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The Effect of Eggshell Powder (ESP) Filler on the Properties of Purple Sweet Potato (PSP) Starch Bioplastics

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ABSTRACT

Petroleum-based plastics are derived from non-renewable sources and are supremely utilized in packaging industries due to their superior flexibility, mechanical and barrier properties. However, due to petroleum-based plastics do not degrading easily, researchers are turning into bioplastics. This study was conducted to examine the effect of eggshell powder (ESP) loadings on the physical and mechanical properties of purple sweet potato (PSP) starch bioplastics. PSP starch was extracted and mixed with glycerol as plasticizer and 0 – 40 % by weight of ESP to fabricate PSP/ESP bioplastic using solution casting method. The incorporation of ESP in PSP starch matrix (in terms of functional groups and bonding existed) was analyzed by using Fourier Transform Infrared spectroscopy (FTIR-ATR). The physical property of PSP/ESP bioplastics is characterized through water absorption test. Whereas the mechanical properties (tensile strength, Young's Modulus and elongation at break) of bioplastics was analyzed by tensile test. From FTIR analysis, it can be summarized that the PSP/ESP bioplastic was successfully synthesized. The tensile strength and modulus of this bioplastics increase from with the addition of ESP up to 20 wt.%. This is because further addition of ESP above 20 wt.% reduces tensile strength and modulus of elasticity of this bioplastic. In terms of elongation at break, a slight decrease in elongation at break as the ESP loadings increases. Similarly, the water absorption capacity of this bioplastic significantly *decreases as the percentage of ESP increases. The incorporation of ESP into this bioplastic able to reduce rate of water absorption from 26.32 % to 12.5 % in 72 h. Therefore, these bioplastics exhibit good physical and mechanical properties that can be used as alternatives for synthetic plastic to cope with waste generation and disposal problems, especially in the food industry.*

Keywords: Bioplastics; Starch; Purple Sweet Potato; Eggshell

INTRODUCTION

The issue of waste recycling and environmental protection has received much attention worldwide due to the increased awareness of the adverse effects of plastic pollution. Traditional plastics, which are derived from petroleum-based polymers, have raised major environmental concerns, including resource depletion, non-degradability, and the generation of microplastics. Therefore, the use of plastics from renewable and sustainable sources has emerged as an important alternative to petroleum-based polymers [1].

Currently, bioplastics, which are mainly derived from renewable resources, have been gaining considerable interest as alternatives to petroleum-based plastics. Compared to petroleum-based plastics, bioplastics have superior environmental properties such as biodegradability and low carbon dioxide (CO_2) emissions [2]. Bioplastics are mainly derived from biological materials, including proteins, lipids, and polysaccharides. Among the different types of bioplastics, polysaccharide-based bioplastics, such as starch, chitosan, and cellulose, have been widely investigated due to their abundance, renewability, biodegradability, and biocompatibility [3]. Starch has been said to be a promising candidate in the making of bioplastic due to its complete biodegradability and good physical properties. Starch is the second most abundant biomass material in nature after cellulose, it is composed of two different types of glucose polymers, which are linear amylose and branched amylopectin. Nonetheless, starch has poor mechanical properties, including brittleness and low tensile strength, as it consists of long and rigid linear amylose and highly branched amylopectin molecules [4]. To improve the mechanical properties of starch-based bioplastics, various fillers, including wood flour, plant fibers, and mineral-based materials (e.g., clay, calcium carbonate, and calcium phosphate), have been incorporated into these starch bioplastics [5]. These fillers have been used as reinforcing agents to enhance the mechanical properties of starch-based bioplastics. In addition, the moisture sensitivity and high hydrophilic properties of starch-based bioplastics are two major factors that limit their practical applications. Thus, the modification of starch-based bioplastics has been extensively studied in recent years.

