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The Mechanical and Water Barrier Properties of Cassava Starch/Citric Acid Incorporated with Palm Oil

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Starch-based bioplastic is susceptible to degradation due to water absorption. The addition of citric acid and palm oil may improve the mechanical and water permeability of bioplastic films produced with cassava starch. In this study, four bioplastic films were prepared with different concentrations of citric acid (5% and 10% w/w) and palm oil (2% and 4% w/w) using the solution casting method and glycerol as the plasticizer. To determine the influence of citric acid and palm oil on the films, physical (i.e., thickness, tensile strength, elongation at break, moisture absorption, moisture content, water vapor permeability, and water contact angle) and chemical analyses (i.e., thermogravimetric analysis, differential scanning calorimetry, and Fourier transform infrared spectroscopy) were measured. Bioplastic film containing 5% citric acid and 2% palm oil (Sample E) has the highest tensile strength (1.60 MPa) and the lowest water vapor permeability (1.16±0.02% w/w). The analyses of differential scanning calorimetry and Fourier transform infrared spectroscopy have confirmed that the enhanced mechanical properties were due to the formation of crosslinks. Moreover, crosslinks may have increased the bulkiness and the water contact angle. The addition of palm oil further increased the water contact angle to enhance the resistance of cassava starch film against moisture absorption and water vapor permeability.

Keywords: Bioplastic; cassava starch; citric acid; palm oil

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Packaging film is vital for food hygiene, particularly in minimizing exposure of perishable foodstuff to moisture and microbes. Most of the packaging films are produced from non-biodegradable polymers such as polyethylene or polypropylene. Widespread use of these materials has caused disposal problems and is currently the major source of marine microplastic pollution. A natural polymer such as starch can be used to produce biodegradable packaging film. Cassava starch is a suitable material to produce packaging material. However, due to its abundance of hydroxyl groups, starch is naturally hydrophilic and attracts water molecules, forming a gel mass and losing its mechanical strength [1]. Chemical modification with a natural organic acid that possesses multiple binding sites can form linkages and enhance the properties of the starch film [2]. The addition of citric acid may react with hydroxyl groups to form crosslinks to improve starch stability and reduce water vapor permeability [3]. Citric acid can strengthen the intermolecular bonding of hydrogen bonds by introducing covalent bonds through crosslinks, causing low water vapor uptake and strengthening tensile properties [4].

Palm oil is widely available and is a cheap source of lipids in Malaysia. Furthermore, the addition of lipids such as palm oils may further enhance the hydrophobicity of the starch film. Lipid repels water and is an efficient barrier to water vapor [5]. According to [6], an improved chitosan film with good water vapor barrier properties will be acquired when lipid is present. In fact, the addition of citric acid alone can reduce water vapor permeability [7]. Both palm oil and citric acid can be used simultaneously with cassava starch to produce a film with enhanced mechanical properties and resistance to high moisture conditions. With the addition of palm oil to the crosslinked starch film, the diffusivity coefficient of water vapor decreased and the flow of water vapor into the film can be reduced.

The concentration of both polysaccharides and lipids is very important in film formulation because it can affect the performance of the film. The water vapor easily penetrates the film at a low content of palm oil. However, excessive palm oil may produce an oily surface, inelastic and brittle starch film.

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According to [8], the addition of palm oil can lower the tensile strength of the starch-based film. To the best of our knowledge, the properties of starch-based films incorporated with both citric acid and palm oil have never been reported. This study investigates the effects of various contents of palm oil and citric acid on the mechanical properties and water vapor permeability of the cassava starch-based film. Thermal and spectroscopic techniques were used to elucidate the reaction mechanism of the resulting films. A water contact angle was conducted to study the hydrophobicity of the film.

EXPERIMENTAL

Chemicals and Materials

Cassava starch (Kapal ABC brand) was prepared according to Table 1 using the procedures reported by [9]. A solution was prepared by mixing 10 g of cassava starch (20% amylose and 75% amylopectin) with 3 mL glycerol (Friend/Schmidt; 99% AR grade) in 150 mL of distilled water for 5 min. The starch solution was heated at 60ºC and stirred continuously with a hot plate (IKA, Germany) for 30 min. To prepare the crosslinked starch solution, various concentration of citric acid (Systerm; 5% and 10% of starch dry weight basis) and palm oil (Buruh brand) was added to the starch solution along with 1 mL of Tween 80 (Merck). Then, 20 mL of the solution was poured onto a Petri dish. The solution was dried in an oven (Memmet, Germany) at 40ºC. Finally, the dried film was peeled off and stored in a desiccator with silica gel 60 (Merck; 0.063-0.200 mm).

Characterization Methods

The thickness of the film was examined by using a digital micrometer (Digimatic Micrometre 293-340, Mitutoyo Corp, Japan). The sensitivity of the film was set to 0.001 mm. The thickness of each dried film was measured at three distinct positions: the top, middle, and bottom of the film. Tensile strength (TS) and elongation at break (EAB) of the film were determined according to ASTM D638-14 [10] using a tensile tester testometric (Testometric Co. Ltd., United Kingdom). The dried film was cut to a uniform size (7 cm x 1 cm). The initial grip separation was set to 40 mm, while the crosshead speed was set at 5 mm/min. Tensile strength tests were replicated twice on each variation of the bioplastic composition at 23±2 °C and 50±5% relative humidity. The tensile strength (TS) was calculated with Eq (1):

$$\mathrm{TS} = \frac{Fmax}{A} \qquad \text{Eq (1)}$$

where $Fmax$ is the maximum force (N), and A is the area of the film (mm^2). The elongation at break (EAB) was calculated with Eq (2):

$$\mathrm{EAB}\ (\%) = \frac{X}{Xi} \times 100 \qquad \text{Eq (2)}$$

where X is the increased length of the film after breakage (mm), and Xi is the initial length of the film (mm). The moisture absorption (MA) was determined with ASTM D570 [11]. The dried film was placed into a desiccator containing silica gels after the initial weight (Wi) was recorded. The film was kept at 25ºC for five days. After that, the final weight (Wf) was weighed, and the MA was calculated with Eq (3):

$$\mathrm{MA}\ (\%) = \frac{Wf-Wi}{Wi} \times 100 \qquad \text{Eq (3)}$$

where Wf is the final weight of the dried film (g), and Wi is the initial weight of the dried film (g).

