Fabrication and characterization starch/chitosan reinforced polypropylene as biodegradable

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Abstract. The production of bioplastic from starch/chitosan reinforced polypropylene with different ratio from 35/65, 50/50 and 65/35. In present study, bioplastic was investigated by using tensile strength test, X-Ray diffraction (XRD), and Fourier transform infra-red (FTIR) spectroscopy, and respectively. XRD analysis shows that the sample have amorphous phase structure with the main broad peaks 18° to 30°. FT-IR used to investigate functional group and the result analysis show that the main bonding is of O-H hydrogen bonds (carboxylic acid), C-H alkanes, C=C alkenes and C-O alcohols. The tensile strength obtained for bioplastic were 68.41Mpa at ratio 65/35, respectively. These bio plastics have exhibited mechanical properties with high biodegradability that makes them a suitable alternative for the existing conventional plastics.

1. Introduction
Plastic waste problems are increasing every year in the world. The use of non-environmentally-friendly plastic products causes a variety of serious environmental problems. The increasing in environmental damage effect is the reason for the development production of natural-based plastics [1]. Bioplastics can use to maintain a sustainable environment and to prevent the disposal of synthetic plastic wastes [2]. Synthesis plastic takes 50 years to decompose nature, while bioplastics requires 10 to 20 times faster to decompose in nature [3]. From the previous study it was found that there are several natural bioplastics-based materials such as PVA / Chitosan [4], PVA / pineapple fibber [5-6] and gelatin / chitosan [7].

Thermoplastic starch is a renewable natural polymer [8] which passes through thermomechanical process in a mixture of suitable plasticizers such as glycerol [9]. The disadvantages of thermoplastic starch are poor mechanical properties, due to the intramolecular and the intermolecular bonds contained in starch [8]. This is supported with addition (1% and 2%) chitosan to show good mechanical properties for 2% [10]. In addition, chitosan has been proved and considered a non-cytotoxic material that can biodegrade and has some interesting biological activities [11].

Plastic waste especially polypropylene (PP) can be able to decompose in nature by mixing natural ingredients such as starch and chitosan to increase accelerate degradation process. A low-cost composite with excellent mechanical properties can be made from starch and polypropylene (PP) [12]. Polypropylene (PP) is an amorphous thermoplastic polymer and is widely used as a thermoplastic engineering material, because it has several vital and useful properties such as transparency, dimensional stability, fire resistance, high temperature heat distortion, and high mechanical strength [13].

In this study, we investigated the effect of additional polypropylene as a reinforced in bioplastics (starch / chitosan), to the mechanical properties, strong bonding characteristics and good structure properties of materials which are determined by FTIR and XRD and the length of decomposition time by microorganisms in the degradation process, respectively.
2. Experiment

2.1. Material
Polypropylene composite has been synthesized from glass plastic waste, aquades, sago starch, chitosan (deacetylation rate of 94.88%; molecular weight, 200 Kda-500 Kda; 200-300 mesh particle size; viscosity 55.31 mPa), Glycerin (Merck), Acetic Acid (CH3COOH) (level 6%) (Merck).

2.2 Bioplastics synthesis
Making of bioplastic was carried out by mixing starch with chitosan, and glycerol as plasticizer, at temperature of 350°C. Bioplastic synthesis was performed by weighing polypropylene 2 grams. Samples of different ratios of starch (S)/chitosan (C) are 35/65, 50/50 and 65/35. Similar procedure is also applied for sago starch until all the starch dissolves. A glass beaker containing a starch solution was placed on a hot plate while heated. Mixing was carried out on a hot plate at a constant temperature of 85°C and magnetic stirrer velocity of 80 rpm for 10 minutes. 25 ml aquades was added into the sample then heating process on the hotplate to form a gel. Polypropylene which has melted then poured into a beaker containing starch. Chitosan solution adding 10 ml of acetic acid for each composition. Both solutions are mixed in a beaker on constant heating temperature 85°C for 15 minutes. After the sample begins to form the gel, the sample is poured into the mold and dried in an oven at 85°C for 12 hours.

| Table 1. The mass compositions of bioplastics synthesis in this study |
|----------------------------------------------------------------------------------------------------|
| Chitosan/Starch (%) | Starch mass (g) | Chitosan mass (g) | Total mass (g) |
|---------------------|----------------|------------------|----------------|
| 65/35               | 2.08           | 1.12             | 3.20           |
| 50/50               | 1.60           | 1.60             | 3.20           |
| 35/65               | 1.12           | 2.08             | 3.20           |

2.3 Characterization of Bioplastic
2.3.1 X-ray diffraction (XRD). This test was performed to information about the crystallinity by using Shimadzu 7000 X-ray diffractometer with CuKα radiation (λ = 1.5405 Å) was recorded between 15° ≤ 2θ ≤ 60°, operates at 30 kV and 10 mA.

2.3.2 Fourier Transform Infra-Red (FTIR). FTIR absorption analysis was carried out by using IRPrestige-21 FTIR spectrometer (Shimadzu Corp.) to determine the functional groups in bioplastic samples.