The need for material with good physical and mechanical properties is crucial in developing packaging material suitable to be used in the food industry. This can be achieved by the addition of inorganic particles such as calcium carbonate to improve the properties of the film. In recent years, many researchers have also focused on the combination of biopolymers with inorganic nanoparticles to develop composite materials with improved physical and mechanical properties. Among all natural sources of calcium carbonate, eggshell is the most suitable due to its high calcium carbonate ($CaCO_3$) content around 95% [6]. The use of eggshell powders in new materials has been suggested as alternative fillers in polymers, paints, ceramic tiles, mortar, and concrete [7]. Compared to conventional $CaCO_3$ composites, the mechanical properties of eggshell powder (ESP)-filled biocomposites, such as the tensile strength and Young's modulus, can be improved [8,9]. The incorporation of ESP into polylactic acid, thermoplastic starch, and poly (butylene succinate) (PBS) has been proven to improve the thermal stability, mechanical properties, and/or water resistance of these biodegradable materials [10,11].

To produce a more attractive bioplastic, purple sweet potato (PSP) can be used since this type of potato is unique compared to other types of tubers due to its high anthocyanin content and bright purple are useful marker or indicator. The above works served as inspiration for the current work, which fabricate bioplastics that comprise natural polymer and inorganic particles have gained more interest as environmentally friendly and bifunctional materials due to fascinating properties such as biocompatibility and biodegradability. In this work, a simple and eco-friendly approach have been used to fabricate PSP/ESP films by the solution casting method.

EXPERIMENTAL DETAILS

Extraction of Purple Sweet Potato (PSP) starch

100 g of purple sweet potatoes, PSP (without skin) was weighed and used in this study. Then, 100 mL of distilled water was added to the PSP and the sample was grind using mortar and pestle. The mixture then was poured through a strainer into a beaker leaving crude starch settling on the strainer. The PSP starch was dried to remove the moisture, ground to obtain in powdered form.

Preparation of PSP/ESP Bioplastic

Ground-up eggshells were used as filler. Eggshells were collected from Arau, Perlis. The samples were washed with water, to remove the white membrane inside the eggshells and, subsequently was sun-dried. The eggshells were then grounded into powder using kitchen mixer. Later, the PSP starch and ESP were used to prepare five PSP/ESP bioplastic samples with various compositions of ESP. A constant weighed of PSP, constant concentration of plasticizer (glycerol) and varied composition of ESP (0, 10, 20, 30 and 40 wt.%) were used in this experiment. Generally, 2.5 g of PSP starch was dissolved in 25 mL distilled water together with various compositions of ESP as shown in Table 1. Next 2 mL hydrochloric acid (HCl) and 2 mL of glycerol were added into the solution. The solution was heated at medium heat with constant stirring until gelatinization. The solution was cast into petri dish and even out with glass rod. Sodium hydroxide was used to neutralize the pH of the mixture before casting step (if necessary).

Table 1: Formulation of PSP/ESP Bioplastics

Sample	Composition (g/25 mL distilled water)		
	PSP starch	Glycerol	ESP
ESP 0%	2.5	2	0.00
ESP 10%	2.5	2	0.25
ESP 20%	2.5	2	0.50
ESP 30%	2.5	2	0.75
ESP 40%	2.5	2	1.00

Characterization and Testing PSP/ESP Bioplastics

Fourier Transform Infra-Red Attenuated Total Reflectance (FTIR-ATR)

The extracted PSP and ESP were analyzed using Fourier Transform Infrared spectroscopy in Attenuated Total Reflectance mode (FTIR-ATR, model Frontier 100842 Perkin Elmer, UiTM Perlis Branch). The powdered samples were analyzed at range 4000 to 400 cm^{-1} to determine the functional group and to study the effect of various ESP composition in the PSP starch bioplastics.

Tensile Testing

The tensile properties (Tensile Strength (TS), Young's Modulus (YM) and Elongation at Break (EAB)) of PSP/ESP bioplastics were analyzed using Universal Testing Machine (Instron 5567 Tensile Tester Machine, UiTM Perlis Branch) using ASTM D882 method. The films were cut into rectangular strips of 75 mm x 13 mm with triplicate specimens for each PSP/ESP bioplastics. Each of the specimen's thickness was measured using Digital Thickness Gauge and the crosshead speed for the test was programmed to 2.00 mm/min. The specimens were placed in the grips of the Universal Tester and were pulled until failure.

