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Original Article

Chemical modification of biodegradable cassava starch films by natural mono-, di- and tri-carboxylic acids

Jutarat Prachayawarakorn[1, 2*] and Jintapa Tamseekhram[1]

[1] *Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Lat Krabang, Bangkok, 10520 Thailand*

[2] *Advanced Materials Research Unit, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Lat Krabang, Bangkok, 10520 Thailand*

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Abstract

Starch is the most important polysaccharide polymer used to develop biodegradable films, mainly used for packaging applications. Due to high hydrophilicity and poor mechanical properties of biodegradable starch film, different types of natural carboxylic acids were introduced into cassava starch film. These were lactic acid (LA), malic acid (MA) or citric acid (CA), classified as the mono-, di- and tri-carboxylic acid, respectively. It was found from Infrared (IR) spectra that new IR peak position arisen from the ester group and new hydrogen bond formation were observed for different acid-modified starch films. In addition, the incorporation of different types of the acids into the cassava starch film also caused significant decrease of swelling, water uptake and water vapor permeability (WVP) because of more hydrophobicity of various starch films modified by the acids. Comparison among different types and contents of the acids used for modifying cassava starch films was performed. Furthermore, morphological, thermal and biodegradable properties were also investigated.

Keywords: acid, biodegradable polymers, modification, starch

1. Introduction

Starch is a naturally polysaccharide that has been extensively studied for many years in the field of renewable materials to replace synthetic oil-based materials as biodegradable films. Cassava (*Manihot esculenta*) is an important vegetal crop in tropical regions; where, on a food energy production basis as resource of complex carbohydrates, it ranks fourth after rice, wheat and corn. The main composition of these roots and tubers is: 70-80% water, 16-24% starch and small quantities, 4% of proteins and lipids (BeMiller & Whistler, 2009).

However, hydrophilic character of starch is a major restriction that seriously limits the development of starch-based materials. Chemical modification has been explored as a way to solve the problem and to create more water resistant materials. Depending on nature of substituents and on degree of substitution, properties of modified starch can be varied expansively (Xie, Lui, & Cui, 2005).

One approach to modify starch is via cross-linking. Chemical cross-linking has long been examined as a way to reduce low water sensitive and to produce high strength materials. Examples of cross-linking reagents include glutaraldehyde, boric acid and epichlorohydrin (Xie, Lui, & Cui, 2005). Nevertheless, some of these cross-linking agents always present toxicity and thus their potential applications as biomaterials are limited. To overcome these advantages, certain non-toxic functional additives and simple modification techniques are required to improve properties and water resistibility of biodegradable starch films.

Natural organic acids such as lactic acid (LA), malic acid (MA) and citric acid (CA) can be used to modify starch. They are found all over the nature or can be produced

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*Corresponding author
Email address: jutarat.si@kmitl.ac.th

in large scale mainly by biotechnology techniques. They are generally added in different foods as acidity regulator, antimicrobial or flavoring agents to provide sour or fruity taste or flavor (Theron & Lues, 2011). One of the most important applications of organic acids in food industry is LA.

For monocarboxylic acid, LA, it is white and water-soluble. With a hydroxyl group adjacent to a carboxyl group, LA is classified as an alpha-hydroxy acid (AHA). LA is also used in a wide range of food applications such as bakery products, beverages, meat products, confectionery, dairy products, salads, dressings, ready meals, etc. LA in food products usually uses as either as a pH regulator or as a preservative. It is also served as a flavoring agent. It was mentioned that addition of LA to either cassava or corn starch decreased their intrinsic viscosity due to acid hydrolysis (Bertolini, Mestres, & Colona, 2000; Martinez, Amaya, Cabajal, Chang, & Zazueta, 2007). Zhong, Song, and Li (2011) claimed that LA decreased degree of crystallinity of Kudzu starch/chitosan blended films (Zhong *et al.*, 2011).

Another organic acid widely used in food industry is MA, a dicarboxylic acid organic compound. It is made by all living organisms, contributes to the sour taste of fruits, and is applied as a food additive. It is also used with or in place of the less sour citric acid in sour sweets. It was reported that MA could reduce intrinsic viscosity, degree of crystallinity and gel hardness of both native and crosslinked wheat starch (Majzoobi, Beparva, Farahnaky, & Badii, 2014). It was also mentioned that the use of MA increased elongation and solubility but decreased tensile strength including swelling of blended corn starch/PVA films (Yoon, Chough, & Park, 2006b).

