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Effects of Rice Husk Ash Loadings on the Tapioca Starch-based Film Composite

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Abstract

Plastics are majorly produced from petrochemicals which lead to several problems such as the depletion of fossil fuel and environmental pollution due to their nature of being non-biodegradable and overflowing landfills. To overcome this problem, researchers have begun to develop bioplastic which is plastic made from a renewable source such as starch. However, the starch-based bioplastic is moisture sensitive due to its hydrophilic nature, which makes it easily swells in water and leads to a decrease in its tensile strength. Therefore, modification of the starches polymer matrix was conducted by blending starch with low-density polyethylene (LDPE), with the addition of glycerol as a plasticizer and rice husk ash (RHA) as filler. The produced film composite was then subjected to tensile test and swelling test. It was found that the presence of RHA improved the mechanical properties of the film composite by increasing the tensile strength and Young's modulus of the film. The integral stability of the film composite also increased which was displayed through a decrease in the swelling percentage. RHA with 9 wt.% yielded a film composite with better strain without jeopardizing its strength and waterproofing property.

Disciplinary: Polymer Science and Engineering, Chemical Engineering, Sustainable Technology.

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1 Introduction

Bioplastic is a type of plastic partly or wholly made of renewable biomass sources such as starch, woodchips, vegetable fats and oils, and recycled food waste. It is developed because it could help lessen the problem of conventional plastic, which is derived from petrochemicals. This type of plastic pollutes the environment as it takes up a long time to decompose in landfills. The upper hand of using bioplastic is that it can be recycled naturally through biological processes. This would then reduce the use of fossil fuels to produce plastics. Bioplastic has been around for a long time in a variety of products such as food containers, groceries bag, food packaging, and even auto parts. In 1941, Ford invented the first 'green car' using the plastics auto part derived from hemp, wheat, flax, and soybeans. Unfortunately, World War II happened shortly after its debut which made the idea of making plastic derived from the plant was forgotten until the 1990s when people started searching for an alternative to petroleum-based plastic [1].

Starch has been one of the most promising sources for various applications as a renewable raw material, among natural polymers due to its price, wide availability, and thermoplastic behavior [2]. Starch can be found abundantly in leaves, flowers, fruits, seeds, stems, and roots of a plant. According to a few references, the source of starch affects the properties of the produced bioplastic due to the different content of amylose and amylopectin and their molecular structure [3]–[5]. In the study by Hulleman et al. [3], samples using potato, corn, and wheat starch with around 25% of amylose were proven to have a higher tensile strength than the sample using waxy corn starch that contains less than 1% amylose. The difference in the tensile strength value can be associated with the small amount of B-type crystallinity difference since crystallinity increases stiffness and stress at break.

This could also affect molecular mobility and the ability to form an association. Tapioca starch is reported to have 16.04–26.95% amylose content [6]. In another study, tapioca starch from Ng Nam Bee Marketing, Singapore reportedly contains 24.12% amylose [7]. Cassava or tapioca starch as a polysaccharide synthesized by plants has become an attractive source of biopolymer due to its low cost, high availability, and biodegradability despite its hydrophilic structure that makes it highly swelling in water [8]. Typically, a good bioplastic must be flexible and strong with low water absorbability, high thermal stability, and aesthetically pleasing.

Since starch-based bioplastic has limitations such as brittleness and high-water solubility, this has led researchers all over the world to embark on research to find the best formulation to produce a good bioplastic [9]. It is widely reported that waterproof starch-based films are difficult to fabricate. This is because starch contains a large number of hydroxyl groups which develop a hydrophilic nature in starch and set limitations to the development of starch-based materials [10]. Schmidt et al. [11] studied the effect of the degree of acetylation, plasticizer concentration, and relative humidity on cassava starch films properties by using acetic anhydride as the esterification reagent. A total of twelve formulations were studied by using fixed concentrations of cassava starch, with two different concentrations of starch acetate and glycerol respectively. The study has proven that acetylated starch films with improved mechanical properties, lower water solubility, and permeability to water vapour were obtained when starch acetate with 0.6 degrees of substitution and low glycerol concentration was used. A blend of starch with synthetic polymer and modification of starch through compositing is one of the efforts to improve the properties of the starch-based film [12]. The studies on the biodegradability and mechanical properties of the plastic from a blend of polyethylene (PE) with starch have been widely reported, where a high concentration of starch in the blend causes an incompatible mixture that leads to low mechanical and rheological properties of the polymer [13]. Deepshikha et al. [13] reported on the fabrication of biodegradable film from a blend of low-density polyethylene (LDPE)/corn starch incorporated with nano-silica, with a weight ratio of 80/20 LDPE to corn starch.

