Morphological Properties of Cassava Film 
Influence by Plasticizers in Zinc-air Fuel Cell

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Abstract  The effect of plasticizers, glycerol, sorbitol, and sucrose on structural, mechanical, and chemical properties of cassava starch film has been investigated. The morphologies of cassava films were studied by the addition of a different type of plasticizer. Mixtures of cassava starch and distilled water with the combination of glycerol, sorbitol, sucrose as plasticizers. Dried films plasticized showed the results under a scanning electron microscope (SEM) as smooth film surfaces were observed in a mixture of glycerol, sorbitol, and sucrose because glycerol and sucrose are more hydrophilic than sorbitol, thus the presence of more hydroxyl groups (-OH groups) in the molecule, sorbitol interacted with water by hydrogen bonding resulting in less plasticizing effect compared to glycerol and sucrose. As a result, the presence of sorbitol as a plasticizer with glycerol and sucrose in cassava starch films provided a more compact and homogenous surface, improves the stability and flexibility of cassava starch films.

1. Introduction
Over the past century, biomass and petroleum have emerged as powerful platforms for fuel sources. In recent study suggested that the rising demand for fuel lead to the increasing of oil prices in global economic growth due to the high demand for energy suppliers, especially in transportations. The issue of the increase in air pollutions emits carbon monoxide and carbon monoxide as its by-products have received considerable critical attention and became a shock throughout the world.

Therefore, to overcome these problems, there has been renewed interest in technologies in which the development of fuel cell was created recorded as eco-friendly compared to the biomass because they produce only water and heat as their by-products. Fuel cells are promising as a new potential candidate for an alternating current generator due to their low gas emission [1]. There has been growing interest in the use of zinc-air Fuel Cell (ZAFC) due it can be the best candidate for alternative energy generator because it is environmentally safe and does not use the high cost of a catalyst which is platinum (Pt) made it became more comfortable and affordable to use [2].

Discovery set out to investigate the usefulness of starch thin film on the fuel cell. This is due to starch is known as a completely biodegradable polymer in soil and water. It also has two molecular components which are identified as amylose and amylopectin with the linear component of α(1→4) bound glucose molecules and important for energy storage, water binder, emulsion stabilizer, and gelling agent [3].

Therefore, in this study, cassava starch thin film is applying to Zn-air fuel cell to identify the capability of ZAFC when the cassava thin-film applying to it [4]. The cassava thin film acts as a separator to allow the proton to easily passed through from Zn-anode to the cathode. This is because cassava thin film is highly ionic conductivity but electrically non-conductive, which enables high ions movement capability and chemical stability [5].
2. Methodology
2.1 Materials.
Cassava starch purchased from Thye Huat Chan Sdn. Bhd. (Malaysia) as a raw material in the preparation of cassava films. Glycerol, D-Sorbitol (analytic reagent with 97% purity), Sucrose were used as plasticizers, and trioctylammonium chloride (Aliquat 336) as plasticizer and ion carrier. Indeed, the water used in this experiment was free from ionic impurities.

2.2 Preparation of Cassava Starch Film.
The cassava film was prepared to utilize a related technique to that described [6]. Cassava starch powder (5 g) was dissolved with a mixture of glycerol, sorbitol, sucrose with the ratio of 1:1:1 and distilled water to completed 100 g of solution. The homogenous solution was stirred for 30 minutes until entirely gelatinized. After vigorous stirring, Aliquat 336 (0.5 %, 1.0 % w/w) was added and the solution was continuously stirred for an additional 30 minutes. The mixed solution was permitted to gradually evaporated in acrylic sheet mold (9.0 cm³) and dried in the oven at 35 °C for 16 hours. The film thickness was cut and measured by digital Vernier caliper with 0.01 mm standard deviation over five times readings.

3. Results and Discussion
3.1 Visualization of cassava films.
Figure 1 shows a transparency visualize of cassava films with and without plasticizers. The images promoted that all films have the same visualization when observed by naked eyes.

