The Effects of Clay Nanoparticles as Reinforcement Agent on the Properties of Starch-Protein Edible Film

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***Abstract*— In order to reduce the environmental damage to the environment, the edible film made from starch-protein was conducted which may replace the non-degradable material which is plastic that commonly used. As to increase the properties of film, the addition of clay to the starch-protein film is made which the objective is to study the mechanical and physical properties of the starch-protein film. The water-vapour permeability (WVP), water solubility and mechanical test (tensile strength and elongation at break was conducted. Montmorillonite (MMT) clay was used in this researched. As the result, in the presence of MMT in the film decreased the value of WVP (3.377×10^{-9} g/m.s.Pa to 1.0918 $\times 10^{-9}$ g/m.s.Pa) and percentage of water solubility (98.72% to about 50%). The different amount of clay 5%, 10%, 15% and 20% from weight of starch-protein is performed and showed inconsistent result. Result for mechanical properties showed the decreased in tensile strength and elongation at break as the addition of clay to the starch-protein film. At the end of this study, can be conclude that 5% clay film is the most suitable composition for food packaging application. The highest elongation at break for 5% clay film is significantly higher than other.**

Keywords*— *starch-protein film, edible film, clay nanoparticle, montmorillonite, mechanical properties.

I. Introduction

Edible film is a thin layer, which can be consumed, coated on a food or placed which function to act as barrier between the food and the surrounding environment (Skurtys et al., 2010). Films is purposely used to protect foods mechanically, prevent the contamination from microorganism and protect foods against quality loss due to mass transfer such as moisture. Previously, non-degradable synthetic materials is used for food packaging. The increasing usage of non-degradable materials cause the increasing of environmental pollution which driven to do research on the uses of edible film. Then, the research on the edible film is continued and the demand of edible film increase due to the advantages of using it as food packaging. Edible film able to longer the shelf-life and enhance the quality of fresh foods as well as environmentally friendly food packaging. Sausage meat in casing is the one of the example of edible packaging where the casing is not removed and can be cooked and consumed. The biomaterial film may also be used to enhance the quality and stability of pharmaceutical solid. (Talja, 2007)

The edible films are classified into three categories taking into account the nature of their components: hydrocolloids (containing proteins, polysaccharides or alginates), lipids (constituted by fatty acids, acylglycerols or waxes) and composites (made by combining substances from the two categories) (Skurtys et al., 2010). Biopolymers used to prepare edible films are proteins from fish gelatin and polysaccharides including starch like cassava starch, corn starch and potato starch. The materials used for biopolymer film have advantages over the synthetic polymer in term of environment. However, biopolymer film have poor mechanical properties and high permeability to water vapor. The improvement is made by adding plasticizer such as glycerol to obtain good properties of edible film.

For film made from starch, the mechanical strength can be improved with the addition of glycerol. However, barrier properties of starch films like protein films change and weak with the addition of plasticizer (Torabi & MohammadiNafchi, 2013). Thus, this research is done to figure out the improvement can be made by the addition of nanoparticle towards the starch-protein edible film properties. Nanoparticles is a filler that show a high level of efficiency to enhance the physicochemical and mechanical properties of starch-based films (Sun, Xi, Li, & Xiong, 2014). Nanoparticle that is used in this research is montmorillonite (MMT).

The technique used to produce edible film is casting method. The amount of MMT particles is varied to analysis the suitable amount of MMT needed to produce edible film which have function as good food packaging. Mechanical and physical analysis, water vapor permeability and solubility will be analyzed.

Recently, people have begun to realize the importance of protecting the environment. Non-degradable packaging can affect the environment and could be a contributing factor to environmental pollution. The step to try to reduce the use of plastic is applicable. However, it is really hard to completely stop using plastic as the food packaging. Synthetic plastics are still being used commercially. Non-degradable packaging is commonly used in food industry as to protect the food from chemical, biological and environmental factor which can change the characteristic of the food. In order to reduce the use of synthetic plastic, the film made from biodegradable polymer is studied to replace the packaging that used synthetic material. This will give good impact to the environment as bio-packaging can reduce the amount of plastic wastes (Skurtys et al., 2010).