CA, tri-carboxylic acid, exists widely in citrus fruits and pineapples, where it is the main organic acid. CA is generally recognized as safe according to FDA and is thus suitable for use in food packaging. As a result of its tri-carboxylic structure, interaction could take place between carboxyl groups of CA and hydroxyl groups of starch. Such an interaction would improve the water resistivity due to reducing available OH groups of starch. It was described that CA could form strong hydrogen bond interactions with starch and improved its water stability (Reddy & Yang, 2010; Yu, Wang, & Ma, 2005). Furthermore, because of the tri-carboxyl structure, CA may serve as a cross-linking agent and CA was shown to improve mechanical properties by reducing tensile strength and increasing elongation of corn starch which was attributed to cross-linking (Reddy & Yang, 2010). It was also mentioned that blended corn starch/PVA film modified by CA caused the increase in elongation at break but degree of swelling and solubility of the blended film were found to decrease (Yoon, Chough, & Park, 2006a). Moisture content and water permeability of corn and potato starch films were displayed to improve by using CA (Olsson, Menzel, Johansson, Anderson, & JärnstrÖm, 2013b; Reddy & Yang, 2010;). A concurrent reaction to cross-linking in response to CA addition is hydrolysis due to lowering pH. It was previously shown that high temperature, high CA concentration, and low pH increase degradation rate of starch (Curvaho, Zambon, Curvelo, & Gandini, 2005; Menzel *et al.*, 2013; Olsson, Menzel, Johansson, Anderson, & JärnstrÖm, 2013b).

Most of published papers reported on properties of starch modified by acids normally used for food applications. In case of casted films, they were commonly prepared from blended films between starch and other synthetic polymers such as poly (vinyl alcohol). Therefore, further works are required to examine the effect of different natural organic acids on properties of the cassava starch films. To the best of our knowledge, there is no published information showing the effects of different types and contents of LA, MA and MA on characterization and properties of the cassava starch films which was followed in this research.

2. Materials and Methods

2.1 Materials

Cassava starch, approximately contained 20±1 %wt amylose and 75±2 %wt amylopectin, was obtained from Thaitam (Chonburi, Thailand). Glycerol was purchased from Lab System Co., Ltd. (Thailand) and used as a plasticizer. LA, MA and CA (food grade) (Figure 1) were purchased from UCS 1986, Co. Ltd. (Thailand).

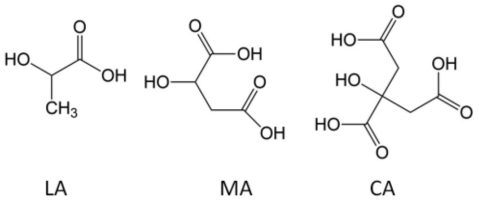

Figure 1. Chemical structures of LA, MA, and CA.

2.2 Sample preparation

Cassava starch films were prepared by dispersing 10% (w/w) starch in water with 15% glycerol by weight of the starch. The starch dispersion was heated on a hot plate (IKA, Germany) to 65°C and maintained at the temperature for 45 min. under vigorous stirring. Different LA, MA or CA concentrations (10% and 20%w/w starch); designated as LA10, LA20, MA10, MA20, CA10 and CA20, were added to the gelatinized starch after cooling down to room temperature. After that, 50 grams of the sample were poured into a polypropylene tray and dried at 70 °C for 5 hrs with subsequent curing by a hot-air oven (Memmert, Germany) at the temperature of 150 °C for 10 min. The non-modified starch film (A0) was used to compare with different acid-modified starch films.

2.3 Fourier Transform Infrared spectroscopy (FTIR)

FTIR spectrum of a sample was recorded via a Spectrum 2000 GX spectrometer (Perkin Elmer, USA) using KBr disk technique. A resolution of 4 cm^{-1} with a spectral range of 4000-400 cm^{-1} was applied. Each spectrum was collected from 16 scans.

