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An investigation into the morphology, thermal properties and photodegradation of cassava residue-fatty acid complex

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Abstract
The environmental problem of packaging usage has traditionally been solved through the use of incineration and landfills. However, these solutions cause an increase in pollution, which greatly impact global warming as a consequence. In this research, natural materials were applied, including cassava residue as the main material. The primary advantages of cassava residue comprise its classification as a renewable resource and its abundancy. However, a drawback of cassava residue is its ability to dramatically absorb water. Cassava residue can be enhanced by fatty acids along with a coupling agent in order to increase the efficiency of its mechanical and water-resistant properties. Besides the incorporation of antioxidants to enable protection in electronic device packaging, it causes damage to packaging properties and protects electronic devices. The results of experimentation exhibited that the modification of cassava residue with lauric acid and stearic acid led to the increase of water resistance. The addition of polymethyl methacrylate, a compatibiliser, led to increments of smooth surfaces in samples that were modified by fatty acid. Further, the tensile strength and compressive strength of modified samples were better than those of unmodified samples. The best properties were obtained with a S80AL20C2. In addition, the morphology, thermal properties, and photodegradation of samples modified with long-chain fatty acids were investigated. The incorporation of ZG-262 Eastmantenox ^{TM}, antioxidant, in cassava-residue-fatty acid complex led to an increase in the degradation temperature at 50 wt% loss, temperature of first-stage degradation, temperature of second-stage degradation, and remained weight at a temperature of 650 ^{o}C.

Keywords: *Cassava residue, Fatty acid, Morphology, Thermal properties, Photodegradation.*

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I. INTRODUCTION

Due to environmental problems and environmental awareness, attention on the utilisation of biodegradable and renewable resources has increased significantly [1, 2]. One interesting candidate that meets the criteria of being biodegradable and renewable is starch-based material. Because of their processing properties, the compatibility of the material, and other thermal and mechanical properties, starch-based materials have been considered a potential substance that could replace fossil-based materials. Starch is a natural biopolymer candidate to replace synthetic polymers and is one of the promising renewables being researched [3]. The disadvantages of using starch in applications are its poor mechanical properties and water sensitivity. Attempts have been made to improve the mechanical properties of starch-based biodegradable materials by using various methods [4]. To reduce the hygroscopicity of cassava residue, the addition of fatty acid has been considered, which exhibits good hydrophobic properties in starch-based biodegradable materials containing cassava residue. The use of cassava residue, agricultural waste (agro-waste), in the production of bioplastic represents an exciting new challenge [5, 6]. There are various agricultural waste products which have the potential to be employed as bioplastics, such as bagasse, cellulose, sago, corn cob, and chitin. Because it is less expensive and easily available, the use of agro-waste as a source for the production of biodegradable plastics is expected to increase. Biodegradable materials obtained from cassava residue (renewable resource) have a large amount of starch and fibre. This has led to increased attention towards combining the environmental and functional benefits [7]. A few years ago, the current group studied the mechanical properties and surface characteristics of blends between thermoplastic starch containing tapioca residue and fibre [6]. Based on a similar approach, the present study deals with an investigation into the morphology, thermal properties, and photodegradation of cassava residue-fatty acid complex produced via fatty acid addition. The aging resistance of these materials, especially to ultraviolet (UV) light, is relevant for outdoor applications since degradation usually shortens their shelf-life [8]. The photodegradation of cassava residue-fatty acid complex is caused by the absorption of photons, particularly at those wavelengths found in sunlight.

While photodegradation is the alteration of materials by light, resulting from the action of sunlight and air, it also includes the change of a molecule's shape to make it irreversibly altered because a common photodegradation reaction is oxidation.

