STRUCTURAL AND MECHANICAL PROPERTIES STUDY OF THERMOPLASTIC STARCH REINFORCED WITH RICE HUSK BIOCHAR

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Abstract—The morphological and mechanical properties study of thermoplastic starch (TPS) film from *Tacca leontopetaloides* reinforced with rice husk biochar (RHB) was investigated in this study. *T. leotopetaloides* was chosen as a good source of starch since it is cheap, readily available, abundance in nature and it is not a staple food in Malaysia. Using *T. leontopetaloides* starch as the main ingredient for TPS is a new idea to produce biodegradable compound in order to control environmental problem by reducing the agricultural waste disposal problem. The TPS/RHB biocomposites were developed from casting method. RHB infiltration into TPS was performed by rolling them with roll mill. The improvement of the properties of TPS with biochar has significantly increased the tensile strength and elongation at break properties of TPS. X-ray Diffraction analysis showed that the TPS/RHB blends displayed crystallinity characteristics at peak of 22°. Based on the results potrayed by the analyses, it was clearly proven that the incorporation of RHB into TPS has brought a great improvement of mechanical properties of TPS.

Keywords— **Thermoplastic starch, Rice Husk Biochar, *Tacca leontopetaloides*, Plasticizers**

I. INTRODUCTION

Development of biodegradable products based on agricultural materials has achieved a great progress in recent years (Curvelo, 2001). Starch is one of the most promising raw materials for the purpose of producing biodegradable plastic since starch is a renewable source of carbohydrate obtained from a great variety of crops. Starch is cheap, readily available and considered as a potential source in the production of water-soluble pouches for detergents and insecticides, flushable liners and bags and medical delivery system and devices (Fishman, 2000).

Starch is naturally occurring substance which is in the form of discrete and partially crystalline microscopic granules, held together by an extended micellar network of associated molecules (Dufresne A, 1998). The granular starch is composed of about 15-45% crystallinity and can be processed into thermoplastic starch (TPS) when it is subjected by high temperature and shear (Forsell, 1997).

Tacca leontopetaloides is Polynesian arrowroot starch lies within the species Dioscoreaceae (Ukpabi, 2009). This plant exists and is widely distributed from Western Africa through southern Asia to northern Australia. This plant is commonly used as food source for many Pacific Island cultures and as material to strengthen fabrics in some of the islands (Kay, 1987).

The production of TPS involves the usage of starch as main ingredient. Starch is cheap, abundant and renewable, thus makes it has a lot of advantages (Nurul Shuhada Mohd Makhtar, 2013). Water and plasticizers play important roles as they help in forming hydrogen bonds with the starch. Starch is a multi-hydroxyl polymer with three-hydroxyl group per monomer. Plasticization of the starch is displayed when the plasticizers form hydrogen bonds with the starch, thus destroying the original hydrogen bonds between hydroxyl groups of starch molecules (Hulleman, 1998).

However, utilization of TPS only as alternative for other plastics is a poor choice as it has many drawbacks in terms of mechanical strength and high water susceptibility (Carvalho, 2003). The high water absorption can be overcome by blending it with biodegradable polymers (Averous, 2000), adding certain synthetic polymers, inorganic materials (Huang, 2004) or lignin (Baumberg, 1998). For improving the mechanical properties, the TPS films can be reinforced with fibers such as micro-fibers, natural fibers and commercial regenerated cellulose fibers.

Rice husk is a waste product from agricultural industries of the rice production. In China, a large amount of rice husk are produced per annual and leads to the problem of waste management to the country and the waste have to be burnt in open environment. Rice husk currently has been used as bio-fuel to generate electricity (Shackley, 2012). Thermochemical conversion of rice husk gives raise to the formation of rice husk biochar (RHB). RHB has been used as biofuel and also applied in amendment of new soil. Recycling of RHB causes no adverse effect to the soil's health as reported by Oguntunde, (2008).