2.4 Swelling

A film, with the size of 1×1 cm^2, was weighed and left at ambient temperature in distilled water for 72 h. The film was, then, blotted with a tissue paper and the weight of the film was measured periodically with a microbalance (Presica Instrument, UK) until equilibrium was reached. The degree of swelling was evaluated using Equation (1):

$$\text{Degree of swelling} = (m_2\text{-}m_1)/m_1 \times 100 \qquad (1)$$

where m_1 and m_2 were weight of film before and after swelling, respectively.

2.5 Water uptake

Water uptake test was carried out according to ASTM D-570 standard method. A newly prepared sample was first dried at 105 °C for 3 hrs and then kept in a closed container at 99±1% RH. The amount of water absorbed by the sample was determined for 1, 7 and 14 hrs. The percentage of water uptake was calculated as Equation (2):

$$\text{Water uptake} = (w_2\text{-}w_1)/w_1 \times 100 \qquad (2)$$

where w_2 and w_1 were the wet and the dried weights of the sample, respectively.

2.6 Water vapor permeability (WVP)

WVP test was carried out according to ASTM E96 using desiccant method. Each film sample was fixed to a circular opening of a permeation cell (area of 5 cm^2). The interior of the cell was filled with silica gel and stored at 38°C in a desiccator that contained saturated $CaCl_2$ solution (90%RH). The sample was re-weighed daily for seven days. The changes in the weight of the cell or weight gain (G) were plotted as a function of time (t). The water vapor permeability (WVP) was obtained using Equation (3):

$$\text{WVP} = G/tA = (G/t)/A \qquad (3)$$

where G/t was the slope of the straight line and A was the sample permeation area.

2.7 Morphology

An EVO MA 10 scanning electron microscope (Carl Zeiss, Germany) was employed to study phase morphology of a sample, operated at an acceleration voltage of 5 kV. To prevent electrical charge during observation, each tested sample was sputter-coated with a thin layer of gold. The sample was immersed into liquid nitrogen before being fractured. Images were taken of the fractured surface at the magnification of 1,000×.

2.8 Mechanical properties

Mechanical tests were conducted according to ASTM D-638 standard method at a temperature of 23±1˚C and relative humidity of 60±5%. Testing was performed for ten samples each, measuring 10 cm × 1 cm randomly cut from a cast film. The sample was conditioned at the specified test for 24 hrs prior to the test. Measurement of each specimen was carried out using a Universal Testing Machine (Lloyd Instrument, LR 5K, West Sussex, UK) with a 1 kN load cell and a crosshead speed was maintained at 40 mm/min.

2.9 Biodegradation by soil burial test

A sample was cut in rectangular shape of 10 cm × 1 cm. The sample was buried below 10 cm of soil under ambient temperature (32±1 °C). Water content and pH of the soil were controlled at 5-10% and 7±1, respectively. After that, tensile test was carried out to determine the tensile properties of the sample after burial in soil for 0, 5, and 10 days.

2.10 Thermogravimetric analysis

Thermogram of a sample was recorded by a thermogravimetric analyzer (TGA) (Perkin Elmer, Pyris 1, U.S.A.). The sample was tested within a temperature range of 50-600 °C and at a heating rate of 10 °C/min under nitrogen atmosphere.

3. Results and Discussion

The use of mono-carboxylic acid (LA), di-carboxylic acid (MA) and tri-carboxylic acid (CA) can cause not only acid hydrolysis at low pH but also esterification reaction between carboxylic group of acid and hydroxyl group of starch. However, crosslinking reaction via esterification is only expected for MA- and CA-modified starch films due to the di-and tri-functional groups of the acids, respectively. Based on chemical structure of tri-carboxylic CA-modified starch film (Olsson, Menzel, Johansson, Anderson, & JärnstrÖm, 2013b), possible chemical structures of mono-carboxylic LA, di-carboxylic MA -modified starch films are proposed in Figure 2, showing only esterification by the use of LA but crosslinking via esterification by the use of MA.