Incorporating fiber fillers could also improve the strength and heat resistance of the film composite [12]. Natural cellulosic fiber such as sisal, cotton, bamboo, jute, kenaf, and wood has been incorporated in the polymer matrix of starch and was found to improve the mechanical properties of the polymer. Other advantages of fiber reinforcement lie within the use of renewable resources, low cost, low density, abundant and easy processibility [14]. Inorganic nanofiller such as silica, on the other hand, has the advantages of higher surface to volume ratio and higher surface area that lead to the enhancement on the overall properties of the polymer composite due to good adhesion between polymer matrix and the nanofillers [15-16]. Silica is widely used as a mineral filler and can be used in the form of oxide or silicate and in a crystalline or amorphous structure. Silica can be divided into two types which are natural and synthetic. One of the sources of natural silica is rice husk ash (RHA). Rice husk is a side product of the rice milling industry. It is an agricultural waste in many rice-producing countries around the world such as Thailand. In India, it is normally burned in the field which would cause air pollution due to the smoke produced from the combustion process. It has been a common problem for rice farmers since it is resistant to decomposition in the ground, difficult to digest, and has low nutritional value to be fed to animals. Thus, it also contains about 90- 98% of silica [17]. The extraction of silica is economical due to the large presence of silica content in the ash. Thanks to their small diameter, many applications such as thermal insulators and composite fillers use ultrafine silica powders [18]. A lot of researchers have tried to study the characteristic of silica from RHA and its various utilization. Some researchers have also tried a lot of methods to extract silica from rice husk with high purity. A comparison of purification and processing of silica from RHA was conducted in which nine study results that used different purification and processing methods were compared [19]. The utilization of rice husk as fillers in thermoplastics fabrication has gained interest thanks to the need to minimize environmental problems caused by agricultural by-products. Incorporating natural fibres in bioplastic formulation has been proven to increase the tensile strength of a starch-based thermoplastic [20]. The study was done using corn starch with 11% moisture obtained from Langfang Starch Company, China. The fibre used was micro winceyette fibre with a length of approximately 12 mm obtained from Tianjin Textile Industry University. By increasing the fibre content from 0% to 5%, the initial tensile strength increased up to 15.16 MPa. The use of silica as nanofillers is attractive due to its large surface area, high adsorption capability, large pore volume, and smooth surface. Another plus point of using nano-silica from rice husk is the ability to add value and elevate the biomass material to a bioplastic, which could help to solve the accumulation of waste in the world [13].

This study evaluates the effects of rice husk ash incorporated with the blend of tapioca starch/LDPE and glycerol as a plasticizer on the mechanical properties and water solubility of the fabricated film composite. The weight ratio of LDPE/starch used was 16/40.

2 Materials & Method

The tapioca starch used in this study was bought from the store nearby. The glycerol was purchased from Merck Malaysia and the rice husk ash was bought from a local supplier.

2.1 The Fabrication Process of the Composite

Prior to the preparation of the composite, the tapioca starch was dried in a Memmert universal oven at 70°C with medium fan speed for 24 hours to minimize moisture content. For the basis of 40g of starch and 16 g of LDPE, 2.8 g of RHA which corresponds to 5% w/w of the blended polymer was hand-mixed in a beaker. 16 g of glycerol was added and hand-mixed until the mixture was homogenous. The subsequent melt blending process was carried out in the Thermo HAAKE Polylab Internal Mixer at 130°C and 70 rpm for 13 minutes.

The solid produced by melt blending was crushed by a compact crusher. As for sample preparation for subsequent tensile tests, the crushed solid was then subjected to a hot moulding process by using a Cometech Hot Press machine at 130°C for 15 minutes to produce a dumbbell-shaped thin film. The above procedures were repeated by using other concentrations of RHA (7%, 9%, 11%, and 13%). The formulations involved are tabulated in Table 1.

Table 1: Formulation of a film composite with various RHA content

Composition (g)	Code					
	RHA-0	RHA-5	RHA-7	RHA-9	RHA-11	RHA-13
Starch	40	40	40	40	40	40
LDPE	16	16	16	16	16	16
Glycerol	16	16	16	16	16	16
Rice husk ash	0	2.8	3.92	5.04	6.16	7.28

2.2 Characterization of the Composites

2.2.1 Tensile Strength

The mechanical properties of the film composites were tested by using a Universal Testing Machine with a standard procedure of ASTM D638 where the samples had dumbbell-shaped. The load cell used was 500 N with a crosshead speed of 500 mm/min. From the obtained data, the tensile strength was calculated from the maximum load divided by the average cross-sectional area in the gauge length segment of the specimen. Young's modulus was calculated from the initial slope of the stress vs. strain plot.