Each film was cut into a similar dimension (2 cm x 2 cm diameter), weighed, and oven-dried at 100ºC for 24 hours. After that, the cut films were re-weighed. The moisture loss was calculated by differences between the final and initial weight of the cut films. The moisture content (MC) was calculated with Eq (4):

$$\mathrm{MC}\ (\%) = \frac{Wi-Wf}{Wi} \times 100 \qquad \text{Eq (4)}$$

where Wf is the final weight of the cut film (g), and Wi is the initial weight of the cut film (g). The water vapor permeability (WVP) of the film was determined with a modified gravimetric cup technique according to ASTM E96-92 [12]. The dried film was cut into a round shape to cover the top of the vials. The vials were containing 10 mL of silica gels. The initial weight of sealed vials was weighed. Then, the sealed vials were placed in a desiccator that contained a beaker of water. The sealed vials were re-weighed for seven days. The weight uptake by the sealed vials was the water vapor passed through the cups to the films. The WVP of the film was calculated as follows:

$$\mathrm{WVP}\ (\%) = \frac{Wi-Wf}{Wi} \times 100 \qquad \text{Eq (5)}$$

Table 1. Composition of cassava starch, glycerol, citric acid, and palm oil in film samples (A-E).

Formulation/Sample	Cassava starch (g)	Glycerol (ml)	Citric acid (%)	Palm oil (%)
A	10	3	-	-
B	10	3	10	4
C	10	3	10	2
D	10	3	5	4
E	10	3	5	2

where *Wf* is the final weight of the cut film (g), and *Wi* is the initial weight of the cut film (g). For thermogravimetric analysis (TGA), 7 - 10 mg of the film sample was heated from 50 to 700ºC by TG analyzer (Perkin Elmer, Pyris 1, USA) at a rate of 10ºC/min in the nitrogen atmosphere to characterize degradation temperature and thermal stability. For the differential scanning calorimetry (DSC) analysis, 7 - 10 mg of the film sample were weighed and encapsulated in aluminium pans individually by using a DSC analyzer (DSC 204 F1, Germany). The temperature was measured around 10 to 230ºC with a scan rate of 10º C/min.

The FTIR spectra were collected on two film samples (i.e., Sample A and Sample E) using attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectrometer (Nicolet IS10, Thermo Fisher Scientific, USA) at a range of 650-4000 cm^{-1} with a resolution of 16 cm^{-1}.

The water contact angle was measured at room temperature (25ºC). The wetting behavior of the film samples was analyzed using a water surface analysis system (VCA 3000S, AST Products, Inc., USA) and a watered syringe (5 µL of distilled water). A drop of distilled water was dropped on the film samples. The angle of incidence was examined after the water deposition.

Five film formulations were prepared in triplicate. The average values and standard deviation were calculated and reported. The average values of various film samples were compared and analyzed using the analysis of variance (ANOVA) technique.

RESULTS AND DISCUSSION

Film Thickness

Figure 1 shows the film thickness of various film formulations that contained cassava starch, glycerol, citric acid, and palm oil. The result has revealed that citric acid and palm oil affect the film thickness. Generally, a higher concentration of citric acid and palm oil contributes to the film thickness. However, the thickest film is Sample A, which only contained cassava starch and glycerol. This is associated with the influence of glycerol in the rearrangement of the polymer structure and finally increasing the thickness and density of the film [13]. Meanwhile, Sample E contained with 5% of citric acid and 2% of palm oil has the lowest film thickness. The increase of citric acid also contributed to the rearrangement of the intermolecular in the polymer chains. Thus, the film thickness increases as citric acid content increases in the bioplastic increased [9]. It is believed, citric acid also may elevate the solid content in the film and finally will increase the film thickness [14]. The film thickness could also be effected by the casting mold area, and the volume of the solution poured into the mold [13].