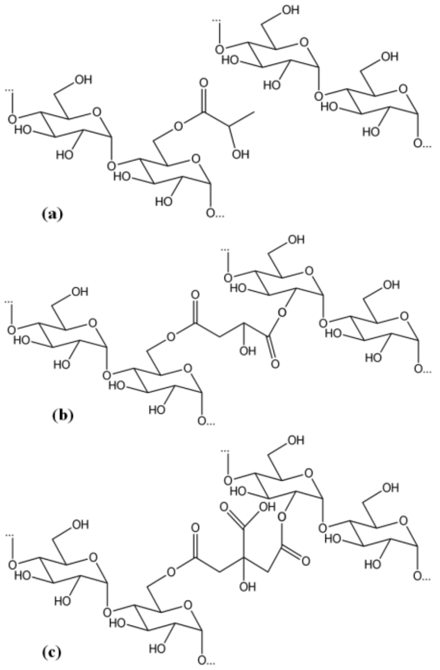

Figure 2. Possible chemical structures of different acid-modified starch films (a) LA (b) MA and (C) CA.

3.1 FTIR spectroscopic study

Figure 3 shows FTIR spectra of different acid-modified starch films. It can be seen that all films presented similar spectra based on carbohydrate structures. The peak positions in the region of 3,300-3,500 cm^{-1} and 2,800-3,000 cm^{-1} were assigned for the O-H stretching and C-H stretching, respectively. The wavenumber at 1,640 cm^{-1} was arisen from O-H bending from bound water; whereas, the peak position at 1,450-1,470 cm^{-1} was designated for O-H bending of starch molecule. Other bands appeared at 1,000-1,200 cm^{-1}, 800-950 cm^{-1} and 765 cm^{-1} were attributed to C-O-H bending, C-H bending and C-H$_2$ rocking, respectively (Bower & Maddams, 1996).

The difference between the non-modified starch (A0) film and the acid-modified starch films is that LA-, MA- and CA-modified starch films showed the extra peak position at 1,737-1,742 cm^{-1}, presenting the C=O stretching of ester bond (Bower & Maddams, 1996). It indicates that the addition of the acids into the starch films caused the esterification reaction between the starch and the acid molecules.

Moreover, the incorporation of LA, MA and CA into the starch films also created the IR peak shift of O-H stretching and O-H bending into lower wavenumbers. The results confirm the new formation of hydrogen bonds between the starch and the acid molecules. The peak shift has also been reported for the cassava starch/carrageenan composites reinforced by pectin particles and cotton fibers (Prachaya warakorn & Pattanasin, 2016) and cassava starch/lignin composites (Kaewtatip & Thongmee, 2013).

3.2 Swelling

Swelling tests were carried out at 1, 5 and 72 hrs and the results are presented in Figure 4. Similar patterns for all films, the great increase of swelling were found for the 1 and 5 hrs of the test. At 72 hrs of the testing, the degree of swelling increased gradually. From Figure 4, all the acid-modified films show the significant decrease of the percentage of swelling, compared with A0 film. This is because the esterification reaction decreases of free hydroxyl groups of starch molecules, resulting in lower degree of swelling. By the results from the swelling tests, it is confirmed that esterification can occur by the use of LA, MA or CA.

Comparison among different types of acids, the degree of swelling of LA-modified starch film appeared to be the highest, followed by MA- and CA-modified starch films, respectively. This could be because of the mono-, di- or tri-carboxylic acids of LA, MA and CA, respectively. The highest degree of esterification is expected to be the highest for the use of CA, generating the lowest degree of swelling.

Because of the monocarboxylic acid of LA molecule, only esterification can occur, resulting in less hydrophilicity and the decrease of the degree of swelling. However, the di-carboxylic acid of MA and tri-carboxylic acid of CA can also cause crosslinking reaction; consequently, the degree of swelling clearly dropped. It can be observed from Figure 4 that the use of CA leads to lower degree of swelling than that of MA, suggesting that more crosslinking was obtained with the use of CA. When the acid content was considered, it was found that high content of the acids caused low degree of swelling, indicating of high esterification and/or crosslinking reaction.

