A preliminary study of bioplastic composites based on carbon materials from paper waste and corn waste

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Abstract. Waste materials continue to increase and have become a major problem in many countries. In this work, waste was recycled to form bioplastic composites. The study focused on the bioplastic (starch-cellulose acetate)-carbon material composites. The Graphene Oxide (GO) and Carbon-dots (CD) were chosen as filler materials. The physical properties of these bioplastics were investigated using tensile test, water uptake test and biodegradation test. Results showed that the addition of GO and CD reduced the tensile strength and elongation. It was also found that the water uptake decreased while the biodegradation rate increased with GO or CD addition. The interaction between the bioplastic starch-cellulose acetate matrix and the carbon materials as fillers can change the mechanical properties of the bioplastics. The carbon materials fill the pores in bioplastics and make the bioplastic more waterproof and their hydrophilic properties attract water faster and help the activation of microbial activity during the biodegradation.

1. Introduction

According to PlasticEurope data, the use of plastic materials worldwide has reached 359 million metric tons. Plastic materials is mostly used for wrapping [1]. This causes plastic waste to continue to increase and become a serious problem in many countries. There are various ways to reduce pollution due to plastic materials such as recycling [2], converting it into fuel [3], replacing with other materials [4] and so on. Replacement of plastic materials with other materials that are similar in nature is one solution that is quite effective. In the development of this substitute material, materials derived from organic materials that have been calculated with some methods [5] to define their properties were selected and made to such materials we known as bioplastics [6-17].

The main ingredients of the bioplastics most commonly used are carbohydrates. There are two main sources of carbohydrates in the production of bioplastics, namely cellulose [8,12,17] and starch [6,7,10,13]. Research on the combination of cellulose and starch to improve the mechanical properties of bioplastics has been carried out [6,14,15]. These studies indicated that with the right combination of the two the quality of the bioplastics can be improved.

One of the main objectives of bioplastic research is to obtain biomaterials with physical properties that are very similar to the plastic used today. One of studies that showed promising results was starch-based bioplastic composites with graphene and graphene oxide (GO) fillers [7,11,12,16]. These studies showed that the addition of Graphene or GO resulted in the increase in the tensile strength of the materials.
This work aims to study the physical properties of composite bioplastic made from combination of starch and paper pulp (cellulose-acetate) with carbon materials as fillers. Carbon materials can take a form of various types such as: activated charcoal, graphite, diamond, carbon nanotubes, fullerenes, graphene [18], GO [19], carbon nanodots (CD) [20–24] and so on. In this work, the carbon materials used as fillers are GO and CD materials because the production of bioplastics using such materials is relatively simple.

The cellulose used in this study was processed from unused paper waste. Paper has a cellulose content of 90-99% [25]. With this large content, a considerable amount of cellulose can be obtained from processing. Here, GO and CD fillers were made from Corn cobs. The production of GO and CDs from corn cobs has been previously done as can be found in [19,20,24], reporting fairly good amount of GO and CD resulted from these carbon materials.

2. Methods

2.1. Pulp

Paper waste was prepared by cutting it into small pieces, then the ink and dust in the paper were removed by soaking the paper in isopropyl alcohol for 5 minutes. The paper was then lifted and dried. About 20 grams of the paper were soaked in 40 ml of 5% NaOH while being heated and stirred for 1 hour with a hot plate at 70°-80°C. The pulp obtained was washed with distilled water and dried at room temperature. The next step was to mix 15 grams of the dried pulp with 36ml of acetic acid while heating and stirring for 30 minutes at a temperature of 70-80°C. The pulp was washed again with distilled water and dried at room temperature. Total of 10 grams of the dried pulp was added with 100 ml of distilled water and heated to form refined cellulose acetate pulp.

2.2. GO

Corn cobs were cut to small pieces and sun-dried. Afterwards, the dried corn cobs were burned in the furnace for 28 minutes at 350°C to produce activated charcoal, which was then ground to a powder. The powder was filtered with 325 mesh sieve to obtain a fine powder. About 1.5 gram of charcoal powder, 0.8 gram of detergent and 250 ml of distilled water were mixed together using a blender for 3 hours. The blended solution was left for 24 hours, so that the GO in the solution was to the surface. Then GO layer was taken to obtain GO solution.

2.3. CD

The small pieces and dried corn cobs were ground again to a fine powder. The powder was then mixed with distilled water and stirred for 30 minutes to obtain a homogeneous solution. The solution was put in microwaves for 5 minutes with medium heating and became a CD solution. The CD solution was then filtered and stored for further processing.

2.4. Preparation of bioplastics Samples

To make bioplastics, 9.5 gram of corn starch, 3 gram of cellulose acetate pulp, 60 ml of distilled water, 5 ml of acetic acid, and 5 ml of glycerol were mixed together. The solution was heated and stirred using a hot plate with a temperature of 70 to 80°C for 8 minutes, until the sample has a glue-like texture. The resulting mixture was poured into the mold and dried for 24 hours. The step was repeated by adding 5 ml of GO (CD) solution to make bioplastic-GO (bioplastic-CD) composites.

2.5. Characterization

The identification of the produced GO and CD was done using a UV-Visible Absorbance Spectrophotometer. Furthermore, the physical properties of bioplastics were investigated using tensile test, water uptake test and biodegradation test.
3. Results and discussion

3.1. UV-Visible absorbance spectra for GO and CD

The UV-Visible absorbance spectra for GO and CD are shown in Fig.1. From the spectra pattern, it can be seen that GO and CD produced were reasonably good. Figure 1.a. shows a peak at 223 nm and a broad peak in range 253 - 260 nm, which is in agreement with the previously reported results [19,26–28]. Figure 1.b. shows broad peak at 260-270 nm and 280-310 nm which is the characteristics of CD [21–23]. These peaks happen because the $\pi \rightarrow \pi^*$ and the $n \rightarrow \pi^*$ transitions which are usually reported for GO and CD. Overall, GO and CD have different properties in absorbance and luminescence. CD has high absorbance above one in almost all UV region and shows luminescence when illuminated with 295 nm UV-lamp (inset in Fig.1.b.).