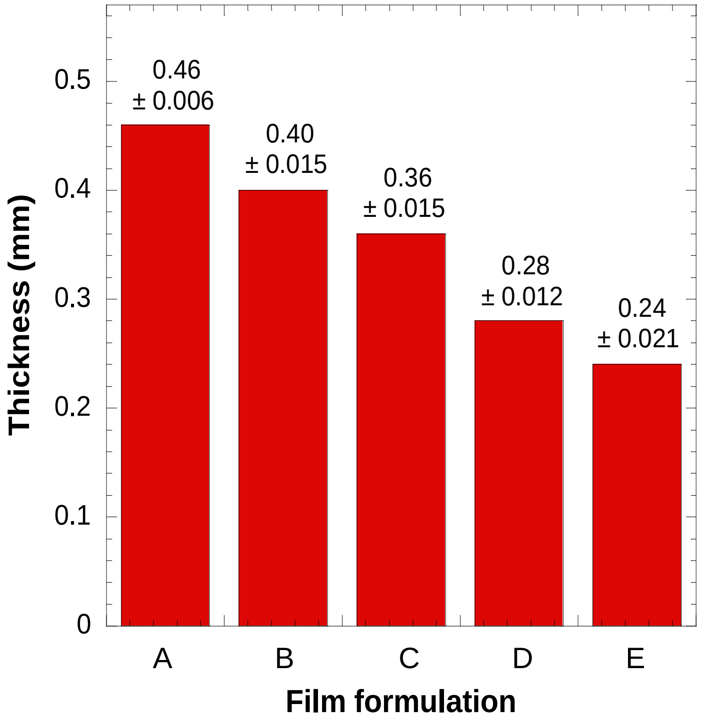

Figure 1. Film thickness (mm) of Sample A (no citric acid and palm oil), B (10% of citric acid and 4% of palm oil), C (10% of citric acid and 2% of palm oil), D (5% of citric acid and 4% of palm oil) and E (5% of citric acid and 2% of palm oil).

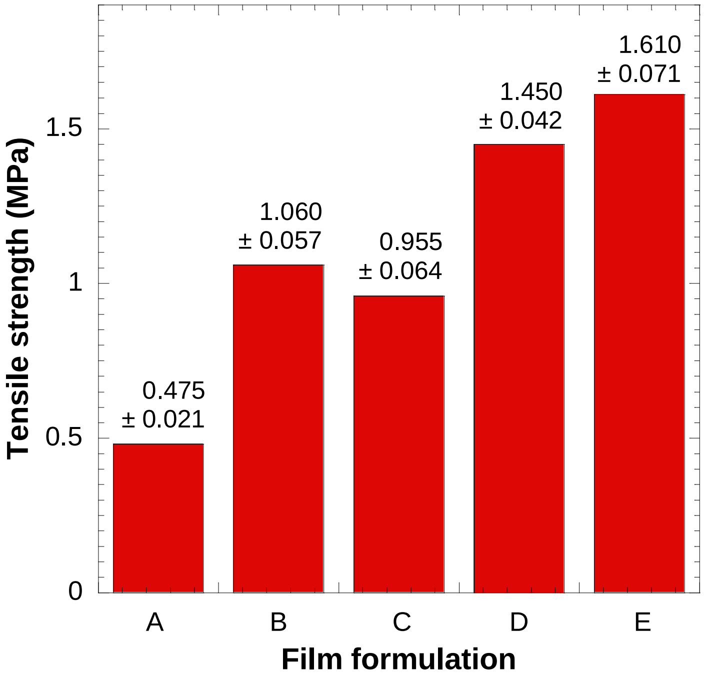

Figure 2. Tensile strength (MPa) of Sample A (no citric acid and palm oil), B (10% of citric acid and 4% of palm oil), C (10% of citric acid and 2% of palm oil), D (5% of citric acid and 4% of palm oil) and E (5% of citric acid and 2% of palm oil).

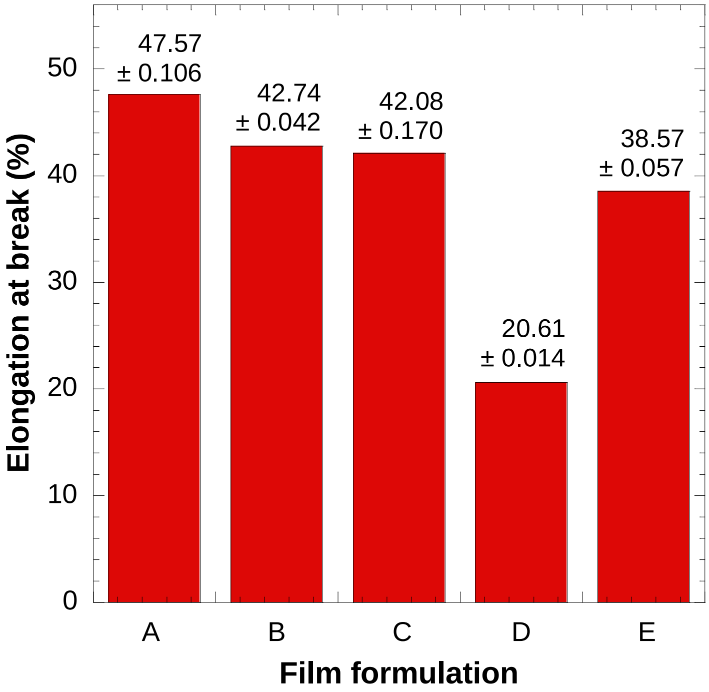

Figure 3. Elongation at break (%) of Sample A (no citric acid and palm oil), B (10% of citric acid and 4% of palm oil), C (10% of citric acid and 2% of palm oil), D (5% of citric acid and 4% of palm oil) and E (5% of citric acid and 2% of palm oil).

Tensile Strength (TS) and Elongation at Break (EAB)

The TS and EAB results of all variation bioplastic film are shown in Figure 2 and 3, respectively. Generally, addition of citric acid into starch-based bioplastic enhanced the TS but marred the EAB of the bioplastic film. The highest TS is 1.6 MPa and was observed at Sample E with the combination of the lowest citric acid and palm oil content in the cassava starch bioplastic. This is due to citric acid forming crosslink in starch chains. Citric acid will be restructuring the starch chains that will allow the additional hydrogen bonds between the starch chains, resulting finally enhanced the TS of the starch bioplastic [16]. However, further increase the citric acid (more than 5%) in starch-based bioplastic will decrease the TS but enhanced the EAB. This happened due to citric acid acting as a plasticizer in the starch-based bioplastic, which will diminish the interaction between the macromolecules in the starch chains. These different functions of citric acid (crosslinking agent and plasticizer) will give contrast results on tensile strength and elongation at break [9,16]. It also believed that decreased of TS possibly due to: (1) the excess citric acid prevented close proximity and decrease the formation of hydrogen bonds between starch molecules [14], or (2) the formation of excessive crosslinks that limits the mobility of the starch molecules [15].