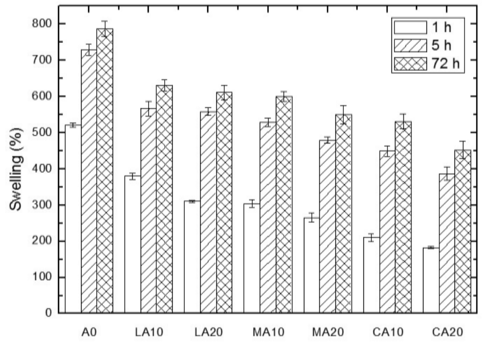

Figure 4. Swelling of different acid-modified starch films.

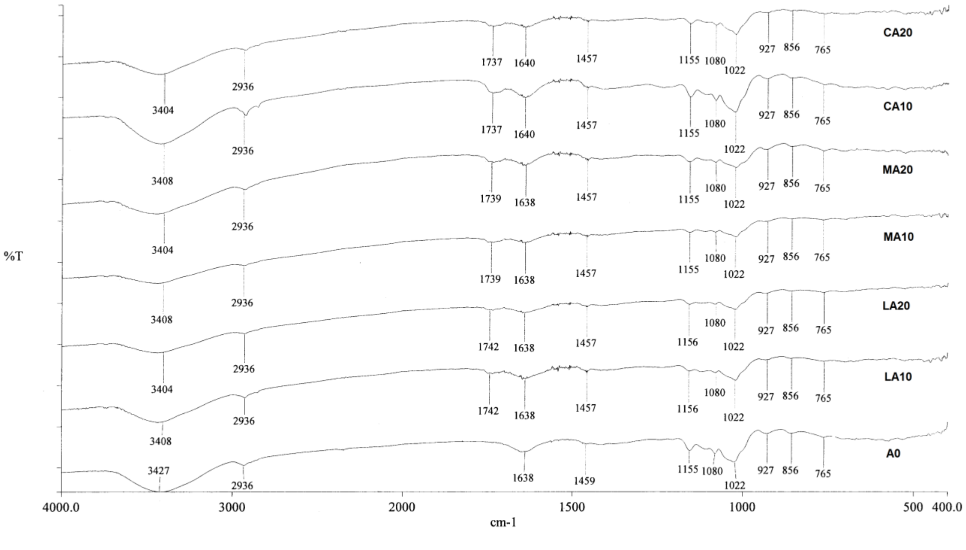

Figure 3. FT-IR spectra of different acid-modified starch films.

3.3 Water uptake

Figure 5 represents water uptake of different films determined at 1, 7 and 14 h at approximately 100% RH. It can be seen that A0 film shows the highest water uptake. However, various acid-modified starch films (LA-, MA- or CA-modified starch films) clearly caused the decrease of the water uptake. This is because of the esterification reaction caused less free hydroxyl groups, resulting in more hydrophobicity and lower water uptake. As expected, the tri-carboxylic CA molecules showed the lowest water uptake, suggesting the highest degree of esterification and cross-linking. The decrease of the water uptake of different acid-modified starch films also related to the results from the swelling test (Figure 4). Moreover, the increase of the acid contents also caused the decrease of the water uptake as shown in Figure 5. The results confirm the reports from Olsson *et al.* that the potato starch film modified by CA noticeably showed the decrease of water absorption and water vapor permeability (Olsson, Hedenqvist, Johansson, & JärnstrÖm, 2013a; Olsson, Menzel, Johansson, Anderson, & JärnstrÖm, 2013b).

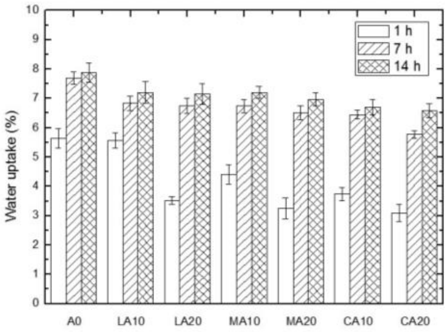

Figure 5. Water uptake of different acid-modified starch films.

3.4 WVP

WVP test was performed by the desiccant method at the temperature of 38°C and 90%RH. The results are shown in Table 1 and it was found that all the acid-modified starch films showed lower WVP than that of A0 film. It indicates that the esterification reaction caused more hydrophobicity of the starch molecule. Comparison among LA-, MA- and CA-modified starch films, it was found that WVP values were ranged in the following order, CA<MA<LA, related to the esterification and crosslinking reaction and the results also correlated to the swelling and water uptake tests (Figure 4-5). In addition, the increase of the acid content tended to decrease WVP as seen in Table 1 due to the more hydrophobicity from the increase of the esterification and crosslinking reaction permeability (Olsson, Hedenqvist, Johansson & JärnstrÖm, 2013(a); Olsson, Menzel, Johansson, Anderson & JärnstrÖm, 2013(b)).