In order to produce food packaging, the durability of the packaging and the product shelf life need to take into account. The factor that is considered as food packaging is the relative humidity and the permeability of water vapor. Edible film made from combination of starch and protein may have problem in their properties as food packaging. Starch-protein edible film have poor mechanical properties, sensitive to moisture content and high permeability to water vapor compared to synthetic material (Torabi & MohammadiNafchi, 2013). Thus, clay nanoparticle is added to improve the edible film barrier properties and physical properties. The addition of nanoparticles may increase the tensile strength, the elongation at break, the decomposition temperature and water vapor permeability in the film (Mbey, Hoppe, & Thomas, 2012). Other than that, starch-protein film is hard and brittle thus glycerol is added which act as plasticizer to reduce the brittleness caused by high intermolecular forces (Sanyang, Sapuan, Jawaid, Ishak, & Sahari).

In this study, the starch-protein edible film which reinforce with the clay nanoparticle is prepared. The test and analysis on the physical and mechanical properties of starch-protein edible film with the addition of clay nanoparticle is performed. The suitable or optimum amount of clay nanoparticle used in developing starch-protein edible film also is investigated.

II. METHODOLOGY

A. *Materials and methods*

Materials

Cassava starch from Thye Huat Chan Sdn. Bhd. , gelatin (powder) from Halal Gel Sdn Bhd, montmorillonite (clay nanoparticles), glycerol from Systerm, distilled water, desiccator, magnetic stirrer, petri dish, test cup, oven, thermometer, spatula, scanning electron microscopy, electronic weighing balance, parafilm, silica gel, hot plate, dropper, micrometer.

Methods

Film preparation

The starch-protein film with the addition of montmorillonite (MMT) is prepared by using casting method. Firstly, gelatin powder is dissolved in distilled water at the temperature 60°C for 30 minutes until form clear solution. Meanwhile in the other beaker, 15g of cassava starch is dissolved in 100 mL distilled water and heated with stirring at the temperature 85°C for 30 minutes until it is completely gelatinized. Then, gelatin solution and MMT is added to the cassava starch solution at 60°C and it is continued to be stirred for 30 minutes. Next, glycerol is added and stirred for another 30 minutes. The MMT was dispersed in distilled water (10 ml) for 24 h, producing a gel which it reach complete hydration as the preparation for MMT (Wilhelm, Sierakowski, Souza, & Wypych, 2003). The preparation is for different amount of clay which are 0 (control starch-protein film), 5, 10,15 and 20% of MMT per dry solid of starch protein mixture (Sothornvit, Hong, An, & Rhim, 2010).

The solution mixture is then cooled at room temperature. 9 mL of the solution is distributed into the petri dish. The volume of solution for every petri dish is constant. The solution is dried in a ventilated oven at 35°C for 24 hours. The dry film is stored in a desiccator prior to characterization (Al-Hassan & Norziah, 2012).

Water-vapour permeability (WVP)

Water vapour permeability to determine the rate of water vapour transmission through unit area of flat material of unit thickness induced by unit vapour pressure difference between two surfaces under specific conditions of 100% relative humidity. The internal diameter and exposed film area of the test cup is determined. Film sample, was sealed with parafilm over a circular opening of the test cup which was stored at room temperature in a desiccator. Silica is placed inside the desiccator and distilled water was placed inside the cup to maintain 100% of relative humidity (RH) gradient across the film. The RH in the desiccator was always lower than inside the cup. The water vapour transferred through the film and absorbed by the desiccant was determined from the weight left in the cup which is recorded for every 1 hour. The cups were weighted initially, then at 1 hour intervals for the period of 6 hours (Alboofetileh, Rezaei, Hosseini, & Abdollahi, 2013). The measured WVP of each film is calculated as follow:

$$\mathrm{WVP} = \frac{\Delta m\,.\,e}{A\,.\,\Delta t\,.\,\Delta P}$$

From the equation above, WVP is the water vapour permeability (g/m.s.Pa); e is the average film thickness (m); $\Delta m/\Delta t$ is the moisture uptake rate (g/s); A is the exposed film are (m²); ΔP is the partial water vapour pressure difference (Pa) across the two sides of the film at 20°C (2.337×10^3Pa vapour pressure;100% RH inside the cup and 28.044 Pa water vapour pressure in the desiccator)(Alboofetileh et al., 2013).