3.2. Bioplastic

The samples of bioplastic made are shown in Fig.2. The bioplastic samples were made with three different variations. Fig.2.a. is the normal one with only starch and cellulose acetate pulp combination without GO or CD mixture, Fig.2.b. is with GO and Fig.2.c. is with CD. The composite of bioplastic-CD was tested with 295 nm UV-lamp and it showed bright yellow luminescence.

3.3. Mechanical properties of bioplastic

Mechanical properties of bioplastics were measured with the tensile test. The results of the test are shown in Table.1. From the results, normal bioplastic had the largest tensile strength and % Elongation, followed by Bioplastic-GO composite and finally by bioplastic-CD composite which had the lowest tensile strength and % elongation. The interaction between the bioplastic with GO changed the bioplastic mechanical properties. From previous results of studies on bioplastic-GO composite [7,11], the addition of GO filler resulted in the increase in the tensile strength and decrease in plasticity of bioplastic, but in our experiment the results showed that both values decreased. The decrease was because the addition of cellulose acetate pulp in our experiment. The cellulose-acetate molecules interact with the GO and can make macro-void in the bioplastic which were shown in previous reported result by Ismail et.al. [12]. This void shown as pores and can be seen clearly (Fig.2.b.). The cellulose acetate-GO interaction overshadow the effect of starch matrix-GO interaction as the result make the tensile strength more weaker.

The bioplastic-CD composite were more rigid and brittle compared to our two other result. CD as the filler decreased the plasticity when filling in the matrix, but because CD molecules do not have
strong network structure like GO molecules, they decreased the tensile strength and %Elongation more as shown in Table 1.

![Image of Bioplastic a) normal, b) with GO, c) with CD (inset show luminescence from UV lamp).]

**Figure 2.** Bioplastic a) normal, b) with GO, c) with CD (inset show luminescence from UV lamp).

### Table 1. The Mechanical Properties of normal bioplastic, bioplastic-GO composite and bioplastic-CD composite.

| Types of Bioplastic | Tensile Strength(MPa) | %Elongation |
|---------------------|-----------------------|-------------|
| Normal              | 1.65                  | 25          |
| Bio-GO              | 0.80                  | 17.5        |
| Bio-CD              | 0.44                  | 5           |

### 3.4. Water-Uptake

The water-uptake properties of bioplastic were calculated with the swelling test. The Swelling test is the test to measure ability of materials to absorb water. The test was carried out by weighting the initial weight of the material measured ($W_o$), then the materials were soaked in aquadest for 30 minutes. Next, the material was removed from water and weighed ($W_f$). The percentage of water absorbed were calculated using the following equation:

$$ Water\ Uptake(\%) = \frac{W_f - W_o}{W_o} \times 100\% $$

(1)

Table 2. shows the water uptake of bioplastic for normal, GO and CD composite. It can be seen that the water uptake decrease for GO and CD composite. Water absorption dependent to the pores in materials, GO and CD in composite fill in these pores and reduce the space for water molecules to be hold.

### Table 2. The water-uptake for normal bioplastic, bioplastic-GO composite and bioplastic-CD composite.

| Types of Bioplastic | $W_o$ (gr) | $W_f$ (gr) | Water-Uptake (%) |
|---------------------|------------|------------|------------------|
| Normal              | 0.25       | 0.41       | 64               |
| Bio-GO              | 0.35       | 0.53       | 48.15            |
| Bio-CD              | 0.28       | 0.40       | 51.43            |

### Table 3. The biodegradation test result for normal bioplastic, bioplastic-GO composite and bioplastic-CD composite.

| Types of Bioplastic | $W_o$ at first day (gr) | $W_f$ at 7 days(gr) | Mass reduce/ 7 days (%) |
|---------------------|-------------------------|---------------------|--------------------------|
| Normal              | 0.25                    | 0.11                | 56                       |
| Bio-GO              | 0.34                    | 0.16                | 52.94                    |
| Bio-CD              | 0.28                    | 0.11                | 60.71                    |
3.5. Biodegradation
One of the aims for making bioplastics were to make materials that could decompose in the environment. Biodegradation test was conducted to find out how much materials degrade in certain period of times. This test was done by planting the sample material in the soil for a week. Table 3 shows the biodegradation test results for the bioplastics samples. It can be seen that the more the GO or CD fillers added, the faster the mass reduced. The GO and CD are known to have the hydrophilic properties. The hydrophilic properties attract water from the environment faster and help the activation of microbial activity during the biodegradation. The bioplastic biodegradation test results can be seen in Fig.3.

4. Conclusions
Bioplastic and bioplastic-carbon material composites based on paper waste and corn waste has been successfully synthesized. The GO addition and CD addition reduced the tensile strength made the bioplastic composites more brittle. Meanwhile, the water uptake decreased when the GO or CD are used as fillers. It was also found that the biodegradation rate increased with GO or CD addition. The interaction between the bioplastic starch-cellulose acetate matrix and the carbon material fillers can change the bioplastic mechanical properties. The carbon materials fill in the pores in bioplastics and make the bioplastic more waterproof. The carbon materials hydrophilic properties attract water faster and help the activation of microbial activity during the biodegradation.

Figure 3. Bioplastics biodegradation test result normal 1st day (left) and after 7 days (right) for a) normal, b) GO composite, c) CD composite.

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