Development of Cellulose-based Bioplastic from Corn Stalks

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Abstract – Due to the abundance of corn available, there is also a large amount of corn residue. The study aims to develop a cellulose-based sheet from corn stalks. The cellulose-based sheet was tested of its density, tensile strength, and percent elongation, and was analyzed with an fourier-transform infrared spectroscopy (FT-IR) to determine whether it is chemically similar with commercial cellophane. Overall, the cellophane sheet was similar to commercial cellophane in terms of the functional groups present but was weaker in terms of it mechanical properties.

Introduction. – Plastics are artificial materials with long, strong chains of molecules known as monomers bonded together and is usually composed of carbon, hydrogen, oxygen, nitrogen, chlorine and sulfur. These are formed usually by the processing of natural products such as oil, coal, petroleum, and natural gases[1]. It can be found everywhere and is used to make up a lot of things such as Polyethylene bottles and grocery bags. For decades, plastics have been widely used due to its functionality and versatility. It is easy to manufacture and cheap to produce. It is also designed to be durable, lightweight, and water resistant in order to meet the needs of people.

Due to the rapid growth of population and industrialization, the demand for plastic has increased which also lead to an increase in human waste. As of 2015, the Philippines places third around the world as to the amount of plastic being deposited into the ocean[2]. This is an alarming news to the country because the Philippines is a group of islands surrounded by bodies of water where unique, diverse aquatic species can be found[3].

Plastics made from renewable raw materials or from non-food source are called bioplastics[4]. Bioplastics can also be defined as plastics having either biodegradable properties or if it is made from biological sources, or having the property of both[5]. Intensive research has been done mostly on two resource materials: cellulose and starch. Starch and cellulose-based plastics are inexpensive to reproduce and have widely available materials. Since starch is used more often as an organic raw material in chemical industries, this study will opt to use cellulose as a potential raw material for bioplastic by utilization of major crop residues after harvesting since they are rich in cellulose[6].

One of the most important crops in the Philippines is corn. Corn also plays an important role to livestock and poultry, serving as the major ingredient to their feeds[7]. When corn is harvested, the remaining residues are mainly corn stalks. Cellulose is most abundant in corn stalks wherein the stalks consist of nearly 50 percent cellulose.

Álvarez-Chvez et al.[8] recommended the usage of agricultural byproducts, one of them being corn stalks, to produce bioplastics to be able to reduce production cost and land used for polymer production while giving economic value to waste products. By subjecting the cellulose-based bioplastic sheet to FT-IR, the molecular compounds present can determined and assessed. In this study, the important analysis needed using FT-IR is the identification of the organic and inorganic compounds with which we could compare with the conventional compounds present in cellophane.

This study aims to develop cellulose-based bioplastic from corn stalks. It specifically aims to:

(i) measure its mechanical properties in terms of its density, tensile strength and percentage elongation;

(ii) compare these properties with that of commercial cellophane;

(iii) identify the functional groups present in the cellulose-based bioplastic using Fourier-Transform Infrared Spectroscopy (FTIR) spectrometer; and

(iv) compare the spectra of the cellulose-based bioplastic with that of commercial cellophane.

By subjecting the developed cellophane sheet to FT-IR, the functional groups present can be determined and assessed. In this study, the analysis using FT-IR serves to identify the functional groups present in the bioplastic formed which can be compared with the functional groups present in commercial cellophane.

Methods. – The methods was done in five general steps and in five repetitions. The five general steps include preparation of stalks, extraction of cellulose, viscose process, casting and drying of sheets, and testing of sheets. Out of the five repetitions, only the first and the fourth repetitions were successful in producing sheets. All of the repetitions followed the general steps unless stated otherwise or specified.

Preparation of stalks. The corns stalks were removed of its dirt and leaves, and the outer sheath were peeled to reduce impurities and to produce a smoother surface. The stalks were chopped, blended, and used immediately after. Using a top loading balance set to 0.1 milligrams accuracy, 200 g of the blended corn stalks were weighed in preparation for the next procedure. The outer sheath was remained intact in the first repetition, but since it resulted to a rough bioplastic sheet in the end, the outer sheath was peeled off in the succeeding repetitions.