Table 1. Water vapor permeability of different acid-modified starch films.

Films	WVP (g/m^2/day)
A0	1,892
LA10	1,874
LA20	1,821
MA10	1,768
MA20	1,669
CA10	1,584
CA20	1,486

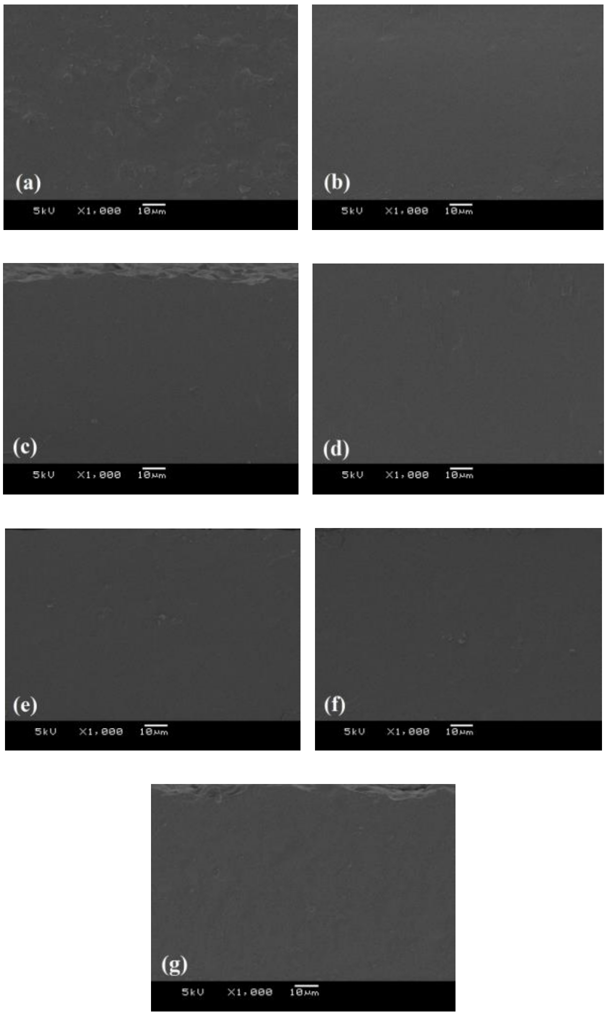

Figure 6. SEM micrographs of different acid-modified starch films (a) A0; (b) LA10; (c) LA20; (d) MA10; (e) MA20; (f) CA10, and (g) CA20.

3.5 Morphology

Morphology of A0 film is represented in Figure 6(a). It can be seen that the film showed continuous and smooth morphology with some unmolten starch. Nevertheless, more homogeneous films were found for all the modified films. LA-, MA- and CA-modified starch films (Figures 6(b)-6(g)) show similar morphology. Moreover, the use of different acid content caused the same phase morphology of the films regardless of the acid types.

3.6 Mechanical properties

Mechanical properties of various acid-modified films are shown in Figure 7. It is clear that A0 film shows the highest stress at maximum load and Young’s modulus as well

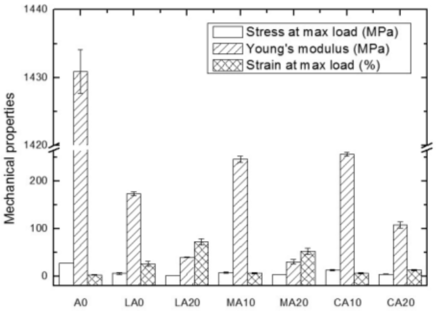

Figure 7. Mechanical properties of different acid-modified starch films.

as the lowest strain at maximum load, indicating of the highest stiffness of A0 film. This is because the polysaccharide chemical structure of starch contains many hydroxyl groups and hydrogen bond formations among the starch molecules. Nevertheless, the inclusion of different types of the acids into the starch films caused the considerable reduction of the stress at maximum load and Young's modulus. As a result, the significant improvement of the strain at maximum load was obtained. This is the evidence for both hydrolysis and esterification reaction, caused the ease for molecular movement under tension. It was reported that at high concentrations of CA, leading to lower tensile strength and higher elongation of the CA-modified corn starch films (Reddy & Yang, 2010).