Water Absorption Test

The water absorption test was conducted following standard ASTM D570 method with slight modification to determine the water absorption behavior on PSP/ESP bioplastic. Each of the samples were cut into rectangular shape with dimension of 2 x 2 cm. Then, the samples were dried in oven at 110 ºC until a constant weight was obtained. This weight was recorded as the initial weight for each of the samples. The samples then were immersed in 50 mL distilled water and left at room temperature for 72 h. Every 24 h, the samples were removed from distilled water and wiped before weighed using weighing balance. The final weight for each sample was recorded and the water absorption for each sample were calculated using Eq. (1).

$$Water\ Absorption\ (\%) = \frac{wt - wo}{wo}\ x\ 100\% \qquad (1)$$

Where wt (g) is the weight of the bioplastic at various times and wo (g) is the initial weight of bioplastic before being immersion in distilled water.

RESULT AND DISCUSSION

Fourier Transform Infra-Red (ATR-FTIR) Analysis

The FTIR spectra of the PSP starch and PSP/ESP bioplastics are shown in Figure 1. Based on the Figure 1, four major absorption peaks are produced by all PSP/ESP bioplastics corresponding to O–H stretch, C–H stretch, C=O stretch and C–O stretch. The most evident peak was at wave number around 3200-3600 cm^{-1} indicating the O–H stretching. The peak is broad and relatively weak in case of PSP starch, while it becomes relatively stronger and narrower in case of PSP starch/ESP bioplastics. PSP/ESP bioplastics have a relatively stronger peak around 3200-3600 cm^{-1} compared to PSP starch as shown in Figure 1. This result is in agreement with the various research in their study [12-13]. The hydrogen bonding is relatively high in PSP/ESP bioplastics, which might be due to the incorporation of ESP into the PSP matrix, which is caused by the strong affinity of calcium and hydroxyl groups in ESP to hydroxyl groups of PSP matrix, forming more strong hydrogen bond between the polymer chains, thereby improving the mechanical properties of the bioplastics. The results of similar band position have also been reported by another researchers [13,14]. At wave number between 2900-3000 cm^{-1} the C–H stretching was observed, the peak position was located at 2937 cm^{-1} for PSP starch while it is shifted to 2933 cm^{-1} and 2936 cm^{-1} for PSP/ESP bioplastics as shown in Figure 1. The shifting of this band could be due to the interaction between hydroxyl groups of PSP matrix and O–H group. These findings are consistent with previous research [14]. These results confirm the occurrence of the shift in the C–O–C stretching which implies that hydrogen bond interaction occurs between the starch and calcium molecules in the matrix of bioplastics.

A vibration band at wave number 16547 cm^{-1} is typically associated with water molecules contained in the structure of starch bioplastics [13]. There is no shifting of the peak position of PSP starch, and it is around the peak of PSP/ESP bioplastics which is located at the wave number of 1650-1640 cm^{-1}. There are several peaks in the range 1100-1300 cm^{-1}, which correspond to C–O–C stretching. For PSP starch and PSP/ESP bioplastics, the peaks appear at the wave number of 1018 cm^{-1} and 1008-1022 cm^{-1}, respectively. The wave number at 1008-1022 cm^{-1} is more intense for PSP/ESP bioplastics than that for PSP starch as shown in Figure 1. The shift might indicate an increase in the intensity of the vibration, which results from the formation of intermolecular bonds between functional groups in PSP matrix and hydroxyl groups in ESP biopolymer matrix. Based on this analysis, it can be summarized that the PSP/ESP bioplastic was successfully synthesized based on the existence of the functional groups.

