H group at the wave number 3340 cm^{-1} is cellulose [6]. The wave number interval for the O-H group is 3200-3500 cm^{-1} [7]. The presence of lignin ~~is~~ was characterized by a C-C bond at the wave numbers 1257 and 1065 cm^{-1} in accordance with the functional groups of lignin. Carbohydrates can be identified by the presence of C-H bonds at 2993 cm^{-1} and O-H bonds, these findings are based on the research by Ibrahim (2006) that the presence of C-H and O-H groups indicates the existence of carbohydrates.[8] Proteins are identified by the presence of the C=O bond at 1728 cm^{-1}, about the 80% of the C=O functional group indicates that it is a protein that is found on the range [9]. Corn husk FTIR spectra in Fig. 1 shows that fibers and carbohydrates have the lowest transmittance values, indicating that the content is dominant in corn husks.

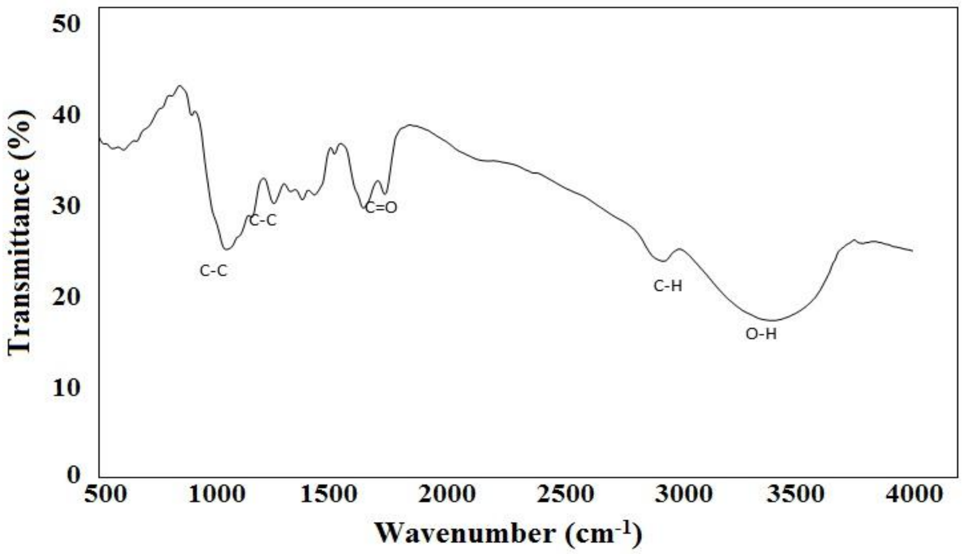

Figure 1. FTIR spectra of corn husks.

SEM Analysis

SEM analysis aims to see the morphology of a sample. The analyzed sample was corn husks with a size of 60 mesh, the results consisted of 30% corn husks and 70% LLDPE extrusion, corn husk biocomposites with 70% LLDPE were mixed with 30% corn husks and 100% LLDPE in a sheet shape. The SEM results can be seen in Fig. 2.

SEM results in Fig. 2 present the corn husk fiber (a) where the fiber seems dominant in the corn husks, this is consistent with the FTIR analysis saying that corn husks have a high fiber content. Fig. 2(b) presents the LLDPE which has been heat-pressed into a sheet shape, based on the figure it can be seen that the surface of the LLDPE looks smooth and this indicates that LLDPE has a high elasticity property. Fig. 2(c) presents the morphology after the corn husks and LLDPE have been extruded with a composition of 30% corn husks and 70% LLDPE, it can be seen that the fibers of the corn husks and LLDPE looks evenly distributed to each section, it means the corn husks and LLDPE are mixed evenly on a mechanical basis [10,11]. Fig. 2(d) presents biocomposites with a composition of 30% corn husks and 70% LLDPE, the surface looks rough and corn husk fibers look evident in these biocomposites. The surface of LLDPE looks smooth while the surface of the biocomposites looks rougher, it implies that corn husks and LLDPE are not fused which later makes their surface does not look homogeneous. Rough surface on biocomposites also indicates that the corn husk biocomposites have a lower level of elasticity than that of the LLDPE [10-12].