Among biopolymers, thermoplastic starch containing cassava residue modified by fatty acids is one biopolymer candidate being considered to obtain polymer products due to its natural origin, processability, and natural origin. Meanwhile, exposure to ultraviolet (UV) radiation causes significant degradation of starch-based material containing cassava residue modified by fatty acids, inducing photooxidative reaction, resulting in the breaking of polymer chains [8, 9, 10]. There is also the production of free radicals and the reduction of molar mass, which lead to the deterioration of biopolymer mechanical properties. In this research work, changes were induced in biopolymer by using UV radiation. Analysis of the temperature of first-stage degradation, temperature of second-stage degradation, degradation temperature at 50 wt% loss and remained weight at a temperature of 650 ºC was carried out.

Some of the cassava residue-fatty acid complex obtained in this research work was incorporated with antioxidants in the matrix to increase the degradation behaviour of the polymer matrix, as reported in composites with micrometric starch. While antioxidants are widely known as an additive for commercial polymer materials to prevent their degradation, there is increasing interest in enhancing the antioxidant functionality of newly-developed polymer materials [11].

II. MATERIALS AND PREPARATION

2.1 Materials

Cassava residue was obtained from RT Agritech Co., Ltd. It was dried at 60 ºC for about 24 h to remove absorbed moisture; long-chain fatty acid, stearic acid (C18:0) were employed as the reagent. ZG-262 Eastman Tenox™ was purchased from Eastman Chemical Company for use as a reagent. In addition, poly (methyl methacrylate) was obtained from Sahachoke Intertrade Co., Ltd for use as a compatibiliser. Both glycerol and hydrogen peroxide, 35 wt% in water, were purchased from Siam Absolute Chemicals Co., Ltd and QRëC™ Company, respectively, for use in analysis.

2.2 Preparation of biodegradable materials of cassava residue-fatty acid complex produced via fatty acid addition

Firstly, the cassava residue was dried, crushed and sieved (through a 40-mesh sieve). The water content in cassava residue was removed by heating in an oven at 60 ºC for 24 hours before usage. Before blending with fatty acids, the cassava residue was mixed with glycerol for 2 hours. After that, the modification of cassava residue with fatty acids such as lauric acid and stearic acid was carried out using hydrogen peroxide as an initiator. Polymethyl methacrylate (PMMA) was employed as a compatibiliser to improve the compatibility in blends by reactive methods. All ingredients were incorporated using a twin-screw extruder with a screw rotation speed of 60 rpm after blending all ingredients with a magnetic stirrer at 40 ºC for 2 hours. The temperatures used in this extrusion ranged from 120 to 140 ºC. The specimens were fabricated into shape by using compression moulding after drying at 60 ºC for 24 hours. The conditions for sample production from the compression moulding process comprised a mild temperature of 150 ºC and mild pressure of 120 bar with a curing time of 10 min. The sample names and compositions are given in Table 1.

Table 1: Sample name and composition of cassava residue-fatty acid complex containing antioxidant property

Sample name	Cassava residue (%wt)	Long-chain fatty acid (%wt)	Glycerol (phr)	Compatibilizer (phr)	Antioxidant (phr)
S80AL20C2	80	20	30	2.0	-
S80AL20C2O5	80	20	30	2.0	0.5
S80AL20C2O10	80	20	30	2.0	1.0
S80AL20C2O25	80	20	30	2.0	2.5
S80AL20C2O50	80	20	30	2.0	5.0

2.3 Sample characterization

Thermogravimetric analysis (TGA) was employed to precisely determine the mass degradation and the degradation temperature of the samples. The samples were loaded into a platinum crucible followed by heating at a temperature range between 25 and 800 ºC at a rate of 20 ºC/min under nitrogen conditions. Nitrogen was employed as a purge gas at a specific gas flow rate.

The photodegradation process was performed by exposing the samples to 336 h UV radiation in a weathering test chamber at a wavelength of 340 nm. The controlled temperature was set at 50 ºC. Descriptions of the characterisation analysis performed before and after exposure to photodegradation for 7 and 14 days were exhibited. Both the weight change and properties of samples were investigated before and after exposure to photodegradation for 7 and 14 days.