For LA-modified starch film, crosslinking cannot occur due to the monocarboxylic group of LA molecule. However, esterification can still take place, resulting in bulkiness of LA-modified starch film; as a result, LA-modified starch film showed lower stress at maximum load and Young' modulus but higher strain at maximum load than those of MA- and CA-modified starch films.

Similarly, for dicarboxylic MA and tricarboxylic CA acids, lower stress at maximum load and Young' modulus including higher strain at maximum load than A0 film was found. On the contrary, crosslinking reaction can occur; therefore, higher stress at maximum load and Young's modulus than those of LA-modified starch film can be obtained. The results also showed that CA-modified starch film represented higher stress at maximum load and Young's modulus; and subsequently, lower strain at maximum load than MA-modified starch film and this suggests higher degree of crosslinking in CA-modified starch film than MA-modified starch film. The results clearly correspond to the degree of swelling test (Figure 4).

When the acid contents are considered, it can be seen from Figure 7 that the starch film modified by 20 wt% acid presented lower stress at maximum load and Young's modulus than those by 10 wt% acid modified starch film. Consequently, higher strain at maximum load was obtained from the film with 20 wt% acid because of more esterification and/or crosslink sites. This finding agreed with N. Reddy and Y. Yang who reported that high acid content caused the decrease of tensile strength due to the excess crosslinking (Reddy & Yang, 2010) and also to the lower molecular weight of starch (Olsson, Menzel, Johansson, Anderson & JärnstrÖm, 2013b). Similar observation was also found in starch/PVA blended films modified by MA and CA (Yoon, Chough, & Park, 2006a; Yoon, Chough, & Park, 2006b). Comparison among different acid-modified films from this present study, it was observed that the highest stress at maximum load and Young's modulus was found in CA10 film; however, the highest strain at maximum load was obtained from the LA20 film. It should be noted that stress at maximum load of CA10 film is comparable to that of commercial low-density polyethylene film (Rapra Technology, 2017; MatWeb, Material Property Data, 2017) and biodegradable low-density polyethylene film (Nguyen, Do, Grillet, Thuc, & Thuc, 2016).

3.7 Biodegradability by soil burial test

Soil burial test was performed to study biodegradability of different starch films. Figure 8 shows tensile properties of the films after burial under soil for 0, 5 and 10 days. It was found that the stress at maximum load and Young's modulus for all starch films were significantly decreased after burial under soil surface. On the contrary, the strain at maximum load appeared to increase substantially. The change represents the biodegradability of the films from microorganisms and from the moisture existed in soil (Seligra, Jaramillo, Fama, & Goyanes, 2016). In addition, all the acid-modified starch films present the ability to degrade in soil.

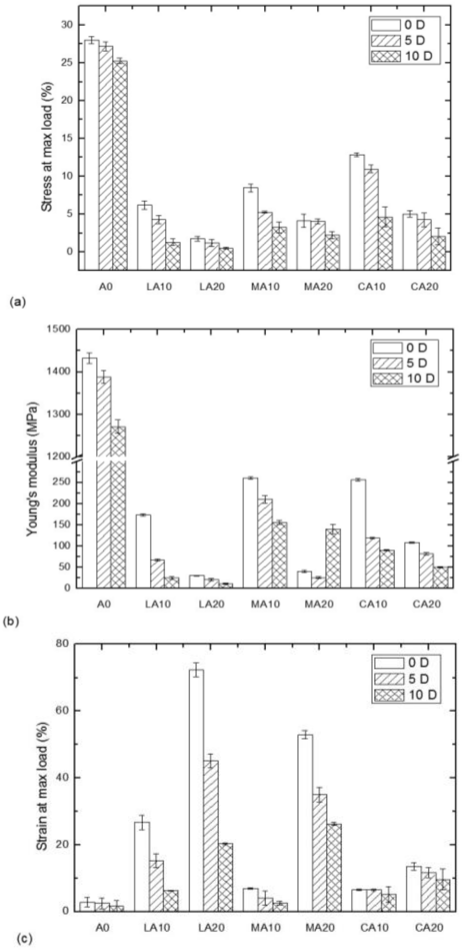

Figure 8. Tensile properties after biodegradation tests for different acid-modified starch films (a) stress at maximum load; (b) Young's modulus and (c) strain at maximum load.