Moreover, the highest EAB is observed in Sample B that contains the highest citric acid and palm oil. This is due to the plasticizer effect of excess citric acid and palm oil in the starch chains. Unsaturated fatty acids present in the palm oil caused the fatty acids to disperse uniformly in the starch chains [29]. This consequently weakened the interfacial bonding in the starch chains, but this effect enhances the EAB of the starch-based bioplastic [16,18].

Moisture Absorption

The percentage of moisture absorption in the starch films is shown in Figure 4. Sample A has the highest moisture absorption at 7.42±1.13% w/w with a significant difference at $p<0.05$ compared to other starch-based films. The presence of glycerol enhanced the absorption and retention of moisture in Sample A. The slight decrease in moisture absorption for Sample B corroborates with the result reported by [16]. Starch films that were modified with 10% citric acid (Sample B and Sample C) have significantly higher moisture absorption than those with 5% citric acid (Sample B and Sample C). Unreacted citric acid may have been trapped in the starch molecule, allowing greater diffusion and enhanced moisture absorption [14]. Sample D has the lowest moisture absorption at 1.41±0.06% w/w possibly due to the enhanced hydrophobicity from the larger starch molecule as a result of the crosslinking process, and the incorporation of hydrophobic palm oil in its starch molecules further decreased moisture absorption.

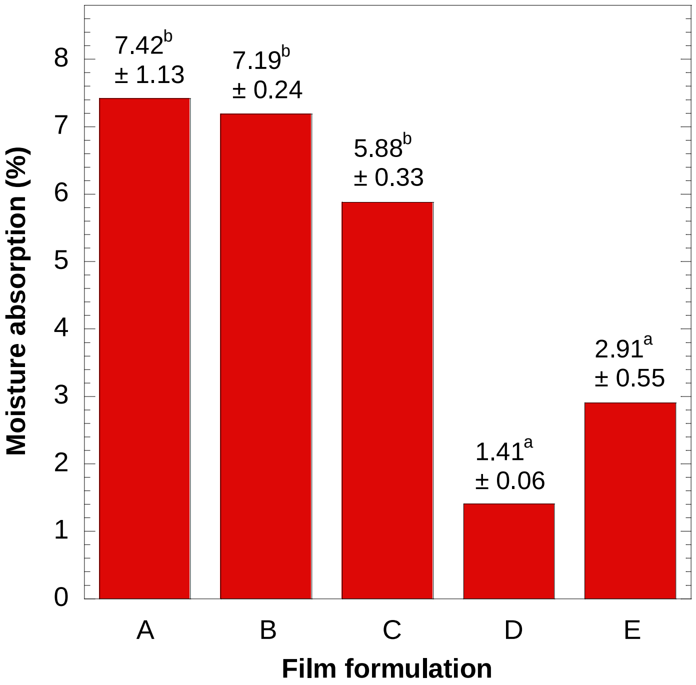

Figure 4. Moisture absorption (% w/w) of Sample A (no citric acid and palm oil), B (10% of citric acid and 4% of palm oil), C (10% of citric acid and 2% of palm oil), D (5% of citric acid and 4% of palm oil) and E (5% of citric acid and 2% of palm oil).

Moisture Content

Figure 5 showed the moisture content of the starch films at various contents of citric acid and palm oil. The moisture content for Sample A (21.08±1.87% w/w) was significantly higher ($p<0.05$) than that of Sample D and Sample E. Again, Sample D has the lowest moisture content with a value of 9.35%±0.93. This is due to the enhanced hydrophobicity caused by crosslinking and palm oil incorporation.

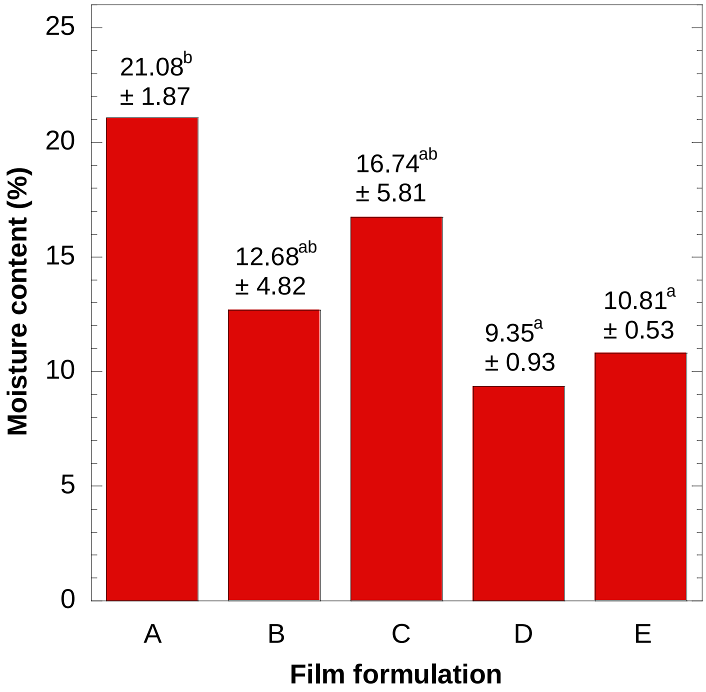

Figure 5. Moisture content (% w/w) of Sample A (no citric acid and palm oil), B (10% of citric acid and 4% of palm oil), C (10% of citric acid and 2% of palm oil), D (5% of citric acid and 4% of palm oil) and E (5% of citric acid and 2% of palm oil).