This study was performed by using scanning electron microscopy (SEM). Surface imaging, wherein the surface of a sample is scanned with an electron beam and secondary and/or backscattered electrons emitted from the sample surface, was investigated by using this complex method. Firstly, each sample was processed by drying before usage at 60 ºC for 8 hours. The samples were placed into liquid nitrogen and then cut to obtain cross-sectional images. Palladium coated samples operated in vacuum mode were obtained and subsequently mounted on stubs.

III. RESULTS AND DISCUSSION

Starch modified with long-chain fatty acids has an important role in the increase of water resistance. Numerous experiments have been conducted using fatty acids and starch to obtain cassava starch at a certain temperature [12]**.** A schematic representation of the reaction of fatty acids with starch to obtain cassava starch is provided in Fig. 1.

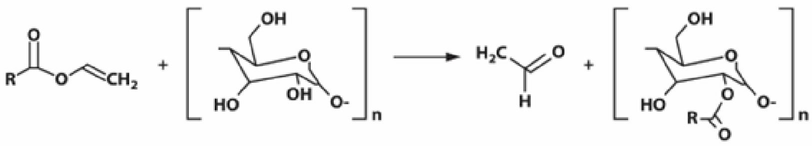

Figure 1: Reaction mechanism between fatty acids and starch obtaining in cassava starch

The process led to the occurrence of ester linkage, whereas Fig. 1 exhibited the reaction mechanism between fatty acids and starch obtaining cassava starch.

3.1 Photodegradation of cassava residue-fatty acid complex produced via fatty acid addition

The effect of photodegradation on the biodegradation of cassava residue-fatty acid complex is shown in Table 2 and Fig. 2. Photodegradation is the degradation of a photodegradable molecule. As a result, the absorption of photons, particularly in those wavelengths found in sunlight, such as infrared radiation, visible light, and ultraviolet light is exhibited. Photodegradation occurs when UV or Vis radiation breaks down the chemical bonds in polymer, then colour changes and loss of physical properties occur so there is the exposure of sunlight and some artificial light. This leads to an adverse effect on the useful life of polymer products.

The effect of antioxidants on the photodegradation process and thermal properties was characterised by the measuring of the degradation temperature at 50 wt% loss (ºC) and remained weight at a temperature of 650 ºC.

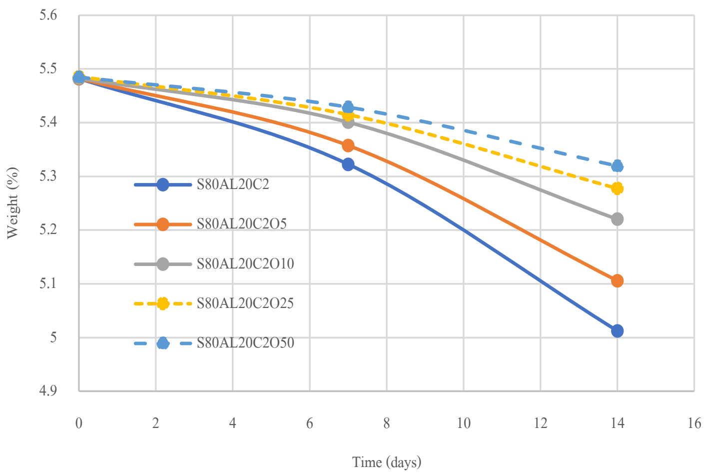

Figure 2: Effect of photodegradation on the biodegradation of cassava residue-fatty acid complex (S80AL20C2) containing various antioxidant content

In this research, the changes induced on cassava residue-fatty acid complex by UV radiation and analysis of the weight of samples were investigated. These results exhibited that the reduction of the weight of samples S80AL20C2, S80AL20C2O5, S80AL20C2O10, S80AL20C2O25, S80AL20C2O50 in order to enable exposure to ultraviolet (UV) radiation causes vital degradation of cassava residue-fatty acid complex, inducing a photo-oxidation reaction. This reaction occurs as a result of the breaking of polymer chains, production of free radicals, and reduction of molar mass. This leads to a decrease in the properties of cassava residue-fatty acid complex. These experimental works are seen to correspond with the results from previous experiments [8].