Extraction of cellulose. In order to delignify the corn stalks, two separate bath solutions were prepared: 15% sodium hydroxide and 15% sodium sulfite. The chemicals weighed were 150 g of sodium hydroxide and 150 g of sodium sulfite, and were each dissolved separately to produce 1L of each solution. The first bath is the 15% sodium hydroxide and was placed on top of a hotplate set to 150°C. The weighed corn stalk samples were slowly added and were heated for two hours. The cooked corn stalks were then filtered using a strainer. Further delignification was performed using the bath of 15% sodium sulfite solution placed on top of a hot-plate set to 150°C for two hours. The cooked corn stalks were then filtered using a strainer to remove absorbed liquids. All of the repetitions followed this method except for the second repetition which used formic acid (90% v/v). However, extraction of cellulose was unsuccessful, which resulted to its end on this repetition.

Viscose process. In order to convert the cellulose pulp to alkali cellulose, the sodium hydroxide solution was prepared by making a 500-mL solution of 18% sodium hydroxide. All of the cellulose pulp are then poured into the beaker containing the solution which was then sealed for 60 minutes, and after which was hand-pressed in a strainer as dry as possible. After breaking up any large lumps into crumbs, the alkali cellulose was transferred to a one-liter media bottle for xanthation. Xanthation was accomplished by adding 7.70 g of carbon disulfide to the alkali cellulose in the bottle and maintaining the sealed bottle at 30C for two hours. The bottle was rotated periodically to insure uniform xanthation. After two hours, the yellow pulp turned to a deep orange color after reacting with the carbon disulfide. The media bottle was opened in the fume hood and 240.28 mL of cold water (5°C) and 48.56 g of 18% sodium hydroxide were added. The mixture started to turn viscous as a thick, orange-colored liquid was formed. The mixture was transferred to a one-liter beaker and was stirred using a handheld electric mixer for two hours. The thick orange-colored solution that resulted was "viscose." The viscose was transferred into a clean media bottle and stored at 5°C in a refrigerator for 24 hours.

Casting and drying of sheets. The cellophane casting stage is when the viscose is poured onto the glass slides and bathed into the chemical baths of 40% ammonium sulfate and 12% sulfuric acid-18% sodium sulfate. In a 250-mL beaker, 200 g of ammonium sulfate was weighed to create 500 mL of 40% solution of ammonium sulfate was created. Subsequently, the sulfuric acid-sodium sulfate bath was made by adding 60 mL of sulfuric acid into a one-liter graduated cylinder. After sulfuric acid, 90 g of sodium sulfate was added. The solution produced was a 12% sulfuric acid-18% sodium sulfate solution. The two baths, ammonium sulfate and sulfuric acid-sodium sulfate baths, were heated over a hot plate up to 45°C.

The sheet of bioplastic was prepared by spreading a thin, layer of viscose on the 1x3x8 inch glass plate using a rubber spatula. The viscose was allowed to coagulate by immersing the sheets in an ammonium sulfate bath (45°C) for 60 seconds. After the immersion, the coagulated sheet that was still on the plate was immersed in a sulfuric acid-sodium sulfate bath (45°C) for two minutes. Upon contact, the yellow sheets gradually turned white and a bubbling effect was observed. The cellulose-based bioplastic films were then soaked in hot distilled water (80°C) for 10 minutes. In order to obtain a more flexible bioplastic, the bioplastic sheets were treated with 5% glycerin solution for 15 minutes. The bioplastic sheets were flipped during the glycerin treatment to allow even plasticizing. The sheets were air-dried for three days at room temperature.

In the first repetition, the viscose was spread onto the inside of the glass slides, which surrounds the viscose with walls. Sheets were successfully made. In the fourth repetition, the chemical used for the first bath was ferrous ammonium sulfate instead of ammonium sulfate. Moreover, the underside of the glass plates which had no walls surrounding was used instead of casting the sheets inside the glass plates with walls. The sheets were then immersed into pans filled with the coagulating and regenerating reagents. Sheets were successfully made. In repetitions three and five, the sheets would tear at every attempt to remove them from the glass since they adhered to the surface of the glass plate.The films were not appropriate for testing since they would tear easily and the sizes of the film were too small.

Testing of sheets. The first and the fourth repetitions were successful in producing solid sheets that could be tested. The first batch was tested of its mechanical properties, particularly the density, percent elongation, and tensile strength as these were the only available tests in Central Philippine University - Packaging Engineering. The fourth batch was tested of its chemical composition using the FT-IR Spectroscopy in Philippine Science High School Western Visayas Campus. All the tests were compared with commercial cellophane.