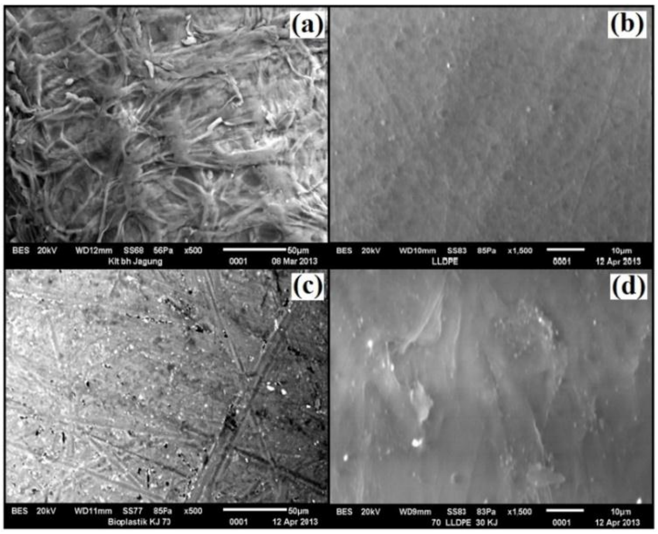

Figure 2. Morphology of samples of (a) Corn husks (b) Hot pressed LLDPE (c) the resulted 30% of corn husks extrusion (d) 30% corn husks biocomposite.

Mechanical characterization

The mechanical testing that was performed consisted of tensile and tear testing using a Universal Testing Machine (UTM) with the Shimadzu brand type AGS-10kNG. The tensile test was adjusted to the ASTM D882 standard, the sampling process was done at a speed of 0-5 mm/ min until the sample experienced a fracture. The tear test was adjusted to the ASTM D1004 standard at a speed of 0 to 51 mm/min.

Tensile strength indicates the ability to bear a load or a strain without damaging the composites or making them break, the testing of the tensile strength generates tensile strength properties, elongation at break and modulus of elasticity [13,14]. Elongation at break refers to the strain of the sample when the sample is broken while the modulus of elasticity refers to the ability to resist permanent deformation deformation due to the loading [15]. When this elasticity limit is exceeded, a material will undergo permanent deformation changes, even though the load is removed. The findings of this research suggest increased tensile strength and elongation at break as the concentration of corn husks is minimized, where the highest value is shown at a concentration of 30% corn husks. Meanwhile, the modulus of elasticity does not change linearly. When the concentrations of corn husks are increased from 70% to 50%, the modulus of elasticity improves but it decreases again when the concentrations of corn husks are reduced from 40% and 30%. The highest value for the modulus of elasticity is at a concentration of 50% corn husks. Higher fiber contents in corn husks make biocomposites more brittle and thus its value of elasticity also tends to decrease when the concentration of corn husks is increased. However, addition of fibers results in increased modulus of elasticity and this modulus of elasticity achieves its peak when up to 50% of fibers is added to the biocomposites. These research findings can be seen in Fig. 3, 4 and 5.

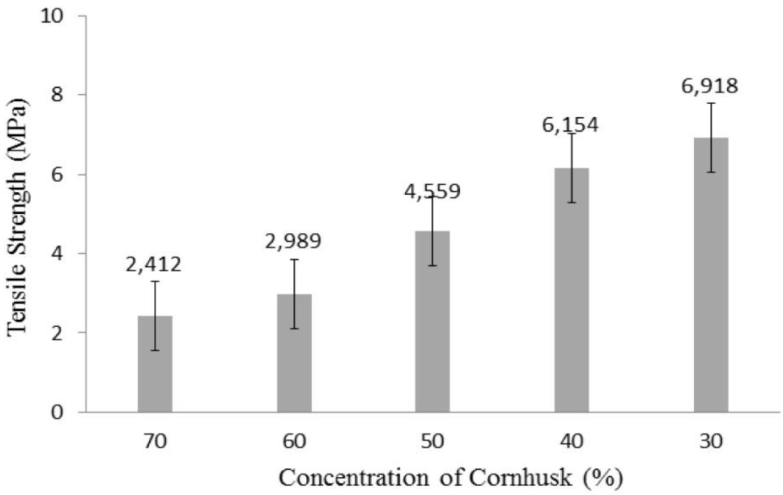

Figure 3. Comparison of biocompocites' tensile strength.

