Effect of Thermal Treatment on Mechanical Properties Rice Husk Ash Filled Tapioca Starch Composite

Dk Norsyafina Binti Pg Adnan , Sazmal Effendi Arshad#
Industrial Chemistry Program, Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, MALAYSIA.
Corresponding author. E-Mail: sazmal@ums.edu.my; Tel: +6088-320000; Fax: +6088-435324.

ABSTRACT
This research presents a biopolymer from tapioca starch (TPS) as the base and rice husk ash (RHA) as the filler material. TPS molding was prepared by gelatinization and casting technique. Rice husk ash was produced from leaching treatment with calcinations at 700°C for 24 hour. The effect of thermal treatment with varying content of rice husk ash (0, 1, 2, and 3 %) on mechanical properties of tapioca starch composite was evaluated in order to get the characterization of the composite. Result shows a decrease in mechanical properties with the increase of rice husk ash content. However, after thermal treatment at temperature 80°C for 24 hrs the tensile strength has an increase of 13%, 125%, 340% and 311%, respectively.

KEYWORDS: Rice husk ash; tapioca starch; mechanical properties; thermal treatment

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INTRODUCTION

Recently, many works have been done in order to produce biodegradable polymers composites which are generally known as 'green' composite or biocomposite. Synthesis of biocomposite is made up from combination of natural fibers and natural matrices (Wan *et al*., 2009) which can help to promote the usage of environmental friendly materials (Sahari & Sapuan, 2011). Starch is known as a natural renewable polymer. Apart from being cheap, it can be found abundantly and is easily biodegradable making it advantageous compared to other polymer (Teixeira *et al*., 2009). Development and characterization of starch based films have been discovered from a few decades ago. Starches are mostly made up from varies of crops such as agar (Rhim, 2011), banana (Zamudio-Flores *et al*., 2006), cassava (tapioca) (Maran *et al*., 2013), corn (Dai *et al*., 2015), maize, rice (Dias *et al*., 2010), sago, sugar palm (Sanyang *et al*., 2015) and yam (Gutiérrez *et al*., 2015).

Septo (2003) stated that since the last decade, many researches have shown great interest in the capability of starch to be converted into a thermoplastic material (TPS). Presence of plasticizer at high condition plays a main role in converting starch into thermoplastic material. Examples of plasticizer that are commonly used are glycerol, sorbitol, urea, formamide, dimethyl sulfoxide and sugars with low molecular weight. Some researchers have managed to develop thermoplastic polymer starches using a simple casting method. A study by Wicaksono *et al*. (2013), for instance has successfully produced tapioca film reinforced cellulose nanofibers through casting method. Other example includes a study by Espinel Villacrés *et al*. (2014), where the team had developed tapioca starch film with hydroxypropyl methylcellulose, glycerol and also potassium sorbate using casting method. However, it was noted that starch biocomposite have shown poor mechanical properties and poor resistance to humidity. In order to solve such issues, a few approaches were taken such as the addition of water and glycerol as plasticizer, which help to enhance mechanical properties of starch composites. Other approaches to overcome these problems were done by adding other material such as synthetic polymer, crosslinking agent or through esterification, lignin, cellulosic microfibrils, natural fibers and commercial regenerated cellulose fibers (Johar & Ahmad, 2012).

There are indeed numerous studies that have already been published which focuses on the usage of combination of starch and natural fibers. Yet, there are only few researches that focused on the usage of rice husk as reinforcement filler for thermoplastic composites. Sarvanan and Kumar (2013) have stated that rice husk which is a popular, common agriculture waste product is suitable to be used as reinforcement filler. Rice husk, an example of lignocelluloses material is abundantly available; provided from rice milling process. Moreover, rice husk is considered as a good source of silica and silicon compound due to its high content of silica, which is about 90-98% after undergoing combustion process. This process turns rice husk into ash, also known as rice husk ash (RHA). Currently, the most popular rice supplying countries which are likely to remain strong in the next decades are situated across Asia and Africa. This fact is supported by a report by Food and Agricultural organization (FAO), which states that the world rice production in 2014 were approximately 741.3 million tonnes and estimate increased to 749.8 million tonnes in 2015 (FAO, 2015). Replacing inorganic substances and synthetic fibers with lignocellulose materials as reinforcing fillers in plastics is therefore advantageous in terms of cost and environmental protection.

To gain new knowledge on this matter, a series of experiments been conducted on the effect of thermal treatment (80°C) on mechanical properties of thermoplastic starch (TPS) based on tapioca starch with rice husk ash (RHA) as filler material. Different rice husk ash content was prepared (0%, 1%, 2%, and 3%).

METHODOLOGY

Preparation of filler

Throughout this study, rice husk were taken from Kg Inobong, Penampang, Sabah, Malaysia. Rice husk was prepared by washing them with water to remove the contaminants and dried at room temperature for 24 hours. Washed rice husk were subjected to chemical treatment via acid leaching. Rice husk were then treated with diluted HCl in water bath at 80°C under constant stirring for 1 hour to remove metallic impurities. After that, drying process in the oven was allowed at 70°C for 24 hours. Then, the rice husk was heated to 200°C for 1 hour to remove the moisture and organic matter. Subsequently, rice husk was heated to 700°C for 12 hour to remove carbonaceous material. Finally, rice husk were cooled down and then grinding step was carried out. The obtained rice husk ash (RHA) (Figure 1a) is used as a reinforcement material for the preparation of composites.