Figure 1. Pure cassava film.

Figure 2a displays the cassava film with plasticizers and cassava film with the addition of aliquot 336 as shown in Figure 2b. It showed the smoother surface of films when adding plasticizers which are sucrose, glycerol, sorbitol, and various concentration of aliquot (0.5 wt%, 1.0 wt%, 1.5 wt%) provided smoother surfaces of cassava films with plasticizers due to less amount of bubbles observed. It is associated with the transparency of films depends on the sizes of a dispersed particle in the starch matrix and revealed by the thickness of films for the period of film preparation [7]. The larger particle sizes observed gave to higher translucent of films. Besides, it is the significance of film thickness that led films to be visible to light.
3.2 Morphological Identification.

Figures 3 shows the SEM micrographs of cassava films without plasticized with the magnification of 500 µm. Films were dried before continuing to the SEM observation. Pure cassava films promoted rough, structured, and porous surface morphology. Cassava films with pure cassava starch behave with higher hydrophilic nature due to hydroxyl groups (-OH bonds) results as the film is fragile compared to films with plasticizers added [7].

Figure 3. SEM micrographs of pure cassava films.

Meanwhile, Figure 4 exhibits the SEM micrographs after the addition of plasticizers which are sucrose, glycerol, and sorbitol that has a different amount of hydroxyl groups gives the smoother surface of cassava films. This is because each hydroxyl group can easily penetrate the bonding in starch due to different amount of –OH bonds in sucrose (contains 8 –OH bonds), glycerol (contains 3 –OH bonds), and sorbitol (contains 6 –OH bonds) promoted a great combination of plasticizers added in films [8-9].

This is due to the higher molecular weight of sorbitol (182 g mol⁻¹) compared to glycerol (92 g mol⁻¹) limiting chain mobility and resulted in films became stiffer [10]. It same goes for the molecular weight of sucrose (342.29 g mol⁻¹) is higher than sucrose and glycerol provided the reduction of hydrophilic behavior of cassava films. Therefore, the addition of many plasticizers results in a smooth morphology surface and has higher stiffness.
Figure 4. SEM images of (a) cassava film plasticized with sucrose, glycerol, sorbitol, (b) cassava film with 0.5 % w/w aliquat and (c) cassava films with 1.0 % w/w Aliquat.

However, films with aliquat 336 (0.5 %, 1.0 % w/w) added represented the smooth surfaces with bubble-like structure lead to an emulsion of aliquat and other plasticizers (sucrose, glycerol, sorbitol) due to the hydrophobicity nature of aliquat and hydrophilicity behaviors of others (Fig 2c & 2d) [11]. Therefore, the attraction bonding between hydroxyl (-OH) groups and amides (-NH) groups is less compatible indicate to non-smooth morphological surfaces compared to films without aliquat (Fig 2a). This is due to the ionic strength presents in aliquat is stable in small amount droplet size which is below 0.5 to stabilize the oil-water bonding in the form of stable emulsions must be 0.5 and below [12]. In addition to the droplet size changes, starch increase to the oil ratio also leads to the distribution of narrower droplet sizes.
4. Conclusion
As a result, dried films plasticized showed the results under SEM as smooth film surfaces were observed in a mixture of glycerol, sorbitol, and sucrose because glycerol is more hydrophilic than sorbitol because of molecular weight of sorbitol (182 g mol\(^{-1}\)) is higher compared to glycerol (92 g mol\(^{-1}\)), meanwhile sucrose (342.29 g mol\(^{-1}\)) higher than both led to restraining the movement of the chain. Films with aliquat 336 (0.5 %, 1.0 % w/w) found as smooth surfaces with bubble-like structure, leading to oil-water ratio must be 0.5 below to stabilize the emulsion form and results as smoother morphological surfaces of cassava films.

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