3.8 Thermal properties

Figure 9 exhibits TGA and DTG thermograms of several starch films. It can be seen that there are three different degradation steps for A0 film. The first degradation steps involved with the evaporation of water in the temperature range of 70-100 °C. The degradation of glycerol plasticizer appeared as the second step at the temperature of 120-220 °C. The third degradation step occurred at the temperature of approximately 320 °C was due to the decomposition of starch (Prachayawarakorn, Chaiwatyothin, Muaengta & Hanchana, 2013).

For various acid-modified starch films, five degradation steps were obtained. The forth degradation step at the temperature of about 250-270 °C was arisen from the hydrolyzed starch and decomposed starch due to curing step at high temperature (Ma, Chang, Yu, & Stumborg, 2009; Reddy & Yang, 2010). It was observed that the thermal degradation temperatures due to the decomposition of starch for all the acid-modified starch films were found to comparable to A0 film. Furthermore, the evidence of the crosslinked starch appeared as the fifth step in the DTG thermograms with the temperature in the range of 320-400 °C (Gilfillan & Doherty, 2016). Moreover, the use of LA, MA and CA seemed to cause the residual weight percentage increased. This could be because the acid molecules could bond chemically with the starch chains (Gilfillan & Doherty, 2016).

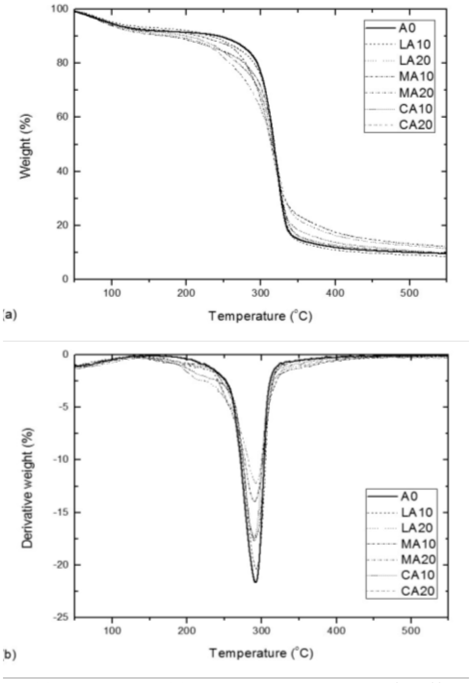

Figure 9. (a) TGA and (b) DTG thermograms of different acid-modified starch films.

4. Conclusions

Different contents and types of natural acid i.e. mono-carboxylic acid (LA), di-carboxylic acid (MA) and tri-carboxylic acid (CA) were successfully used to modify biodegradable cassava starch films. It was observed from FTIR spectra that all of the acid-modified films presented ester functional groups including new hydrogen bond formation. For swelling, water uptake and WVP tests, the results showed similar patterns. Mono-carboxylic LA-modified starch films presented the highest swelling, water uptake and WVP; whereas, tri-carboxylic CA-modified starch films presented the lowest swelling, water uptake and WVP. Higher contents of the acids presented lower swelling, water uptake and water vapor permeability than those of the lower contents. Among different acid-modified starch films, LA20-modified starch film showed the highest strain at maximum load; however, the highest stress at maximum load and Young's modulus were found for CA10-modified starch film. Moreover, all the films showed the ability to degrade, examined by soil burial test. It was also found that thermal degradation temperatures of various acid modified starch films were comparable to that of the non-modified film. Besides, the evidence of both hydrolysis and esterification and/or crosslinking of different acid-modified films could be observed from TGA and DTG thermograms. From this study, the best overall properties were obtained in tri-carboxylic CA-modified starch film at the content of 20 wt%.

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