(a) (b)

Figure 1. (a) The treated rice husk 700°C for 12 hour and (b) final composite of TPS/RHA after thermal treatment at 80°C for 24 hours.

Fabrication of TPS/RHA composites

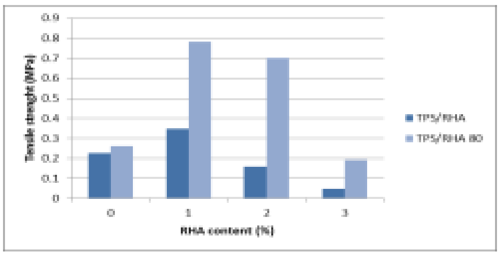
The composites content were a mixture of 85% distilled water, 10% tapioca starch and 5% glycerol. The calculation was made based on Rodney *et al.*, (2015) with slight modification. The mixture was heated on a hot plate under continuous stirring using magnetic stirrer for 30 min until mixtures homogenized well. The samples were prepared using different content of RHA (0%, 1%, 2%, and 3%) where it was subsequently cast in a mould. Then, the samples were left for 24 hours to allow drying process at room temperature. After that, samples were subjected to thermal treatment at temperatures $80^{o}C$. The final composite (Figure 1b) was obtained in the form of plate. Finally composites were labeled as TPS/RHA0, TPS/RHA1, TPS/RHA2, and TPS/RHA3, respectively.

Mechanical properties

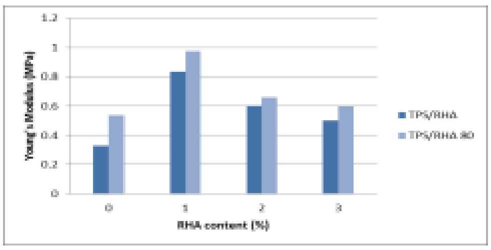
The mechanical properties of the samples were tested based on ASTM D 5083 standard (UTM by GOTECH Al-7000-M). Tensile strength and elongation were determined by using Universal Testing Machine with a load cell of 10kg. Samples were cut using cutter with dimension of 100mm (L) x 20mm (W) x 3mm (T) and five samples for different composite groups were subsequently tested. The samples were clamped between two tensile grips and the initial gauge length was at 50mm. Samples were pulled using a crosshead speed of 1mm/min.

RESULT AND DISCUSSION

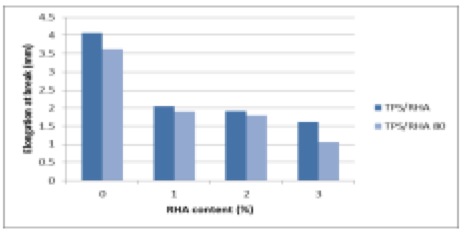
Figure 2(a) shows the tensile strength with increase in RHA content of the tapioca starch composite. The result shows decreasing in tensile strength of non-thermal and thermally composites with increasing RHA content. Maximum decrease in tensile strength at 3% for both composites might be due to the clumping that occurs at certain composition of rice husk ash (Eva *et al.*, 2014). Other influencing factor is the increasing number of silica content (Kord, 2010). Besides that, according to Ahmad *et al*. (2012), higher amount of filler content may cause difficulties in achieving a homogeneous mixture process. Moreover, an occurrence of filler agglomeration process may occur. The dispersion of filler in starch matrix also affects the mechanical properties of composites; therefore if the dispersed filler are well equal in the matrix, the stress will equally transfer into the composite, and vice versa. These actually explain why different composites give different mechanical properties. The evidences are shown in Figure 3 and 4.



(a) Tensile strength (MPa)



(b) Young's Modulus (MPa)



(c) Elongation at break (mm)

Figure 2. Mechanical properties of TPS/RHA composites, before and after thermal treatment at $80^{o}C$ for 24 hours.

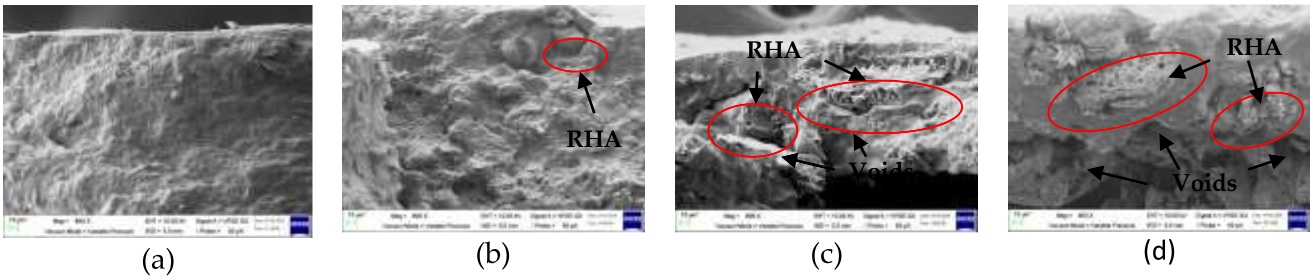


Figure 3. SEM of non-thermal TPS/RHA; (a) TPS/RHA0, (b) TPS/RHA 1, (c) TPS/RHA 2 and (d) TPS/RHA 3.