The combination of TPS with RHB might have a great potential in the field of biodegradable plastics in the presence of plasticizers, which is similar to the conventional synthetic thermoplastic polymers. In this paper, this study focuses on developing the *Tacca leontopetaloides* starch in TPS reinforced with RHB as well as morphological and mechanical properties of TPS/RHB blends. The morphological properties will be conducted using X-ray diffractometer while the mechanical properties will be done using Universal Testing Machine. In this study the concentration of RHB will be varied from 0% to 1%, 3%, 5% and 7%.

II. METHODOLOGY

A. Materials

The *Tacca leontopetaloides* starch powder, rice husk biochar were used as received. The distilled water, 5% acetic acid and glycerol were obtained from the laboratory.

B. Film preparation

Thermoplastic starch was prepared using *T. leontopetaloides* starch together with glycerol, distilled water and acetic acid by using a beaker and hot plate. The thermoplastic starch film was prepared by mixing the 20 g starch powder, 80 mL distilled water, 5 mL acetic acid and 10 mL glycerol in a beaker. The mixture was heated and stirred constantly until it was gelatinized and reached at temperature of 80°C. The homogenized compound was poured into casting plate and cooled for one night. The TPS layer was dried in an oven at 45°C until constant mass was achieved. The combination of TPS/biochar was prepared by rolling the TPS and biochar using roll mill. During compounding process, 0.2 g of sulphur was added prior to the TPS/biochar mixture until the shape of TPS form as sheet with thickness of 3 mm. The concentration of biochar which was used to be added to TPS film were 0% (0g), 1% (1g), 3% (3g), 5% (5g) and 7% (7g). The TPS sheet was cut into smaller size for the purpose of mechanical and morphological analysis.

C. X-Ray Diffraction

X-ray analyses of the samples were performed using a Rigaku X-ray diffractometer operated at 30 kV and 30 mA with CuKα radiation (λ = 1.542 Å). The scanning rate of the diffraction angle 2θ (5-40°) was 2°/min. The samples in the size of 2cm × 2cm and 2 mm thickness were used in the analysis.

D. Tensile properties

The mechanical performance of the TPS films was evaluated in terms of their tensile strength and elongation at break of each film sample at different biochar concentration. Samples of 8 cm, 10 mm in size were cut from the film according to specification to ensure the breakage of the sample occurs within the gauge length. The test were performed according to ASTM D-3500 on five specimens for each biochar concentration. The test was performed using a Tinius Olsen Model testing machine, model H50KT, operated at 10 mm/min and using 2.5 kN load.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

The study crystalline characteristics of TPS film were performed by X-ray diffraction analyses were performed on the composites of different concentration of RHB. The XRD analysis on the RHB which was used to make the blends is presented on Fig. 1.the biochar displayed sharp peak indicated the presence of inorganic components such as SiO_2, KCl and $CaCO_3$ as reported by Weixiang Wu, (2102). The RHB showsThe X-ray diffraction pattern of RHB, plasticized starch, plasticized Starch and rice husk biochar blends are presented in Fig. 2. By referring to the Fig. 2., the TPS exhibits a single diffraction at 22.5°. In a study reported by Xiaofei Ma, (2005), stated that the peak at 22° was attributed to cellulose crystallinity and the addition of fiber to TPS would improve the crystallinity of the matrix. However, mixing of RHB with TPS starting from 1% up to 7% seemed to contribute no significant different with the unfilled biochar TPS. This is because all of them have a single peak at the same angle. The crystallinity exhibited by the TPS/RHB biocomposites is not influenced by the inherent nature of biochar, but rather contributed by high amount of inorganic mineral ash present within them.