2.2.2 Water Absorption/Swelling

The weight of the film composite was measured using an analytical balance. Then it was immersed in 100 mL of distilled water for 24 hours. Next, the sample was removed from the water and wiped gently with tissue paper. Then the weight was measured again. The swelling percentage was calculated as

$$Swelling\ percentage = \left(\frac{Final\ weight - Initial\ weight}{Initial\ weight}\right) x\ 100 \quad (1).$$

3 Result and Discussion

3.1 Tensile Strength

The tensile strength of the bioplastic films with different RHA content is illustrated in Figure 1. Film from RHA-0 that was from pure polymer and without nano-silica showed the lowest tensile strength. The increase in the loading of RHA increased the tensile strength of the film composite, where RHA-13 exhibited the highest tensile strength. The increase in the tensile strength showed that there was a uniform mixing and good compactness between the polymer blend and the silica, which did not cause any disruption on the polymer backbone [13]. The result also implies the fabrication of a homogeneous blend although there is a higher composition of tapioca starch as compared to LDPE in the mixture. The presence of glycerol could also give a substantial effect where it helps to enhance compatibility blend between the matrix of the polymer blend and RHA as the filler [8]. However, based on Figure 2, the opposite trend was observed where the increase in RHA content resulted in reducing the elongation of the film composite except for 9 wt.% RHA. Despite the decreasing trend, 9 wt.% was found to slightly improve the elongation at break for this film composite. It showed that the flexibility of the film composite was not jeopardized even when its strength increased. This phenomenon is reflected from (or in) the homogenous blend of the polymer matrix with a less internal void to provide higher internal bonding [13].

Table 2 shows the values of Young's modulus for each film composite. Young's modulus represents the stiffness of a material. The higher the value shows the film composite possesses good strength that prevents it from experiencing permanent deformation after being stretched out even at lower strain [13]. The value of Young's modulus increased proportionally with the amount of RHA added into the formulation. Based on these results on mechanical properties of film composite, formulation RHA-9, with 9 wt.% RHA incorporated into the polymer blend is the best formulation as it possesses better tensile strength and stiffness with longer elongation as compared to other film composites.

Table 2: Young's modulus for film composite with various RHA content

Formulation code	Young's modulus, MPa
RHA-0	0.0241
RHA-5	0.0271
RHA-7	0.1467
RHA-9	0.1867
RHA-11	0.2133
RHA-13	0.3144