Results and Discussion. – The results of the study are divided into three sections, specifically appearance of the sheet, mechanical properties, and the results of the FT-IR test. Two sheets are used, namely the sheet produced from the first repetition, and the sheet produced from the fourth repetition.

Appearance. The first sheet produced was rough, thick, and opaque. Additionally, prominent fibers were visible on its surface. The sheet was brownish-yellow in appearance. The bioplastic formed was thick and coarse in appearance since the viscose used for casting was a thick liquid. Due to the viscous nature of the liquid, the sheet was difficult to spread in the glass plate using a spatula. Additionally, the viscose used for the first sheet contained corn stalk fibers since it was considered the first batch of viscose among the five repetitions, resulting to its coarse texture. Figure 1 shows the appearance of the sheet.

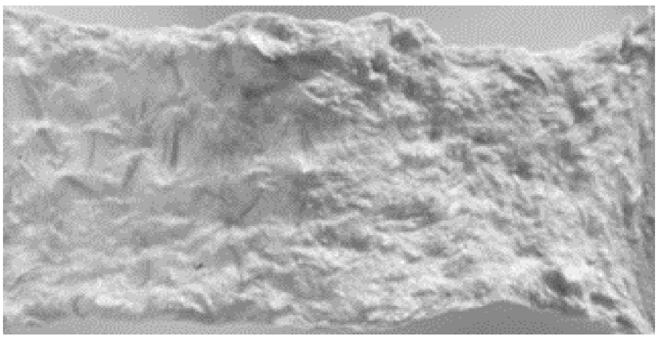

Fig. 1: Appearance of the sheet on the first repetition.

The fourth sheet produced was significantly different compared to the first sheet since it was smooth, thin, and slightly opaque. The fourth sheet was brownish-gray in color due to the presence of Fe3+ ions. Compared to the previous sheet which was thicker and coarser in appearance, the viscose used for casting in the fourth sheet was thin and runny. Hence, the sheet formed was smooth. Figure 2 shows the appearance of the sheet.

Fig. 2: Appearance of the sheet on the fourth repetition.

Mechanical properties. The mechanical properties test was only conducted to the sheets in the first repetition. The results were compared with the commercial cellophane.

Table 1 shows the comparison of the properties between the developed bioplastic sheet and that of the control which is commercial cellophane.

Table 1. Properties of the bioplastic versus commercial cellophane.

	Bioplastic	Commercial Cellophane
Density (g/mL)	0.49	1.24
Tensile Strength (MPa)	1.81	90.12
Percentage Elongation (%)	7.70	8.67

The values of the bioplastic in terms of density, tensile strength, and percentage elongation were lower than that of the commercial cellophane, which served as the control. Compared with the commercial cellophane sold in the market, the bioplastic made from corn stalks had a density which was 60.48% lower, tensile strength which was 98% lower, and percent elongation which was 10.27% lower.

The lower density of the cellulose-based bioplastic could be attributed to its higher thickness and mass. The leftover hemicellulose in the crude alkali cellulose could have deteriorated the strength in the final viscose product which lowered the quality of the film[9]. Consequently, it affected the tensile strength of the cellulose-based bioplastic. Due to the leftover hemicellulose, it may have consumed the chemical substituents during the process before the chemicals had time to react with the cellulose polymers, thus it reduced the availability of chemicals for the cellulose derivatization. This lead to irregularities in the product quality and thus, may have greatly affected its tensile strength and percentage elongation [10].

FT-IR Results. The FT-IR test was only conducted to the sheets in the fourth repetition. Subsequently, the results were compared with the commercial cellophane. Figure 3 represents the comparison in appearance of the spectra of the fourth sheet versus the spectra of commercial cellophane.

The analysis on the spectra will be limited to the region to the left of 1400 cm-1 which is called the functional group region. The range of 600 to 1400 cm-1 which is found in the right region of the spectrum is called the fingerprint region. This region is a complex area, making it complex and difficult to interpret reliably due to the overlapping bands. Lastly, since the researchers are beginners in analyzing the spectrum, discussion will focus on the left region of the spectrum or the functional group region since this is where most of the stretching frequencies occur.