2.3.3 Biodegradation test. Biodegradability material were detected through soil burial test method [14]. In the beginning the samples were weight was recorded as an initial data. This test is carried out by stockpiling the sample under the ground for 3 days, 7 days, 14 days and 28 days. After the periods of stockpiling, the initial weight was determined and the weight after decomposition of the bioplastic was measured [15].

\[ I_b = \frac{W_o - W}{W_o} \times 100\% \quad (1) \]

where, \( W_o \) = weight before placement in soil; \( W \) = weight after taken out and cleaned.

2.3.4 Tensile Strength Test. Bioplastic sample were cut to 5 cm x 3 cm. Mechanical properties of the samples were determined using a tensile tester (Texture Analyzer AND MCT-2150).
3. Results and Discussion

3.1 XRD Analysis
The XRD patterns a shown in Figure 1 presented the structural bioplastic composite for starch/chitosan ratio is 65/35, 50/50, and 35/65 reinforced polypropylene waste. There are two components in sago starch namely amylose which has a linear chain structure and amylopectin which has a branch chain structure [16]. Branch structures make a major contribution in the formation of amorphous structures. Chitosan has a linear polymer chain structure that contributes to the formation of crystalline phases by connecting with each other to form polymer chains regularly [17]. Starch is a semi-crystalline which consisting of crystal unit and amorphous units [18].

![Figure 1. X-ray Diffraction (XRD) spectra of starch and chitosan reinforced polypropylene (35/65, 50/50, and 65/35)](image)

The XRD results from the previous study shows the structure of starch material which is usually characteristics peaks of (amorphous structure) 15° to 25° and chitosan material which shows more broad peaks at 30° to 40° and another broad peak at ref. [19]. The first peak between 18° to 30° indicated the amorphous phase. Peak (A) indicated that contribution from the starch. This peak is increase with the amount of starch and the other one peak (B) is decrease with increasing amount of chitosan.

3.2 FTIR Analysis
FTIR Characterization was carried out to identify the presence of hydrogen bonds that were formed in composition starch and chitosan reinforced polypropylene for composition is 35/65, 50/50, and 65/35. Figure FTIR show for analysis observed the functional group in bioplastics.
In figure 2 we could be seen the presence of O-H hydrogen bonds (carboxylic acid), C-H alkanes, C=C alkenes and C-O alcohols of compound in bioplastic [20]. It can be seen that the three bioplastics samples have the same identical characteristics which means that the bioplastic production process is well carried out and has the same function group.

The FTIR results show the presence of hydroxyl groups for absorption peaks at 3432 cm\(^{-1}\). From the analyzing results the C-H bonding at wave number 2924 cm\(^{-1}\), and C=C bonding at 1641 cm\(^{-1}\) and C-O bonding at 1041 cm\(^{-1}\). The C=C and C-H bonds have a strong relationship with mechanical strain and bioplastic degradation as reported in reference [19] for polymeric materials and the C-O bonds decrease with the increasing amount of starch. The existence of strong bonds with constituent materials makes the absorption intensity of C=C and C-H bonds increases the tensile strength and biodegradable of bioplastic in this research.

3.3 Biodegradation test

Bioplastic biodegradation test results carried out for 3, 7, 14 and 28 days can be seen in Figure 3. Composites with composition ratio 65/35 showed 96.45% degradation percentage compared to other compositions for 28 days. The different is a clearly for low amount of starch is a low degradation also. And when the starch high, the degradation also increases. This is show that starch is play and important role to degradation performance. The heavy loss of bioplastic samples during burial in soil shows the amount of degradation in the natural environment by the action of microorganisms. In cooperation with water and microorganisms, the structure of fibers and adhesive macromolecules break down or decay in different degrees. Destruction of cementation and erosion points in fiber and
resin joints provides more degradation sites for further attacks of microorganisms, which ultimately results in biodegradation.

Figure 3. Biodegradation test for Bioplastics from Starch and Chitosan reinforced Polypropylene (35/65, 50/50, and 65/35)

3.4 Tensile Strength.

Figure 4 shows the results of the tensile strength of starch and chitosan strengthened with polypropylene. The maximum tensile strength of 68.41 MPa was obtained from composition ratio 65/35. This is indicated starch also play in important to increase tensile strength. According to Ref. [21], they stated that the resistance of starch content is different from sweet potatoes compared to another kind of potatoes [21].

Figure 4. Tensile Strength for Bioplastics from Starch and Chitosan reinforced Polypropylene (35/65, 50/50, and 65/35)

4. Conclusion

The study has demonstrated the potential of Bioplastics composite based on starch /chitosan by additional Polypropylene. Bioplastic sample have amorphous-crystalline structure from XRD analysis.
and the FT-IR spectrum shows that the functional groups of bioplastic has similarity with its constituent components. The maximum tensile strength value of bioplastic at 68.41 Mpa was obtained from the composition ratio 65/35. Biodegradation analysis shows that the synthesized bioplastic for composition ratio 65/35 degraded > 95% for 28 days.

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