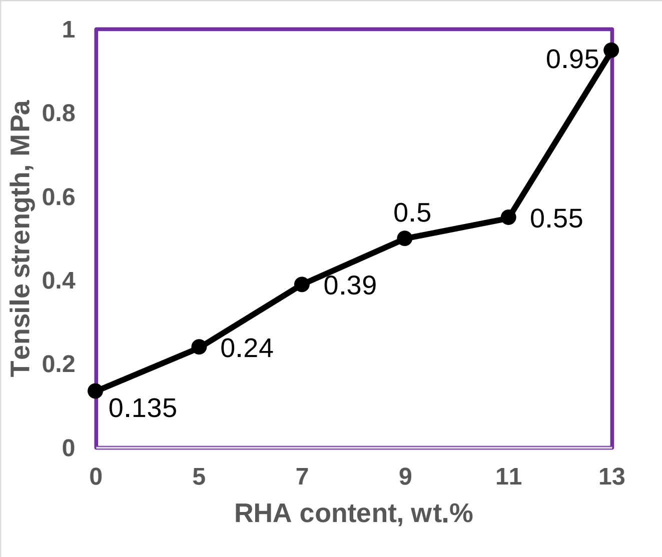

Figure 1: Tensile strength for bioplastic film with various RHA content

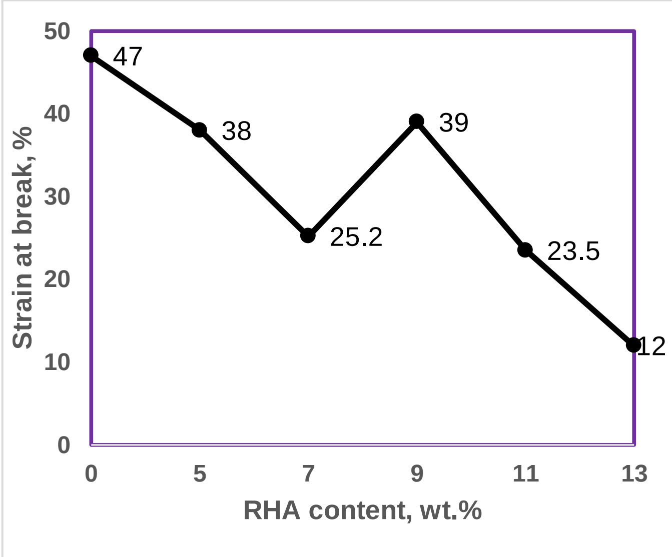

Figure 2: Strain of the film composite with various RHA content

3.2 Swelling Properties

Figure 3 shows the swelling percentage of the film composite at various RHA content. The rapid decrease in the swelling percentage as RHA content increased was shown, where RHA-0 had the highest value of 69.23%. As the main drawback of the starch-based film is its high moisture absorption that leads to the decrease in the tensile strength under higher moisture conditions [12], the incorporation of RHA shows a significant effect to encounter the problem. It was stated by Tianyu et al. [12] that the blend containing starch must have a low percentage of starch in order for the polymer to become hydrophobic and does not swell in water. But this current finding depicts the opposite scenario, where the higher composition of starch as compared to LDPE in the polymer blend did improve tensile strength and waterproofing of the fabricated film composite. A similar trend of the film's strength as with the findings reported by Deepshikha et al. [13] was obtained even when the ratio of LDPE/tapioca starch used was 29/71 as compared to 80/20 being used by the previous research. In terms of the integral stability, the observation of the shape of the film composite after 24 hours of immersion in water was conducted. Figure 4 depicts the shape of film composite from two different formulations, RHA-0 and RHA-5. Based on Figure 4, the film without RHA was almost completely disintegrated in the water to form small pieces while the film with 5 wt.% RHA still retained its original shape.

From the results obtained, obviously, the incorporation of rice husk ash into the film composite formulation has proven to improve the properties of the film. It helps to increase the strength of the film formed, decrease water absorption rate, and help to increase the integral stability of the film even when it is in contact with water. This would mean that the film or bioplastic can be used for applications such as drinking straw or parcel wrappers.

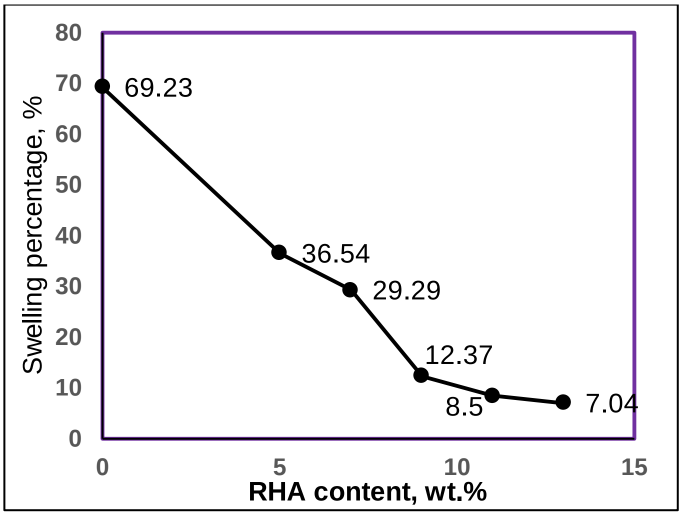

Figure 3: Swelling percentage of film composite at various RHA content

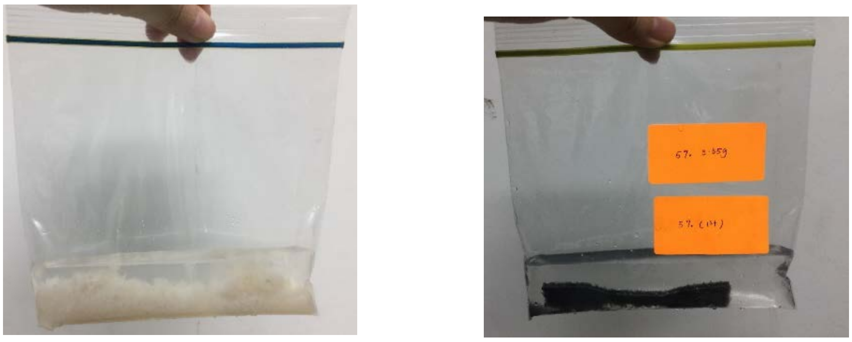
(a) (b)

Figure 4: Pictures showing films composite from 2 formulations (a) RHA-0 and (b) RHA-5, after 24 hours immersion in water

4 Conclusion

In conclusion, film composite or bioplastic with good tensile strength, hardness, waterproof, and good integral stability has been successfully fabricated from a blend of LDPE/tapioca starch with glycerol as a plasticizer and rice husk ash as filler. The higher composition of starch in the blend does not jeopardize the above properties, where it could be reflected through the appropriate fabrication process. It was found that film with 9 wt.% RHA has better elongation as compared to others. The fabricated bioplastics could be potentially used to substitute the conventional petroleum-derived plastic in the future that could help to conserve the environment and to ensure value addition to the biomass of rice husk.

5 Availability of Data and Material

Data can be made available by contacting the corresponding author.

6 Acknowledgement

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