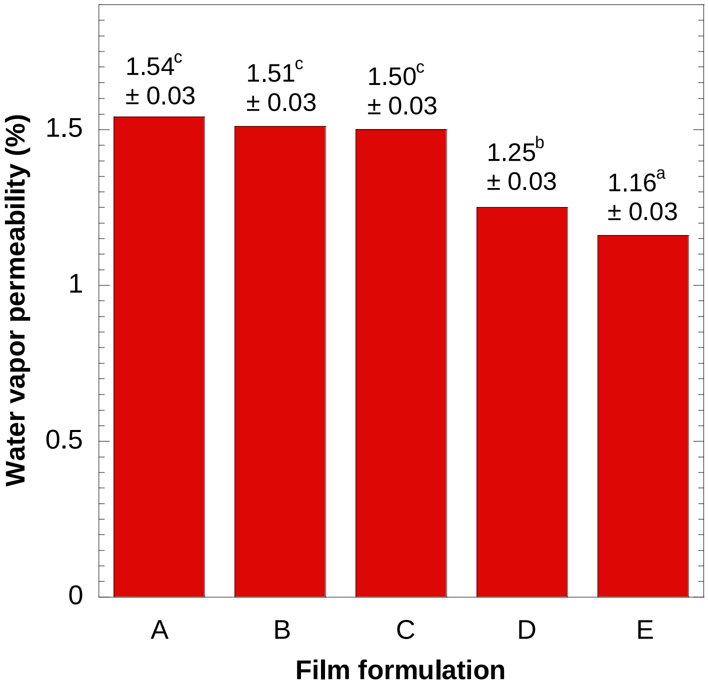

Figure 6. Water vapor permeability (% w/w) of Sample A (no citric acid and palm oil), B (10% of citric acid and 4% of palm oil), C (10% of citric acid and 2% of palm oil), D (5% of citric acid and 4% of palm oil) and E (5% of citric acid and 2% of palm oil).

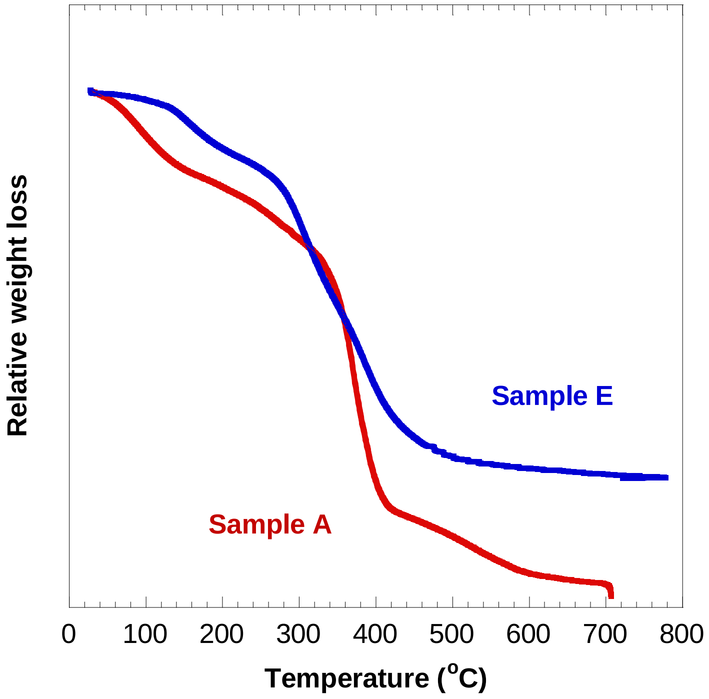

Figure 7. TGA thermograms of weight loss as a function of temperature for (a) Sample A (no citric acid and palm oil), and (b) Sample E (5% citric acid and 2% palm oil).

Water Vapor Permeability

The WVP values of the starch films modified with 5% citric acid (Sample D and Sample E) were significantly lower than that of Sample A, Sample B, and Sample C ($p<0.05$) (Figure 6). The presence of the hydrophilic glycerol in Sample A and the open structure of Sample B and Sample C has allowed greater attraction and penetration of moisture, respectively. The presence of crosslink tightened the structure in Sample D and Sample E, increased hydrophobicity, and reduced WVP [15]. Interestingly, the WVP value for Sample E (1.16±0.03% w/w) was significantly lower than that of Sample D (1.25±0.03 w/w) ($p<0.05$) despite having a lower palm oil content. The decrease in the WVP value of the starch-based film may be due to the starches' hydroxyl groups being substituted with palm oils' hydrophobic ester groups. The palm oil dispersed well in the starch structure at a low content and blocked the water vapor transmission while an excessive amount of palm oil content may be accumulated and eased the water vapor passes through into the films. Although the fatty acids have a hydrophobic characteristic, their molecules contained polar carboxyl groups that may attract water molecules and improve the moisture transfer, thus increasing the WVP of the starch-based film [6].