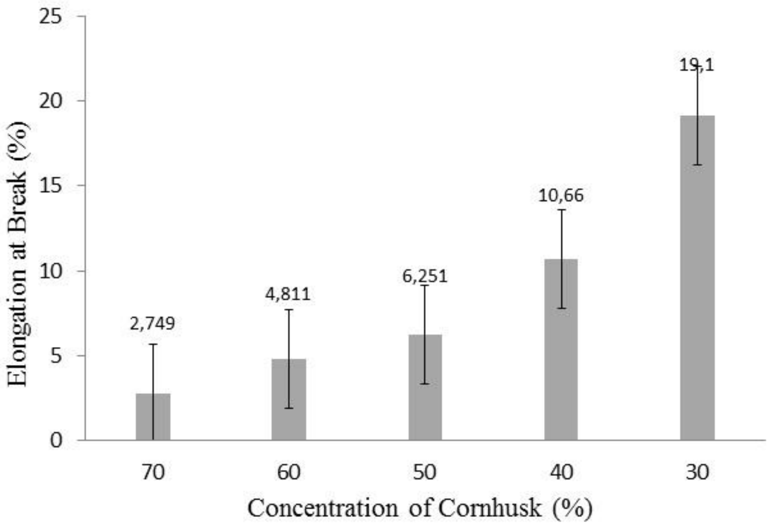

Figure 4. Comparison of biocomposites’ elongation at break.

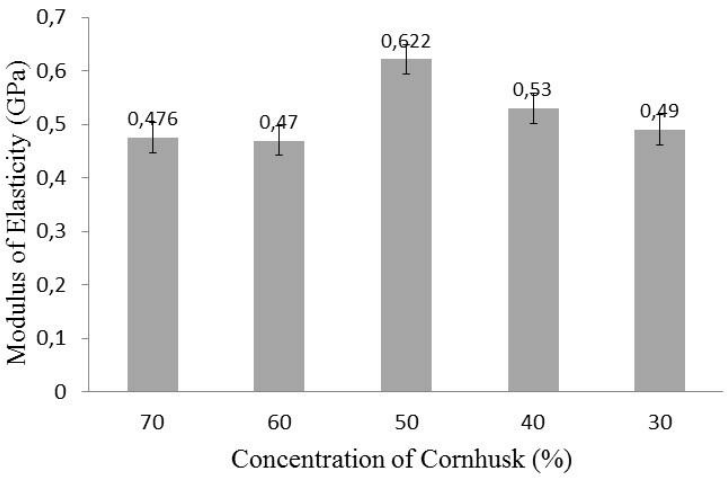

Figure 5. Comparison of biocomposites’ elasticity.

The testing of tear strength aims to determine the resistance of biocomposites to snages. The results of the tear test of the corn husk biocomposites do not differ widely from those of the tensile test, where the greater the concentration of corn husks then the smaller the tear strength (Fig. 6). Decreases in the properties of tensile strength, elongation and tear strength indicate that addition of corn husks on LLDPE will reduce the elasticity property and make biocomposites more brittle since this property is highly dependent on the elasticity of a material [16].

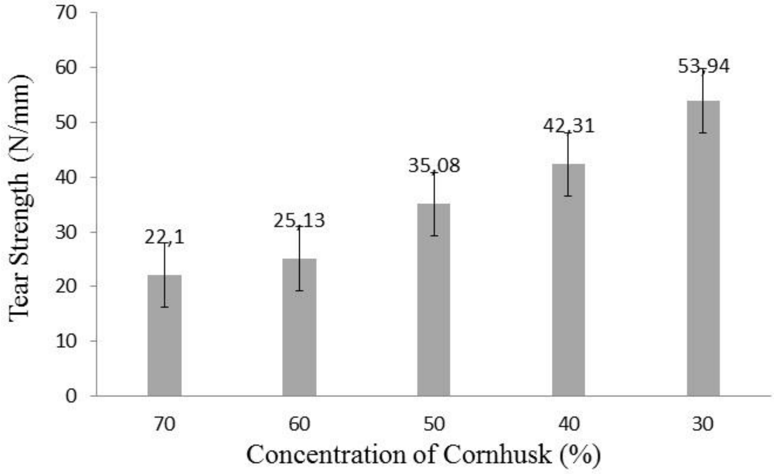

Figure 6. Comparison of biocomposites' tear strength.