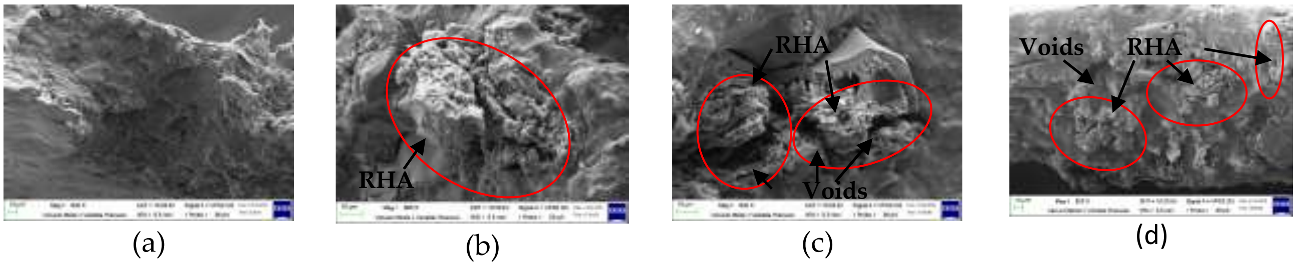


Figure 4. SEM of thermally TPS/RHA; (a) TPS/RHA0, (b) TPS/RHA 1, (c) TPS/RHA 2 and (d) TPS/RHA 3.

In order to increase tensile strength, there is a need to increase the covalent bonding and hydrogen with OH group while also adding the oxygen of from each of carboxyl group bonding between the filler with matrix (Bhat & Abdul Khalil., 2011). Several possibilities that may improve mechanical properties are by taking into consideration the aspect ratio of the filler material, the degree disperse and orientation in the matrix and also adhesion at the interface matrix–filler (Eva *et al*., 2014). However, it was clearly illustrated that, there was improvement of tensile strength after thermal treatment compared than non-thermal treatment composite. The result shows that the tensile strength increase of TPS/RHA matrix was 13% (from 0.23 MPa to 0.26 MPa), 125% (from 0.347 to 0.78 MPa), 340% (from 0.159 MPa to 0.7 MPa) and 311% (from 0.047 to 0.193) respectively, after thermal treatment at 80^{o}C for 24 hours. This enhancement may be due to the removal of moisture from TPS/RHA composite samples, which led to further strengthened bond between the matrix and the fibers. Furthermore, the result of this study is supported by the study done by Ching *et al*. (2014), whom stated that in order to break the samples more energy was needed compared to the non-thermal samples.

Young's modulus of the composites was obtained from slope of the graph of tensile strength vs. elongation at break and the results are shown in Figure 2(b). The tensile modulus shows the relative stiffness property of a material such as the ability of material to resist deformation in tension. Stiffer materials have higher tensile modulus (Sahari *et al*., 2011). It shows that 0% of non-thermal TPS/RHA has the lowest stiffness compared to other non-thermal composites. While the increase in the composite modulus is attributed to the filler modulus, it is to be noted that rice husk ash composites always reveal their weakness in mechanical properties, which a sign of inferior adhesion and poor interaction of the filler with the polymer (Fuad *et al*., 1994). Meanwhile, 1% of thermal TPS/RHA exhibits highest stiffness followed by 2%, 3% and 0% of thermal TPS/RHA composites. The removal of inbound moisture content after thermal aging may lead to the improvement of the tensile modulus, as shown in stiffer composite material (Ching *et al*., 2014).

Elongation at break analysis was shown in Figure 2(c). From the Figure 2(c), it clearly shows that there is reduction in elongation with the increase of RHA content for all samples. The reduction of composite may attribute to the poor interfacial or possibility of void occurring at rice husk-ash-matrix interface. Fracture of composite may occur if the elongated voids merged. Poor relative elongation is also influenced by higher particle size of void; which may cause preliminary failure. Other reason may be due to the higher surface area required by smaller particles for interacting with the matrix polymer (Ahmad & Mahanwar, 2010). Elongation can be increase by reducing the particle size. Meanwhile, decrease of elongation of thermal composites is due to the better aging resistance with the greatest cross-linked structure (Ahmed *et al*., 2014).

CONCLUSION

As a conclusion, the incorporation of small amounts of rice husk ash from 1 to 3 wt% and presence of thermal treatment influences the mechanical properties of tapioca starch material. Thermal treatment further improves the tensile properties of tapioca starch material filled with rice husk ash. Even though rice husk ash filled in matrix showed poor mechanical properties, it still shows better performances compared to tapioca starch in other aspects. Thus, rice husk ash can act as filler in development of biocomposite. This also may help to reduce open burning of rice husk, reduce air pollution and also offers a better solution in making renewable biocomposites.

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