3.2 Thermal properties of cassava residue-fatty acid complex produced via fatty acid addition

The change in the thermal properties of cassava residue-fatty acid complex containing antioxidant property are exhibited in Table 3 as well as Fig. 3 and 4. It was possible to observe significant differences in the thermal properties of cassava residue-fatty acid complex before and after the incorporation of antioxidants. The results of the experiment showed that there was incremental change in temperature during first-stage degradation, during second-stage degradation, and degradation temperature at 50 wt% loss, as well as remained weight at a temperature of 650 ºC with the addition of antioxidants in cassava residue-fatty acid complex. In addition, the temperature for first-stage degradation, temperature for second-stage degradation, degradation temperature at 50 wt% loss, and remained weight at a temperature of 650 ºC in a sample containing antioxidant were higher than in the sample without antioxidants; in order to use the antioxidants for incorporation, these samples were added to prevent their degradation when exposed to ultraviolet radiation, which can cause the remarkable degradation of starch-based material containing cassava residue modified by fatty acids.

Table 2: Thermal properties of cassava residue-fatty acid complex containing antioxidant property

Sample name	Temperature of fist stage degradation (ºC)	Temperature of second stage degradation (ºC)	Degradation temperature at 50 wt% loss (ºC)	Remained Weight at a temperature of 650 ºC (wt%)
S80AL20C2	249.21	359.77	241.49	24.17
S80AL20C2O5	249.42	360.84	242.65	25.90
S80AL20C2O10	250.15	367.92	248.32	30.54
S80AL20C2O25	250.37	369.47	252.92	35.71
S80AL20C2O50	250.58	373.54	256.04	39.26

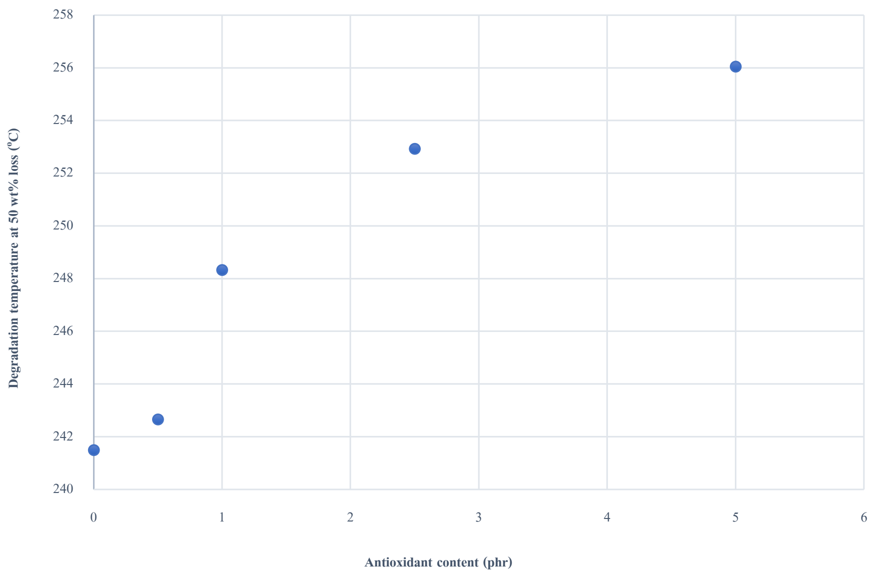

Figure 3: Degradation temperature at 50 wt% loss of cassava residue-fatty acid complex (S80AL20C2) containing various antioxidant contents