Solubility in water

Film solubility test was performed by referred the method from Z. Torabi. Film for each variables were cut into small pieces (2 × 2 cm). Each film was weighed first before start the test. The samples were placed into the plastic cup with 30 mL distilled water. The samples were stirred with constant agitation (100 rpm) for 1 hour at room temperature. The samples were stirred by using agitation shaker. After 1 hour, the remaining pieces of film contained in the water were filtered through filter paper to collect the insoluble pieces of film. The step followed by drying the samples in the oven at 70°C to constant weight (Torabi & MohammadiNafchi, 2013). The calculation for the percentage of total soluble matter (% solubility) was calculated as follow:

$$Solubility = \frac{(Initial\ dried\ weight\ of\ film - Final\ dried\ weight\ of\ film)}{Initial\ dried\ weight\ of\ film} \times 100$$

Mechanical properties

Mechanical property measurements, tensile strength and percentage elongation at break and were obtained using Universal Texture Analyzer. For the film preparation before the mechanical test, the film were cut in strips (60×15 mm^2) and the thickness of each film was measured using micrometer. The strip then were clamped between tensile grips. The force (N) and the deformation (mm) were recorded during extension (Belibi et al., 2013). 25 load cell was used in tensile mode to measure the maximum tensile strength and the percentage of elongation at break of the film from stress-strain curve. The test speed was set to 30 mm/min. The tensile strength and percentage elongation at break was obtained by calculation. Tensile strength was calculated by dividing maximum load that the film can withstand by initial cross sectional area of the strip. Next, for percent elongation at break was obtained as the strain at the strain at the fracture point which corresponds to the ratio of the change of length of the specimen to initial length. The force (N) and the deformation (mm) were recorded during the extension. For each sample, three samples were analysed. The average of three result is reported (Oymaci & Altinkaya, 2016).

III. RESULTS AND DISCUSSION

Water-vapour permeability (WVP)

The water-vapour permeability is performed to determine the rate of vapour pass through the film for a period of time. The WVP calculated for different amount of clay is presented in Table

1. From the result, it shows that the WVP value for 15% of MMT clay was the lowest which is 1.0918×10^{-9} g/m.s.Pa. This value is lower compared to the film 0% of clay. The low value of WVP for the film containing clay caused by the presence of water vapour-impermeable silicate layer in the film. This is the effect from the clay which is MMT. The transmission of water vapour through the layer of film matrix is hindered by the layered structure of MMT caused by the tortuosity of the pathway (Alboofetileh et al., 2013). This make the transmission of water vapour slow for the film contained clay. However, for the 5%, 10% and 20% clay film not have low WVP value. The highest value of WVP is 20% clay film followed by 5% and 10% clay film. This might be happen due to the exposure of the film to the environment while the preparation was done.

Table 1: The value of WVP for each of the film contained different of clay.

Clay	WVP (g/m.s.Pa)
0%	3.3778E-09
5%	4.6061E-09
10%	4.0943E-09
15%	1.0918E-09
20%	5.2202E-09

Solubility in water

Solubility test is performed to analyse the resistance of the film toward water when applied on the surface of food product. The solubility in water also related to the biodegradability of the film. The result for the percentage of solubility of each film with different amount of MMT clay is given in Table 2. From the result, it showed the water solubility is low with the present of clay.

From the result obtained, the percentage of solubility of 0% of MMT clay is the highest which is 98.72%. The percent value is quite high which almost to 100% compared with the film that contained the addition of clay. Film contained 15% of clay was the lowest solubility percentage which indicate less soluble in the water. 15% of clay was the best amount of clay nanoparticles which lead to the lowest value of water solubility. This shows that the presence of clay will be the component that can caused the film to be less soluble in the water. The addition of clay nanoparticle suppressed the diffusion of water into the film structure layer. This due to the clay nanoparticle surrounded the film polymer (starch-protein) and made the water less accessible to the film (Belibi et al., 2013). The water solubility of clay film decreased as the amount of clay increased. However, the water solubility for the different amount of MMT clay in the film was inconsistent. This might happen due the nanoparticle that not fully surround the film polymer and leave the accessible of water in the film structure.