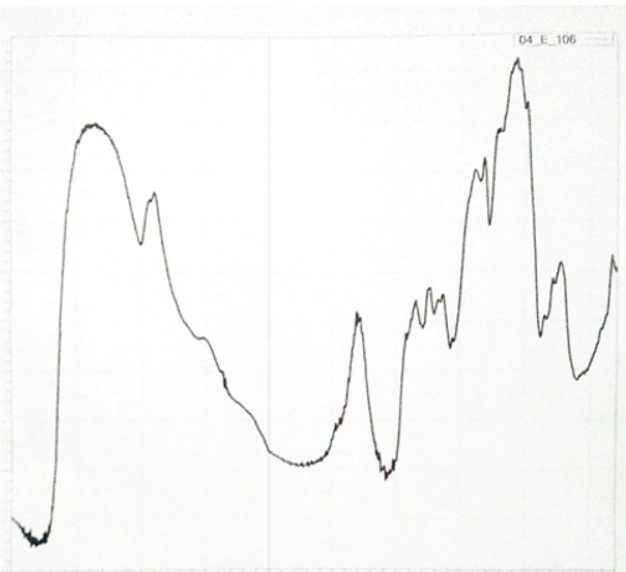

Fig. 3: Spectra of the bioplastic sheet from the fourth repetition.

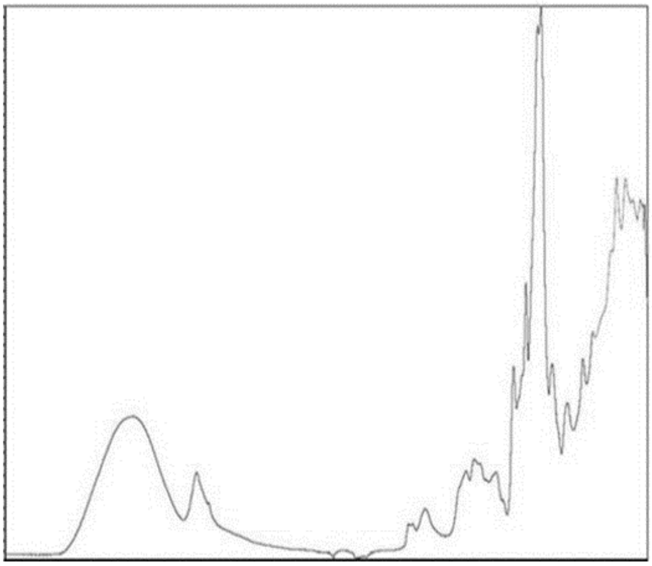

Fig. 4: Spectra of commercial cellophane from Specac (2017).

When the spectra of the fourth sheet (Fig. 3) is compared to the spectra of commercial cellophane (Fig. 4), a general similarity in the peaks can be observed. The spectra used for commercial cellophane (Fig. 4) was based on the analysis done on polymer samples by Specac, a company that manufactures FT-IR accessories and other products related to spectroscopy (Specac 2017). When the two spectra (Fig. 3 and 4) are compared, there is a difference in the intensity of absorption between the bioplastic and the commercial cellophane which is presented in the difference in peaks based on the y-axis. Generally, the spectra for the bioplastic has a higher intensity of absorption. According to the Beer-Lambert law, the thickness of a material is directly proportional to its thickness[11]. Since the bioplastic the researchers produced did not utilize rollers during the process, the sheets were thicker than commercial cellophane which are generally thin and transparent.

Additionally, a larger peak intensity increase indicates that there are more identical functional groups[12]. Figures 5 and 6 present the functional groups present in the spectra. Specifically, the common functional groups present among the two spectra are alcohol and carboxylic acid. Basing on the graph, it indicates that the cellulose-based bioplastic (Fig. 6) has more functional groups, namely alcohol and carboxylic acid, since it has a higher peak compared to commercial cellophane.