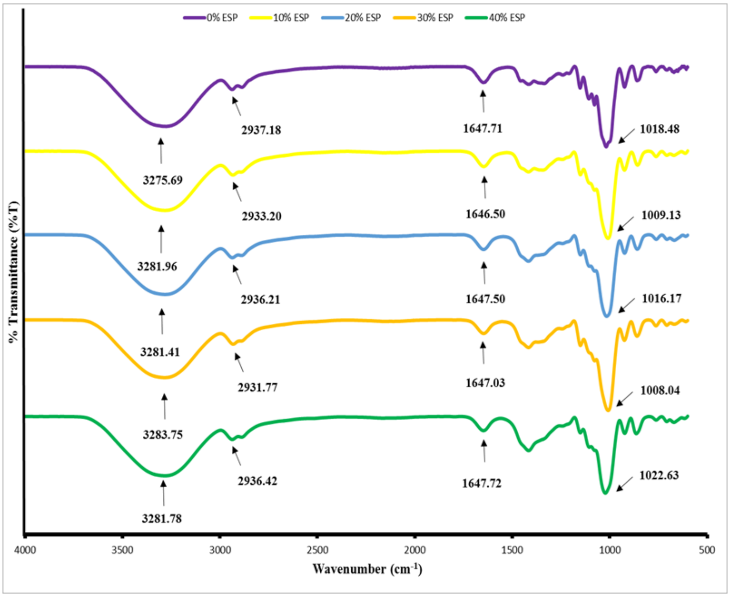

Figure 1: FTIR spectra of PSP/ESP bioplastics

Tensile Test

Figures 2,3 and 4 illustrate the effect of various ESP composition to the mechanical properties (tensile strength (TS), Young's Modulus (YM) and Elongation at Break (EAB)) of PSP bioplastic respectively. Regarding the effect of eggshell powder loadings on the tensile strength of purple sweet potato starch/eggshell bioplastics, Figure 2 exhibited the increasing trend (from 0.3314 MPa to 0.4811 MPa) when the composition of ESP increased from 0 wt.% - 20 wt.% in PSP bioplastic. This might be attributed to the reinforcement provided by the ESP, which acts as a filler material that improves the TS of the PSP bioplastic. Moreover, the existence of hydrogen bonding between the ESP filler and PSP starch matrix, which have been confirmed via FTIR analysis might be contributed to the increasing trend of TS. Furthermore, as the composition of the ESP filler increased in PSP starch matrix, the TS of the bioplastic also increased. Furthermore, the increase in tensile strength may also be due to the presence of minerals such as calcium carbonate in eggshells, which can enhance the mechanical properties of the bioplastic material. Similar trends have been observed in other studies where the addition of eggshell fillers in yam starch bioplastics resulted in increased tensile strength [15]. However, further addition above 20 wt.% of ESP filler reduces its TS due to the presence of porosities and aggregation that occurs in the PSP matrix. Moreover, the existence of porosities and aggregation in starch matrix will lead to the decreasing of interfacial adhesion between the filler and starch matrix [16]. This trend is similar to the previous study that reported that the ESP reduces the TS of the epoxy composites due to the poor adhesion of filler matrix and agglomeration of the ESPs. These possible reasons may lead to a weak ability to transfer stress from the epoxy [17].

In terms of elongation at break (EAB), Figure 3 shows a slight decrease in EAB as the ESP loadings increase. The incorporation of ESP filler into PSP starch matrix led to the decreasing trend of EAB. This decreasing trend can be attributed to the rigid nature of the ESP, which reduces the flexibility of the bioplastic materials. The limitation of ESP filler property will reduce the ability of the bioplastic to elongate before it breaks.

On the other hand, Figure 4 demonstrates that the YM of the PSP/ESP bioplastics increased as the ESP loading increased up to 20 wt.%. This phenomenon indicates that the bioplastics become stiffer and less deformable under applied stress [16]. The incorporation of ESP filler in the PSP matrix increased the YM of bioplastics due to the reinforcement effect provided by the rigid ESP filler particles. However, further addition above 20 wt.% of ESP filler reduces the YM values due to the presence of porosities and aggregation that occurs in the PSP matrix. In summary, the addition of ESP filler can enhance the mechanical properties of PSP starch bioplastics, specifically their tensile strength and Young modulus.