Table 2: The result relationship between the different percent of clay with the solubility percent of the film.

Clay	Solubility (%)
0%	98.72
5%	48
10%	54.72
15%	44.16
20%	53.03

Mechanical Properties

The analysis of mechanical properties of film was analyse by determining the tensile strength and elongation at break. The result was showed in Table 3 was the average from the three samples for each different amount of clay. From the result obtained, the tensile strength for film of 0% of clay was the highest which about 2.63×10^{2} MPa in average compared to the film that contained clay. The film of 15% clay contained result in the lowest tensile strength among the MMT clay film. The percentage of elongation at break for 0% of MMT clay film and 15% of clay film was not really difference. This showed that the film of 0% clay required more force to break the film at the same elongation. From the research (Souza et al., 2012), the study was done for the addition of clay to the cassava starch film. From this research, the increase amount of clay from 0, 0.05, 0.10g with constant amount of glycerol cause the decrease of tensile strength. The present of elongation also was decreased as the amount of clay increases. Excess clay content can caused the phase separation and poor particle distribution and next led to poor mechanism properties which proven by decreased in tensile strength when there is addition of clay to the film (Kampeerapappun, Aht-ong, Pentrakoon, & Srikulkit, 2007). From the Figure 1, the increased amount of clay showed the fluctuate graph. Standard deviation for tensile strength showed low value for all data which indicate the reliability of the testing. However, there was resulted from other researched that stated that the increase of clay amount result in high tensile strength and for the elongation at break percentage will be decreased as the clay amount increase. This result was stated in (De Carvalho, Curvelo, & Agnelli, 2001) research study where the tensile test for starch kaolin film cause increase of 50% tensile strength for 50 phr composition of clay. This may cause by the clay properties that give a strength to the film by hold the polymer molecule together and high force is required to break the film.

Next, the lowest percent elongation of film was 20% MMT clay film. This proved that the increased amount of clay result in the low percentage of elongation. This was the same result like the other researched. The elongation decrease was obtained as the amount of clay increases as showed in the Figure 2. Increase in the amount of clay result in increased the fragility of the composite. The amount of clay or size and the particle distribution may the cause of the effect the properties. For the 5% clay film, the percent of elongation is highest among the other film even the tensile strength is quite same with the 15% clay film. This means that the 5% clay film was less brittle compared to the 15% clay film because 5% clay film able to elongate longer with the quite same force applied to the 15% clay film.

Table 3: The result for mechanical properties, tensile strength and elongation at break.

Clay	Tensile strength, MPa	Standard deviation	Elongation at break, %
0%	**2.63E-02**	**0.0076**	**22.12**
5%	**8.33E-03**	**0.0021**	**60.67**
10%	**1.01E-02**	**0.0018**	**37.17**
15%	**6.74E-03**	**0.0008**	**28.92**
20%	**8.04E-03**	**0.0025**	**12.89**

Figure 1: The graph of mechanical properties for tensile strength.