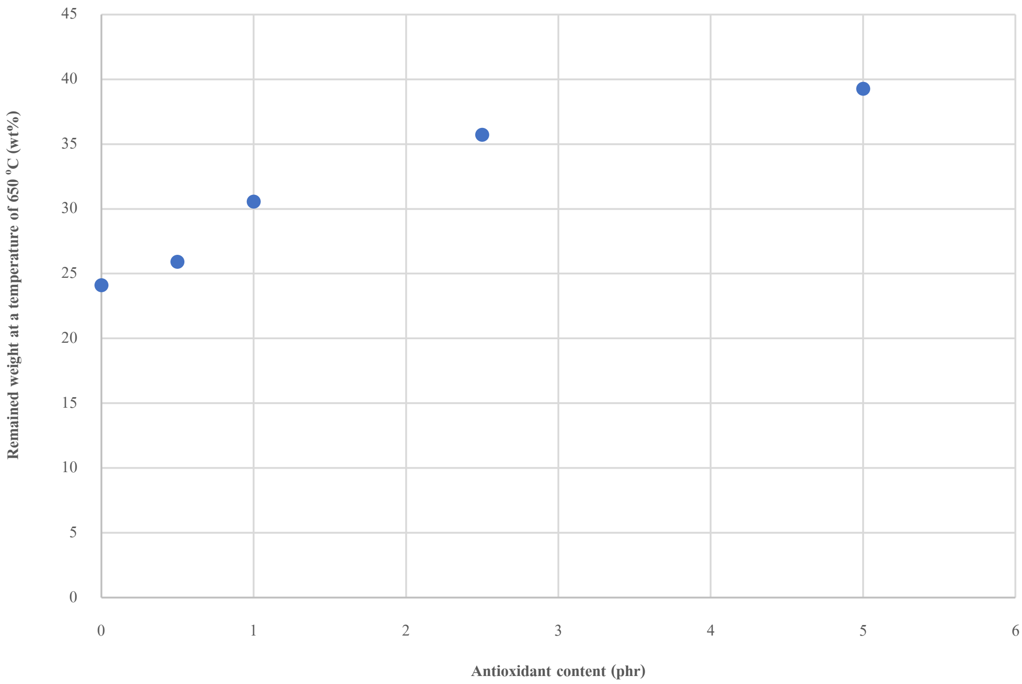

Figure 4: Remained weight at a temperature of 650 ºC (wt%) of cassava residue-fatty acid complex (S80AL20C2) containing various antioxidant contents

3.3 Scanning electron microscopy of cassava residue-fatty acid complex produced via fatty acid addition

As revealed by the cross-sectional and surface morphology of samples, as shown in Fig. 5 and 6, respectively, the SEM technique can only be employed for the evaluation of surface morphology including the homogeneity and roughness of dispersion of nanomaterials in the matrix.

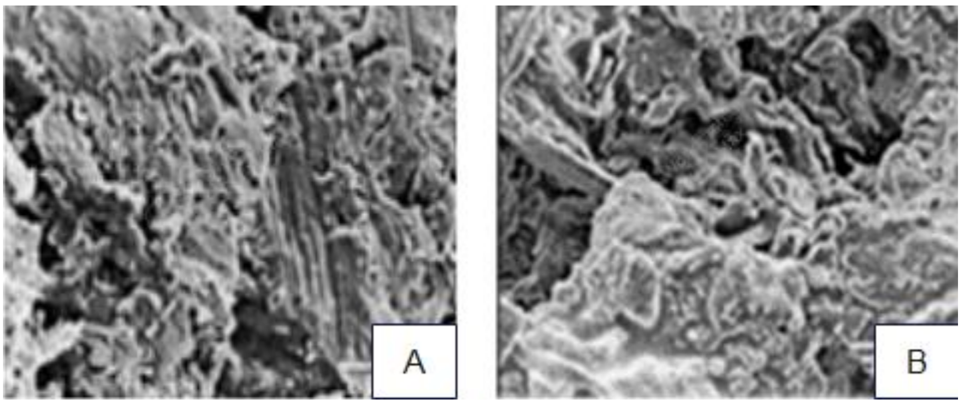

Figure 5: Cross-sectional SEM image of S90AL10C2 (A) and S80AL20C2 (B) obtained at x 350 magnifications