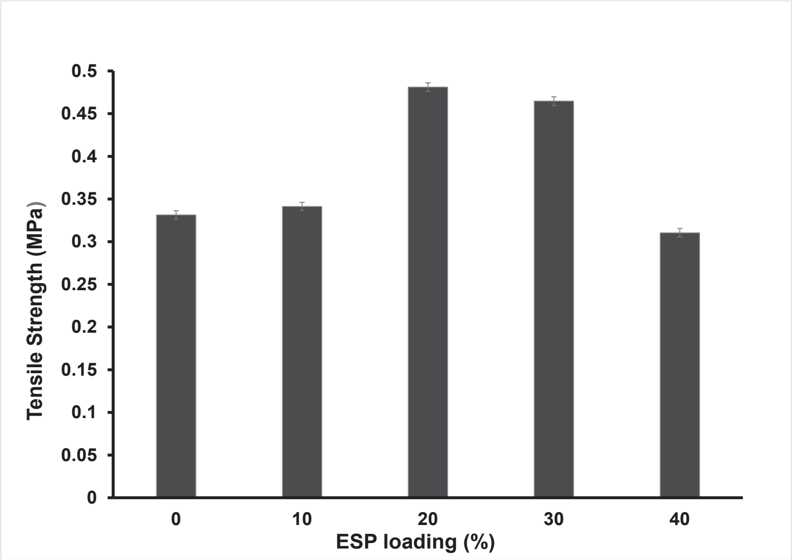

Figure 2: Effect of ESP loadings on the Tensile Strength of PSP bioplastics

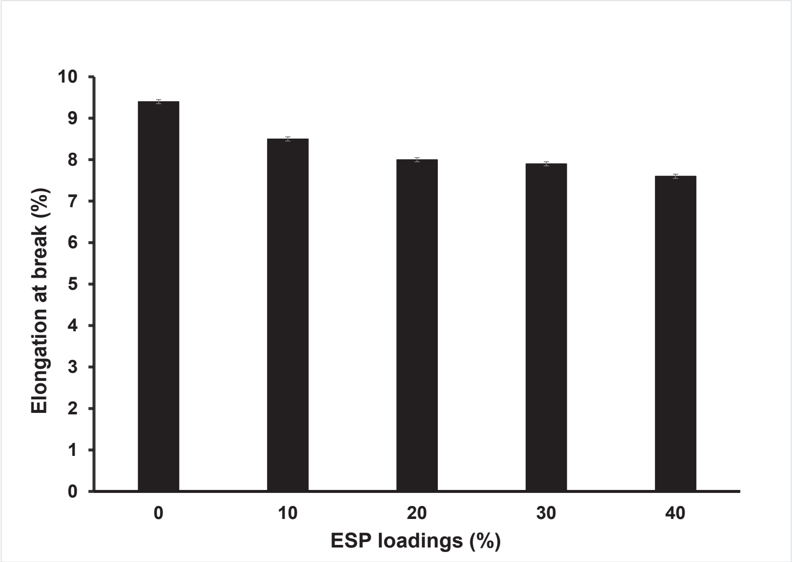

Figure 3: Effect of ESP loadings on the Elongation at Break of PSP bioplastics

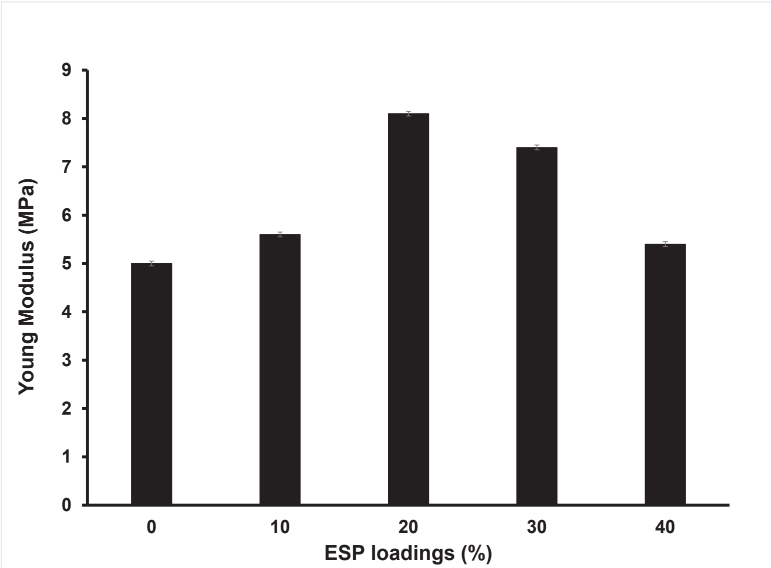

Figure 4: Effect of ESP loadings on the Young's Modulus of PSP bioplastics

Water Absorption Test

Water absorption is an important factor to consider when evaluating the performance of bioplastics. It is crucial to understand how and to what extent bioplastics can absorb water, as this can impact their durability and stability [18]. Figure 5 shows the effect of ESP filler loadings on the percentage of water absorption PSP bioplastics. PSP bioplastic with ESP filler loading (10 wt.%, 20 wt.%, 30 wt.% and 40 wt. %) demonstrated rapid increasing trend until 28 h. However, PSP bioplastic with 0wt% ESP exhibited an increasing trend until 72 h. Moreover, the percentage of water absorption for PSP bioplastic with 0 wt.% ESP increases from 36.36% to 58.82% and 62.16% for the next 40 and 72 h respectively. The increase in water absorption percentage is due to PSP starch matrix, which is highly hydrophilic. The hydroxyl group in PSP strach matrix will interact with water, formed hydrogen bond and increased the films' ability to absorb water [19]. However, the water absorption capacity significantly decreases as the percentage of ESP increases (from 10 wt.% - 40 wt. %). This observation can be attributed to the hydrophobic nature of ESP filler in PSP starch matrix, which limits the ability of water to penetrate and be absorbed by the bioplastic material. ESP filler, which primarily consists of calcium carbonate ($CaCO_3$), may create a barrier that hinders water from being absorbed into the bioplastic material. This result is in agreement with the previous study which concluded that the decreasing trend of water absorption percentage as the ESP filler loading increased in thermoplastic starch-based film [20].