Biodegradable test

A biodegradable test was performed qualitatively using ASTM G-21-70 standard, in which the standard refers to the standard for plastic biodegradable analysis. Biocomposite samples were cut into a 2 x 2 cm^2 size and placed on Potato Dextrose Agar (PDA) media and inoculated using Penicillium sp. and Aspergilus niger molds. The sample was incubated at 28±1^{o}C for a week. The growth of mold colonies were translated into a 0 to 4 ranking, where 1 indicates the lowest mold colony growth, suggesting a low level biodegradability and 4 indicates the highest mold colony growth, suggesting a high level of biodegradability.

The biodegradable test is shown in Fig. 7, where mold cannot grow on LLDPE as the center is not covered by mold. In corn husks with 30, 40 and 50% concentrations, mold grows on less than 10% of the biocomposite area, in other words the composite is ranked 1. In corn husks with a 60% concentration, the mold grows on more than 10% but less than 30% of the biocomposite area, so that the composite is ranked 2. In corn husks with a 70% concentration, the mold grows on more than 30% but less than 60% of the biocomposite area so that the composite is ranked 3.

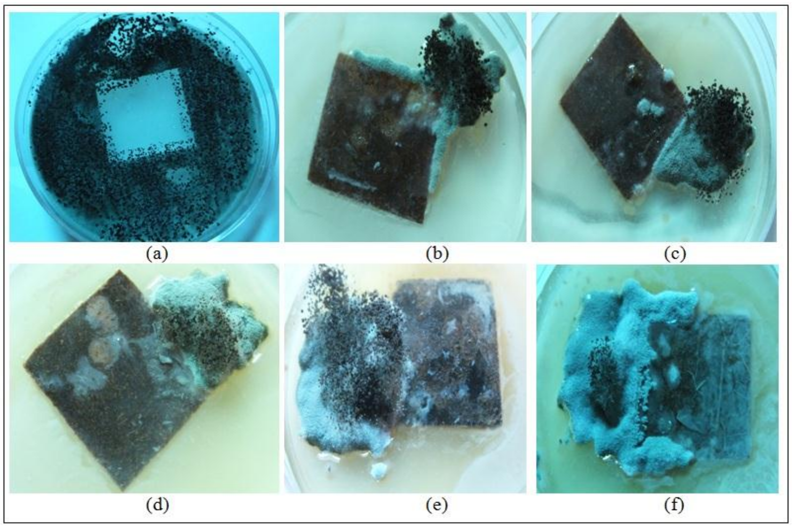

Figure 7. Qualitative *biodegradable* test of corn husks biocomposites using *Penicillium sp* mold (a) LLDPE (b) 30% (c) 40% (d) 50% (e) 60% (f) 70% concentrations of corn husks.

The results of the biodegradability observation suggest that the mold can grow on corn husk biocomposites. Mold growth indicates that corn husk biocomposite can be degraded underground. Mold is one of the most important microbes in degradation because it can produce enzymes which can break complex compounds into simpler ones [17,18].

Conclusion

Corn husks have high fiber content, as seen in slopping O-H peak at 3340 cm^{-1} wave number. This statement is supported by the analysis of corn husk morphology using SEM, where the fibers appeared to be dominant. Corn husks can be one of biocomposite substitution materials. Fibers can strengthen and become the filler for biocomposites. Mechanical analysis results showed that the bigger the concentration of corn husks, the smaller the mechanical characteristics. The 30% corn husk concentration ha~~s~~d the highest mechanical characteristics with 24.77 Mpa tensile strength, 19.10% elongation and 53.94 N/mm tear strength. This analysis of mechanical characteristics was supported by the results of LLDPE and corn husk biocomposite morphology, where the LLDPE surface ~~is~~ was smoother than the biocomposites. The biodegradable test show~~s~~ed that *Aspergilus niger* and *Penicillium sp.* mold can grow on corn husk biocomposites, but it cannot grow on LLDPE. This show~~s~~ed that corn husk biocomposites can be degraded faster than LLDPE. Ranking results showed that the bigger the corn husk concentration in biocomposites, the higher the biodegradability level.

Acknowledgments

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