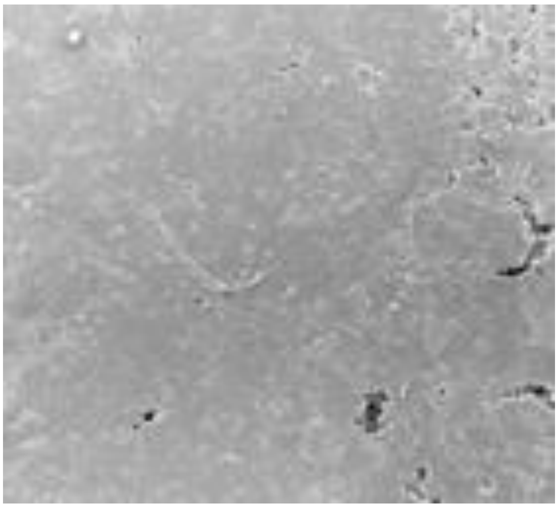

Figure 6: SEM image of surface morphology of S80AL20C2 obtained at x 350 magnifications

The experimental results showed the difference in the morphological characteristics of biodegradable materials in cassava residue and fatty acids when the materials contained different amounts of fatty acid content. Fig. 5 exhibits the presence of black holes on the both of cross-sectional SEM images taken at 350x. The black zone appeared to exhibit little fragmentation. The presence of fatty acid deposits was observed surrounding the granules. This phenomenon plays a vital role in the thermal and structural properties of the starch-lipid mixture. Both S90AL10C2 and S80AL20C2 revealed the same effect in terms of losing the initial semi-spherical shape of starch granules. Fig. 5 illustrates a comparison between SEM images of S90AL10C2 and S80AL20C2. The S90AL10C2 is the sample that has the composition of cassava residue (90 wt%), glycerol (30 phr), fatty acid (10 wt%), compatibiliser (2 phr). It is apparent that S80AL20C2 has higher fatty acid content than that of S90AL10C2. This led to a difference in SEM images, as shown in Fig. 5. Furthermore, scanning electronic microscopy indicated that the surface of the films became smooth after the addition of fatty acids. This led to the higher surface energy of samples because of the reaction. Smoother surfaces were obtained with more homogeneity.

IV. CONCLUSION

Regarding the decreasing of environmental problems, the usage of biodegradable materials is a significant topic of interest. Further, materials consisting cassava residue are garnering attention as an interesting material. However, a disadvantage of this material is its water absorption; potential improvement involves using fatty acids as another composition. The results of this investigation showed that the addition of fatty acids in cassava residue can enable the reduction of hygroscopicity in cassava residue. In addition, the effect of photodegradation on the biodegradation of cassava residue-fatty acid complex was investigated. The results of experimentation showed changes in the sample weight with various times (0 day, 7 days, 14 days) due to exposure to ultraviolet (UV) radiation potentially causing the significant degradation of many materials. UV radiation causes photooxidative degradation, resulting in the breaking of the polymer chains. This leads to the production of free radicals as well as the reduction of molecular weight, whereas the addition of ZG-262 Eastmantenox ™, an antioxidant in cassava-residue-fatty acid complex, leads to an increase in the degradation temperature at 50 wt% loss, temperature of first-stage degradation, temperature of second-stage degradation, and remained weight at a temperature of 650 ºC. In addition, the cross-sectional and surface morphology of samples was investigated by using the SEM technique.

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