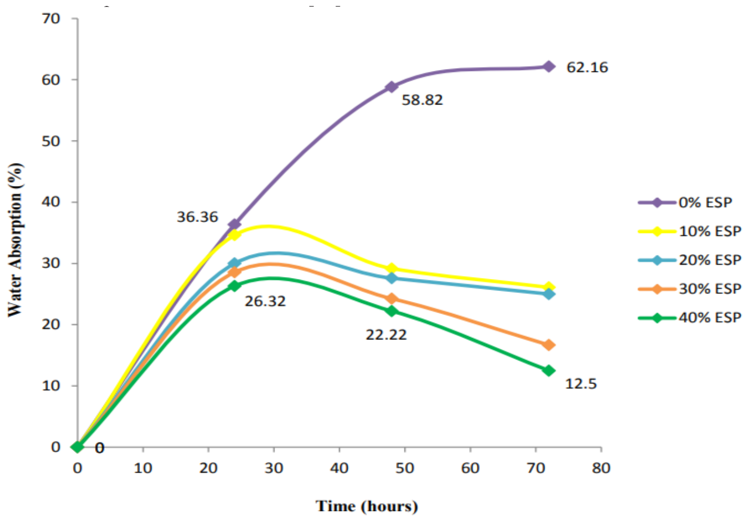

Figure 5: Water Absorption (%) versus Time (hours) of PSP starch bioplastics

CONCLUSION

In this research, PSP/ESP bioplastics were successfully fabricated with various compositions of ESP filler (0 wt.%, 10 wt.%, 20 wt.%, 30 wt.% and 40 wt.%) composition using solution casting method. From FTIR analysis, this bioplastic is successfully fabricated due to the existence of the four functional groups which are O–H stretch, C–H stretch, C=O stretch and C–O stretch. The most evident peak was at wave numbers around 3200-3600 cm^{-1} indicating the O–H stretching. The peak is broad and relatively weak in the case of PSP starch, while it becomes relatively stronger and narrower in case of PSP starch/ESP bioplastics due to existence of hydrogen bonding. As conclusion, the additions of ESP filler into PSP starch matrix are able to increase the tensile strength of the resulting bioplastic from 0.3314 MPa to 0.4811 MPa as the composition of ESP increased from 0 wt.% - 20 wt.%. However, further addition above 20 wt.% of ESP filler reduces its TS due to the presence of porosities and aggregation that occurs in the PSP matrix. YM of the PSP/ESP bioplastics increased as the ESP loading increased up to 20 wt.%, while the incorporation of ESP filler into PSP starch matrix led to the decreasing trend of EAB. From the water absorption test, the water absorption capacity significantly decreases as the percentage of ESP increases due to hydrophobic characteristic of ESP filler. From all the result obtained, PSP/ESP bioplastic may have potential applications in food packaging, medical or pharmaceutical industries as this bioplastic can be used as alternatives for synthetic plastic to cope with waste generation and disposal problem.

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