Thermogravimetric Analysis

The TGA thermograms of weight loss as a function of temperature for Sample A (no starch and glycerol) (Figure 7a) show three phases of thermal degradation: (1) 26 ºC to 100 – 200 ° C; (2) 100 – 200 ºC to 400 – 500 ºC and (3) 500 ºC to 700ºC. The first decomposition phase occurred due to the water evaporation from the starch at temperatures ranging from 26 ºC to 100 – 200 ºC. The second phase appeared at 100 – 200 ºC to 400 – 500 ºC and is related to glycerol degradation and decomposition of hydrolyzed starch. The breakdown of the starch backbone caused the third decomposition phase to occur at around 400 – 500 ºC to 700 ºC [17]. Sample E which was modified with 5% citric acid and 2% palm oil also showed three phases of thermal degradation in its TGA thermogram of weight loss (Figure 7b). The first phase occurred approximately at 20 ºC to 200 ºC due to the evaporation of water from the starch. The presence of citric acid reduced the water evaporation in Sample E compared to Sample A. At 150 ºC, the weight loss occurred due to the degradation of the remaining citric acid in the starch film [18]. The degradation of glycerol and hydrolyzed starch took place in the second phase at around 200 – 300 ºC to 300 – 400 ºC [19]. The third degradation phase occurred at 300 – 400 ºC to 700 ºC due to the thermal decomposition of the starch backbone and crosslinked starch. The citric acid-crosslinked films of Sample E degraded at a higher temperature and lower weight loss than the unmodified film (Sample A), indicating that citric acid improved the binding of glycerol and water to starch [15]. The improvement in thermal stability confirms that adding citric acid improves the binding among citric acid, palm oil, glycerol, water, and starch [20]. Citric acid could strengthen the starch backbone chain and create a tight hydrogen bond linkage with starch than that between starch and glycerol [21].

Differential Scanning Calorimetry

The DSC thermograms for Sample A and Sample E are shown in Figure 8. The differences in enthalpy, onset temperature, and melting temperature of the thermal transition of unmodified and modified starch films are noticeable with the addition of citric acid and palm oil. Sample A (Figure 8a) which consists of starch and glycerol has one peak with an endothermic heat flow recorded at 115.22 °C. According to the DSC result obtained by [15], the starch film containing glycerol showed an endothermic peak at about 100 ºC. The enthalpy value obtained was 14.53 J/g. Glycerol may change the crystalline structure of the film, thus increasing the film's enthalpy value [22]. Glycerol may interfere with the hydrogen bond in the hydroxyl groups, resulting in the retrogradation of starch. The addition of starch did not influence the glass transition temperature of the standard starch film because the glass transition temperature of starch always cannot be observed on the DSC graph [23]. Amorphous chains surrounded by crystalline domains, moisture, physical crosslinks inhibiting the mobility of the amorphous chain segments, and the presence of inter-crystalline phases that do not show normal thermal behavior could all contribute to the absence of a clear glass transition temperature.

Figures 8b shows the DSC curves of Sample E contained 5% citric acid and 2% palm oil shows three peaks. The endothermic temperature at the first peak was 132.22 ºC with an enthalpy value of 5.39 J/g. The enthalpy value of 9.39 J/g was obtained along with an endothermic temperature of 150.22 ºC during the second peak. According to [15], 5% of citric acid reached an endothermic peak at around 150ºC. Next, the endothermic temperature at the third peak was 164.22 ºC with an enthalpy value of 0.86 J/g. The DSC curve obtained is non-reversible and associated with the degradation process. The melting temperature at the final peak is due to the decomposition of citric acid [24]. The onset temperature, melting temperature, and enthalpy were increased with the presence of citric acid in the starch film. This is due to citric acid lowering the intra-molecular and inter-molecular bonds of starch structure and strengthening the hydrogen bond interaction with the starch, thus increasing the melting temperature [25]. The high melting temperature was achieved because citric acid can form a stronger and more compact structure. The result agreed with the study of [15] and [23].

In contrast, glycerol also affected the enthalpy and melting temperature because glycerol tends to absorb water from the film [26]. The glass transition temperature decreased when glycerol was introduced. The decrease in the cohesive forces of attraction in polymer chains caused the glass transition temperature and enthalpy to decrease. The smaller plasticizer molecules entered the starch polymer matrix to establish the polar attractive forces between the plasticizer and starch chain. As a result, decreased the cohesive forces and the glass transition temperature. Generally, the presence of citric acid content made water evaporation more difficult. Citric acid improved the hydrogen bond of the starch hydroxyl group by lowering the molecular interaction between the starch chain resulting in more trapped hydroxyl groups that are difficult to evaporate [27]. The crosslinking reaction will reduce the molecular segment's movement producing a higher glass transition temperature. On the other hand, the enthalpy value may also decrease as citric acid increases due to the decrease in the inter-molecular forces' decrease when citric acid cross-linked with glycerol [23].

The melting temperature of a starch film with palm oil rises as the palm oil content increased. According to [26], palm oil with a composition of 5% to 7.5% presented a melting peak near 100 ºC. Palm oil can lower the melting temperature of the starch film due to the free water content volume dropping, and the film structure changing, thus increasing the endothermic energy of the film. According to [28], the glass transition temperature rises when the palm oil content increases because the moisture content decrease, thus reducing the film structure's movement.