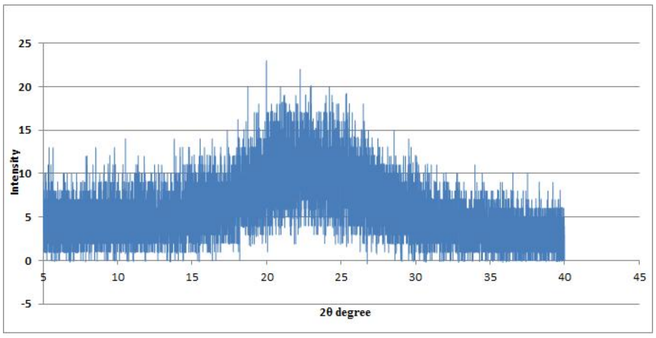

Fig. 1: X-Ray Diffraction pattern of RHB

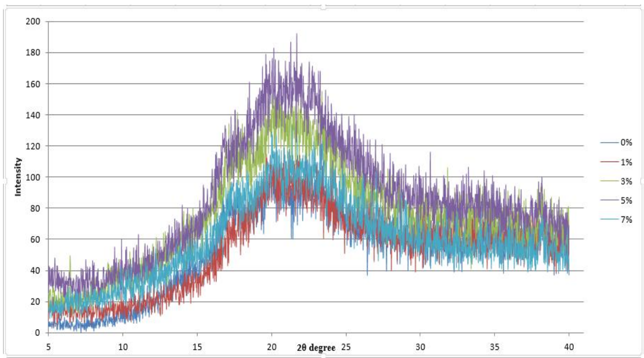

Fig. 2: X-Ray Diffraction patter of TPS/RHB composites at different RHB loading

B. Tensile strength

Table 1 summarizes the tensile strength and elongation at break of TPS/RHB composites at different RHB loading. Mechanical properties of TPS/RHB blends resulted from tensile test are shown in Fig. 3. Tensile strength refers to the maximum stress which a particular composite can withstand before failure occurred during external force was exerted to pull the composite. The stress-strain curves of TPS showed that the TPS with low biochar content represented the typical pattern rubbery starch plastic material. It was observed that there was increment in stress from 0% to 1% RHB concentration, then decrease slowly from 1% to 3% and then increase from 3% to 7%. The plots were essentially linear at low strain and curved towards the strain axis at higher strain. It was clear that the increase of biochar content, the height of plateau was increased although the length was shortened. It was obvious that the TPS/RHB blends exhibits high tensile strength compared to no RHB mixture on the TPS. The TPS containing 7% RHB showed the highest tensile strength about 73% compared to no biochar TPS. However, there is fluctuation to the value of stress may be due to moisture condition of the film when the film was tested on tensile machine. Thus the reading was affected.

The changes in mechanical properties of the TPS/RHB blends is due to the characteristics exhibited by the added RHB and caused the interaction between the composites to be different. It was clear that the addition of RHB has improved the tensile strength as compared to the unfilled TPS. More RHB added into TPS indicates more carbon content in TPS/RHB composites. The porosity of RHB allows it to penetrate into TPS and provides more reinforcement as the interaction of RHB and TPS (Das, 2016). Therefore the tensile strength of the TPS/RHB blend increased when RHB increase from 0% to 1% and from 3% to 7%.

Table 1: Tensile strength and elongation at break of TPS/RHB composites at different RHB loading

Parameters	**RHB loading (wt %)**				
	0	**1**	**3**	**5**	**7**
Tensile strength (MPa)	12.50	21.00	12.35	17.15	25.00
Standard deviation	± 0.25	± 0.00	± 0.65	± 1.15	± 2.00
Elongation at break (%)	21.00	4.95	9.85	4.65	14.65
Standard deviation	± 1.50	± 0.75	± 0.05	± 1.15	± 2.35

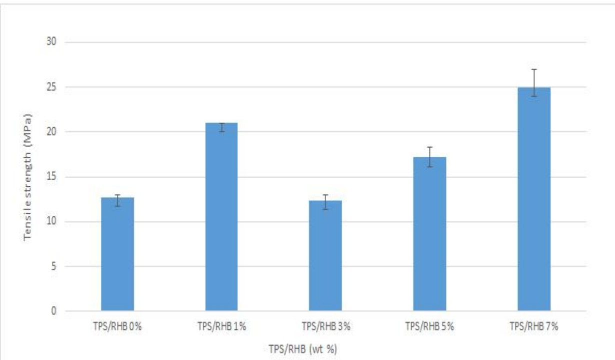

Fig. 3: Tensile strength of TPS/RHB composites at different RHB loading

However, the TPS/RHB blends lost its strength when RHB loading was increased from 1% to 3%. This kind of pattern can be seen from the study reported by Oisik Das, (2015). The decresase value of tensile strength due to the presence of voids within the composites. The possible reason is because of the biochar particles formed into a mass which caused the strength of the composite to be deteriorated. Despite of fluctuation of the tensile strength value, it can be seen that infiltration of RHB into TPS has yielded strong mechanical properties of the biocomposites.