Conclusion. – A cellulose-based bioplastic made from corn stalks was possible. However, its mechanical properties are weaker compared to commercial cellophane. Its weaker properties may be attributed to the impurities present in the sheet, and the methods used were limited to a laboratory scale, which is Millers method[13], which does

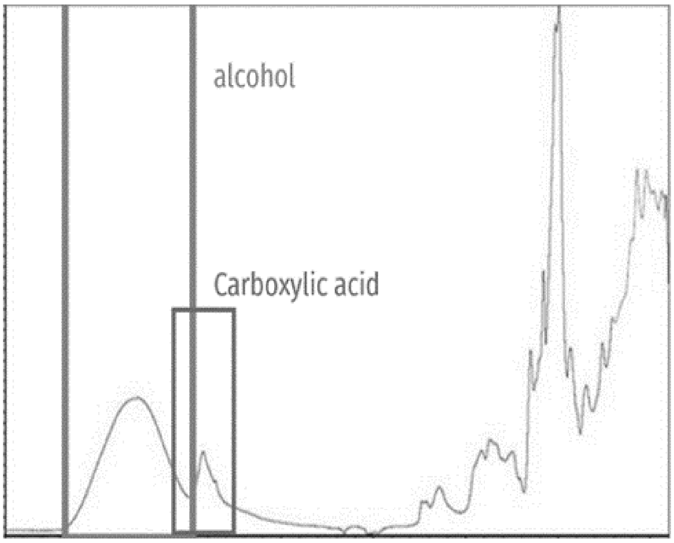

Fig. 5: Functional groups present in the cellophane spectra. The peaks in the cellophane sheet indicate the presence of functional groups, such as alcohol and carboxylic acid.

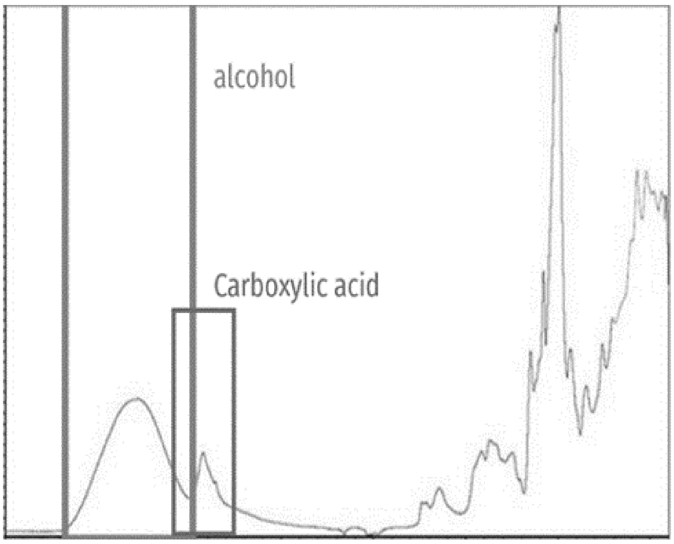

Fig. 6: Functional groups present in the bioplastic spectra. The peaks in the bioplastic sheet indicate the presence of functional groups, such as alcohol and carboxylic acid.

not utilize high-power equipment. The cellulose-based bioplastic is similar to commercial cellophane in terms of the functional groups present. The difference between the cellulose-based bioplastic and commercial cellophane is their appearance wherein the cellulose-based bioplastic is thicker, coarser, and more opaque. Among the five attempts done to develop a cellulose-based bioplastic, the fourth repetition which used ferrous ammonium sulfate yielded to a sheet which is similar to cellophane chemically. However, the current study is limited to the basic knowledge of the researchers in terms of analyzing the FT-IR results.

Recommendations. – In order to obtain bioplastic that possesses better characteristics, it is highly recommended to:

a) Use the corn stalks freshly harvested to ensure the cellulose inside does not degrade over time.

b) Opt for mature stalks than young stalks because plants generally have more cellulose as they age.

c) Change the variety of the corn used may also be done to determine which variety yields to more cellulose.

d) Use a cellulose extraction procedure specifically for corn stalks which results to high yield and purity.

e) Search for a recent method on how to cast cellophane which enables the user to cast thin sheets.

f) Use a more delicate procedure in casting and in bathing the sheets so that the regeneration of the sheets will be even and will not cause holes when pouring the reagents on the sheets.

g) Search and utilize a more efficient method in casting in order for the sheet to be more consistent chemically and physically.

h) Consult an expert who specializes in using the FT-IR to enable more in-depth analysis and interpretation of the sheets.

i) Calibrate the FT-IR machine properly before use.

j) Use a Scanning Electron Microscope to determine whether the commercial cellophane tested is indeed microfibrillated cellulose.

k) To determine what causes the eccentric waves in the spectras.

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