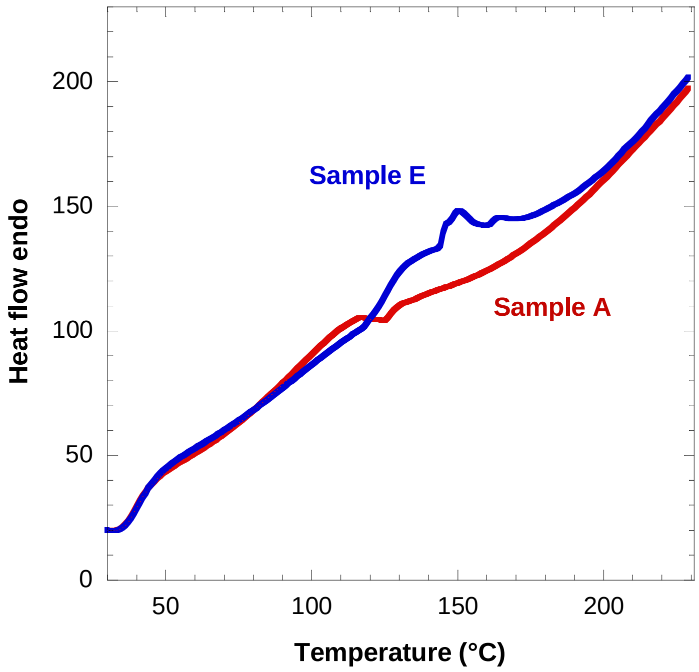

Figure 8. DSC thermograms of (a) Sample A (no citric acid and palm oil), and Sample E (5% citric acid and 2% palm oil).

Table 2. DSC parameters (onset temperature (ºC), peak temperature (ºC), end temperature (ºC), and enthalpy (ΔH) (J/g)) of Sample A and E.

DSC parameters	Sample A	Sample E		
		First peak	Second peak	Third peak
Onset temperature (ºC)	95.22	127.22	145.22	162.23
Peak temperature (ºC)	115.22	132.22	150.22	164.22
End temperature (ºC)	123.35	142.10	157.09	167.23
Enthalpy (ΔH) (J/g)	14.53	5.39	9.39	0.86

ATR-FTIR

The FTIR spectrum and wavenumbers of the Sample A film (i.e., cassava starch + glycerol), respectively, and the interpretation of each band is presented in Table 3. The vibration band at 3273 cm^{-1} and 2929 cm^{-1} represents the stretching of O-H and C-H groups, respectively [9]. The O-H band showed the interaction of hydrogen bonds between the starch chains. The vibration band at 1643 cm^{-1} was due to the bending of the C=O. The asymmetric stretching of C-O-C was indicated by a band at 1148 cm^{-1}, while the C-O-C ring vibrations bands of the starch molecule appeared at 996, 928, and 856 cm^{-1} [29]. Another absorption band located at 924 cm^{-1} showed the O-H bending, indicating that the glycerol molecule can create hydrogen linkage with the starch molecules [30].

The strong, broad, and unsymmetrical band at 1797 – 1712 cm^{-1} may consist of several vibrational bands, namely, the stretching band of C=O for carboxyl and aliphatic ester groups from citric acid and palm oil, respectively [27]. The presence of a band at 1645 cm^{-1} may be due to the aliphatic amides C=O stretching vibration of the protein in cassava starch [26]. The CH_2 stretching band for aliphatic hydrocarbon is located at 1490 cm^{-1}. Bands at the range of 1147 – 1076 cm^{-1}, were due to the stretching vibrations of C-O bonds from the starch's glycosidic bond. During the synthesis of Sample E, palm oil and starch did not form a homogeneous mixture due to the contrasting nature of palm oil (non-polar) and starch (polar). Thus, palm oil is not likely to form strong bonds with cassava starch [28]. However, citric acid is polar and is likely to form crosslinks with several adjacent starch molecules via the esterification process [15].

Table 3. Wavenumbers of vibration bands (cm^{-1}) of Sample A (starch and glycerol), and Sample E (5% citric acid and 2% palm oil)

Functional group	**Wavenumber (cm^{-1})**		
		Sample A	Sample E
O-H stretching	3700 – 3100	3273	3304
C-H stretching	2950 – 2840	2929	2925
C=O bending of amide I	1637 – 1646	1643	1645
C-O-C asymmetric stretching	1250 – 1050	1148	1490
C-O stretching	1200 – 800	996	1147 – 1076
C-O-C ring vibration of carbohydrate	920 856 758	928 856 759	

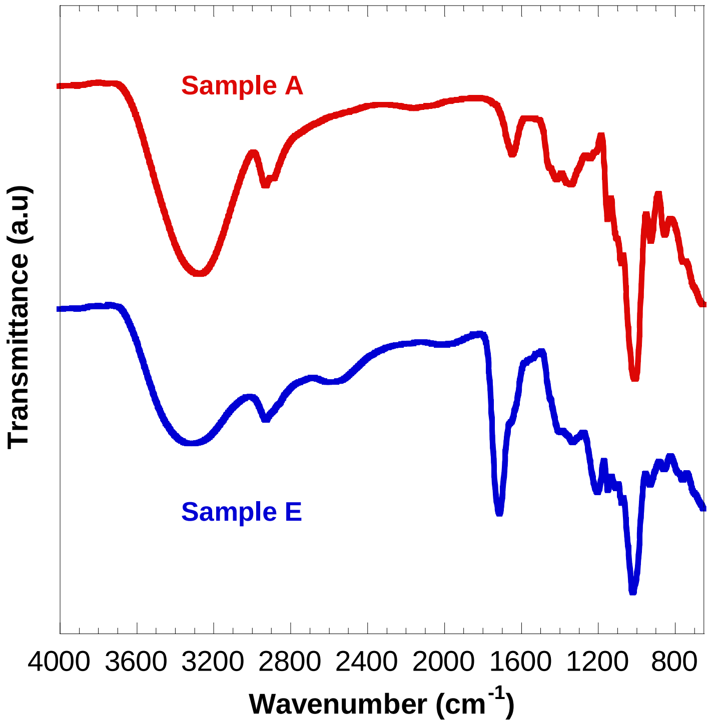

Figure 9. FTIR spectrum of (a) Sample A (starch and glycerol without citric acid and palm oil), and (b) Sample E (starch and glycerol with citric acid and palm oil)

Water Contact Angle

Figure 10 shows that there was a significant difference between the WCA value of all films sample at $p<0.05$. Sample A, which only contained starch and glycerol, has the lowest WCA value at 48.82 ± 5.41° and has a significant difference compared to Sample D at $p<0.05$. The result indicated that the surface of the film is the most hydrophilic than other films. The result obtained is the same as with the study of [31] on corn, potato, and wheat starch films.