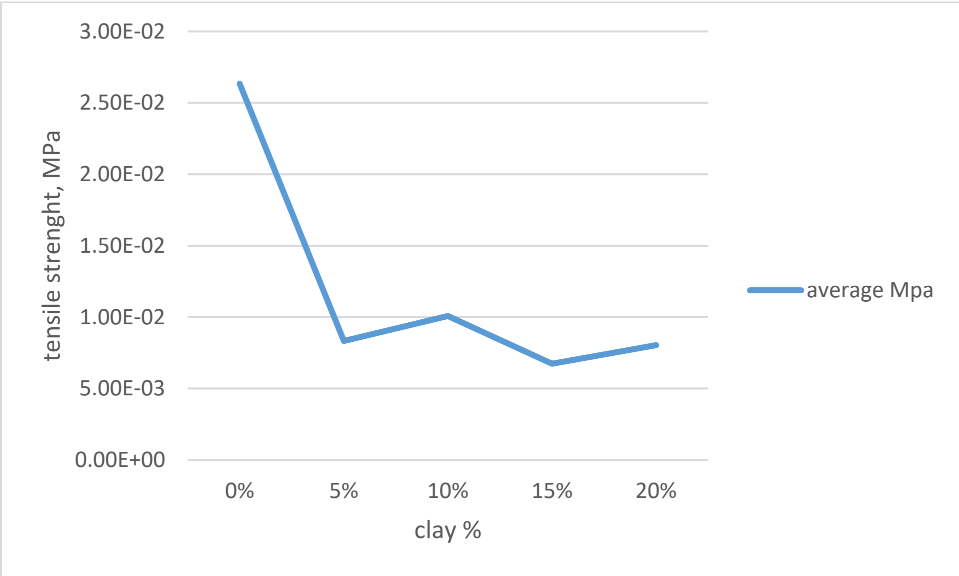
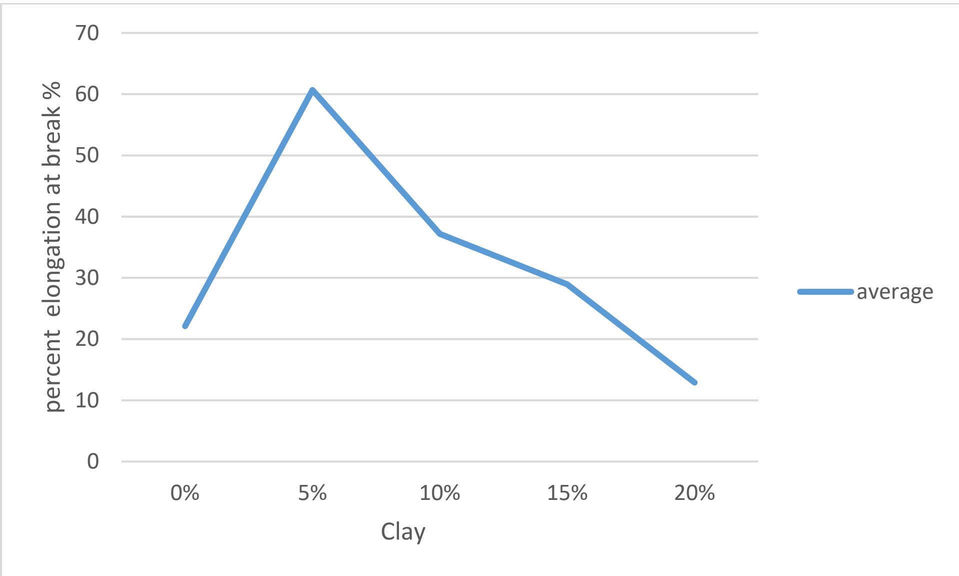


Figure 2: The graph of mechanical properties for percent elongation at break.



I. Conclusion

In this study, the influence of MMT clay content on the properties of the edible film made from starch-protein film was investigated. The used of MMT clay reduced the percentage of solubility of film in the water. This was related to the accessibility of water into the layer of the clay film. The resulted for water solubility for different amount of clay in the film was not consistent. Sample can be improved during the preparation of the experiment. The presence of clay also decreased the rate of water vapor permeability. There was inconsistent result for where the value of WVP should be decreased. This may happened due to the exposure of the film while preparing the experiment. Next, the presence of clay cause the tensile strength decreased and the elongation at break also decreased. The mechanical properties of composite material can caused by the amount of clay and the particle distribution. Incomplete dispersion of MMT clay decrease the reinforcing effect of MMT. At the end of this study, can be conclude that 5% clay film is the most suitable composition for food packaging application. The highest elongation at break for 5% clay film is significantly higher than other. In term of tensile strength value, 5% clay film is the third highest among the sample tested. High percentage of elongation at break is preferred because it showed the film is toughed when force applied to it. The film that have high value of tensile strength with the low percentage of elongation at break is can be brittle.

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