C. Elongation at break

In terms of strength, the increase amount of biochar resulted in the increase of tensile strength, while the incorporation of biochar led to decrease of elongation at break from 0 % to 7 %. A comparison between the elongation and stress was displayed in Fig. 4. It was shown that the increasing of RHB content has led to the decreasing value of elongation. The elongation falls from 21% to 4.95% and then increases up to 9.85%, decrease to 4.65% and increase again up to 14.65%. The inverse trend of tensile strength can be observed across the entire range of the data set, that is, the increasing of RHB amount has reduced the ductility of biopolymer. In a study by Wetzel, (2003), the inverse relationship between the filler concentration and elongation was due to the increase of the brittleness of the composite material and thus will affect in reducing the percentage of elongation at break. Most of the deformation under high strain comes from the polymer due to the rigid nature of the fillers. The differences of rigidity between the matrix and te fillers has led to this result. Most of the deformation under high strain comes from the polymer due to rigidity of the fillers. Other study by Angellier, (2006) reported that the viscoelastic properties of unfilled matrix plays its role in causing the composites to posseses low tensile strength and high strain. The fluctuation of the value displayed on the figure indicates that there was an optimum concentration of biochar to be incorporated with the TPS. Therefore it is possible to use biochar up to 7% without losing its ductility and at the same time posseses high strength in replacing synthetic polymer with biocomposites. A significant increases of tensile strength indicates that TPS matrix is suitable to be suited with RHB.

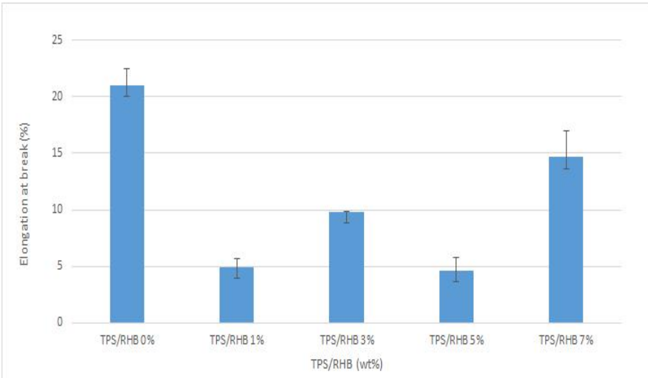

Fig. 4. Elongation at break of TPS/RHB composites at different RHB content

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IV. CONCLUSION

The usage of biodegradable composites is one way to reduce environmental effect. The development of *T. leontopetaloides* as the main material to produce TPS is one invention that can give rise to many benefits due to its advantages. The TPS films produced from this study are homogenous and have good properties. The XRD and Tensile strength results are complementary to each other. Analysis shows that processing of TPS film has changed the properties of the film. The properties are compared with the unfilled TPS and the outcomes from the study has been discussed. All the analyses have been performed on X-Ray Diffraction, Tensile strength and elongation at break by X-Ray Diffractometer and Universal Testing Machine.

Following conclusions have been made:

- Adding 7% RHB resulted in a composite which have the highest tensile strength and low value of elongation at break.
- TPS with unfilled RHB has the lowest tensile strength highest value of elongation at break.
- Addition of RHB into TPS gives no significant effect on the crystallinity of the biocomposites.

This study attempts to improve the value of biochar as product from pyrolysis, in the production of high quality biodegradable thermoplastic processing. It is envisioned that the biochar based biocomposite can be compete commercially as other conventional reinforcement material for other composites. Lastly, biochar is one step of exploring the wide usage of biochar in other field.

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