Both Sample D and E contained 5% citric acid with 2% and 4% palm oil. The WCA values of Sample D and E were 68.85 ± 7.09° and 63.35 ± 7.03°, respectively. Sample D has a significant difference at $p<0.05$ compared to other starch-based films. The result showed that the hydrophobicity of the starch-based film associated with citric acid and palm oil is improved. The result corresponds with the study of [26]. The concentration of palm oil improved the hydrophobicity of starch film, although the WCA degrees could not achieve 90°. Tween 80 is an emulsifier and aids in strengthening the bond between palm oil and starch. Thus, the starch's' hydrophobicity rises gradually. According to [32], this is related to the hydrophobic ester groups of citric acid formed when combined with starch which allows a reduction in the polar groups, preventing the water absorption from the film's surface. In addition, the rough surfaces of the film may have a larger WCA value due to heterogeneous wetting.

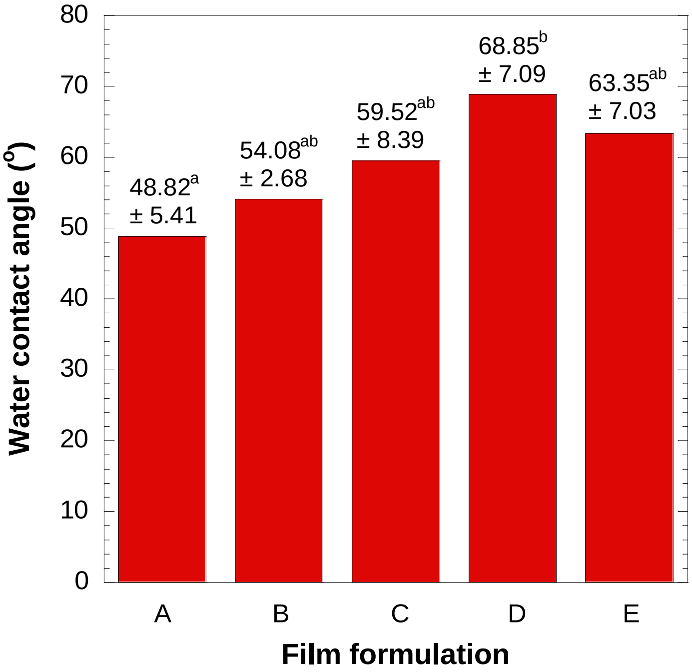

Figure 10. Water contact angle (°) of Sample A (no citric acid and palm oil), B (10% of citric acid and 4% of palm oil), C (10% of citric acid and 2% of palm oil), D (5% of citric acid and 4% of palm oil) and E (5% of citric acid and 2% of palm oil)

Next, the WCA values of Sample B (10% citric acid and 2% palm oil) and C (10% citric acid and 4% palm oil) were 54.08 ± 2.68° and 59.52 ± 8.39°, respectively. Sample B and C have no significant differences compared to other film samples at $p>0.05$. The WCA value showed that the surface hydrophobicity of the film has reduced. From the result, the WCA value of 5% citric acid incorporated into the starch film showed a good result toward the wettability compared to 10% citric acid. According to Wu et al. (2019), the WCA value decreased when added 20% of citric acid was into the starch-based film because the free hydrophilic groups from excessive citric acid solidified crystals on the film's surface [14]. Moreover, it could also be due to incomplete gelatinization of starch structure that makes the water molecules absorbed easily.

CONCLUSION

The effect of citric acid and palm oil on the characterization, mechanical properties, water barrier properties, and thermal properties of cassava starch-based film was successfully determined. Citric acid and palm oil were used to improve the thickness, TS, and EAB. The WVP, moisture absorption, and content were also successfully measured. The wettability of the film was improved by WCA analysis with citric acid and palm oil. Citric acid and palm oil interaction in cassava starch were observed using TGA, DSC, and ATR-FTIR analysis. It was observed that hydrolysis and esterification of citric acid and palm oil with cassava starch were presented in TGA and DSC thermograms. Citric acid and palm oil added into cassava starch showed ester functional groups in the ATR-FTIR spectra.

Generally, Sample E shows the best formulation of the films. The results revealed that all the starch-based films tested, with 5% citric acid and 2% palm oil, had better tensile strength and water vapor permeability. The incorporation of 10% citric acid slightly reduced the mechanical strength and water barrier properties due to participation. The incorporation of 2% and 4% palm oil only showed a slightly improved WVP, and reduced moisture in the film. Thus, this study provided a suitable formula for developing the interaction of citric acid and palm oil with cassava starch.

Extensive research is still needed to assess the biodegradability of the films before they can be used as food packaging films. In addition, it is recommended to produce a protein-based film for film packaging. The protein-based film has a greater protein content which allows them to have good biodegradability, mechanical, and water barrier characteristics than starch-based film. Besides, the research can be done by using other lipid compounds such as palm stearin or palm kernel oil. Additionally, studies of more characteristics of the starch films such as sensory and antimicrobial analysis could be conducted to evaluate the potential in the broader application of food packaging.

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