# DEVELOPMENT OF POLYVINYL ALCOHOL/CARBOXYMETHYL CELLULOSE/STARCH BIODEGRADABLE FILM FOR ACTIVE PACKAGING

By

MISS Chanya BOONTHOD

A Thesis Submitted in Partial Fulfillment of the Requirements
for Master of Engineering (CHEMICAL ENGINEERING)
Department of CHEMICAL ENGINEERING
Graduate School, Silpakorn University
Academic Year 2021

# การพัฒนาฟิล์มโพลิไวนิลแอลกอฮอล์/คาร์บอกซีเมทิลเซลลูโลส/แป้งที่ย่อยสลายได้ทางชีวภาพสำหรับการบรรจุภัณฑ์แบบแอคทีฟ

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Title		Development of Polyvinyl Alcohol/Carboxymethyl Cellulose/Starch
		Biodegradable Film for Active Packaging
By		Chanya BOONTHOD
Field of Study	(CHEMICAL ENGINEERING)
Advisor		Associate Professor Sirirat Wacharawichanant , D.Eng.

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MISS CHANYA BOONTHOD : DEVELOPMENT OF POLYVINYL ALCOHOL/CARBOXYMETHYL CELLULOSE/STARCH BIODEGRADABLE FILM FOR ACTIVE PACKAGING THESIS ADVISOR : ASSOCIATE PROFESSOR SIRIRAT WACHARAWICHANANT, D.Eng.

In this study, biodegradable films of polyvinyl alcohol (PVA)/carboxymethyl cellulose (CMC)/starch were prepared by solution casting method. The properties of PVA/CMC/starch films without citric acid (CA) and with CA were investigated. The Fourier-transform infrared spectroscopy (FTIR) studied functional group of the molecule on surface films appeared chemistry surface of composite films. This result indicates the interaction of crosslinking between the polymer chain. PVA/CMC/starch/CA films have reduced degree of swelling and water solubility which are better than without CA. The morphological analysis revealed the 10 phr of glycerol was used as a plasticizer in PVA/CMC/starch films due to the addition of glycerol resulted in more motion of the polymer chain. The surface becomes more homogeneous and smoother. The incorporation of PVA/CMC/starch/CA films resulted in a greater tensile strength when compared to other films. When CA was added to film, the Young's modulus was likewise raised. The thermal properties show the cross-linking between the modified PVA with the CMC and starch becomes more compact due to the addition of CA to the PVA/CMC/starch films and the stability of the films is enhanced. The PVA/CMC/starch films with CA added still had higher film transparency than the main film. Simultaneously, the UV absorption value is greater than. The water vapor transmission rate was found to be satisfactory for bioplastic films. The gas transmission rate values for the films tested were very good for both oxygen transmission rate and carbon dioxide transmission rate, which are important parts of active packaging. The PVA/CMC/starch/CA films showed better radical scavenging activity compared to other film, this may be due to the presence of CA in the film. Biodegradability test of bioplastic using soil burial test. Furthermore, it has the highest resistance to biodegradation, which was crosslinked with CA.

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# CHAPTER 1

# INTRODUCTION

Food packaging is a crucial part of food products, as it protects food quality and safety while also increasing the added value of food items. With the advancement of contemporary biotechnology, biodegradable films have gained increased attention as environmentally friendly materials and have developed into a new generation of hot research and development projects, as well as a critical component of a global economic sustainable development strategy. Food packaging materials with suitable mechanical properties, thermal properties, biodegradability, barrier properties, antibacterial and antioxidant features are important for food safety and lengthening the shelf life of packed foods [1]. Chemically synthesized polymeric films are frequently utilized in the food industry for packaging because they are simply and affordably manufactured from homogenous basic components and are both flexible and durable. A significant downside of these films is their non-biodegradability. Concerns about nonbiodegradable polymers made from petrochemicals have sparked research in biodegradable alternatives obtained from renewable sources [2]. Due to the environmental damage caused by synthetic plastic use, there is increased interest in biodegradable materials that may be safely and efficiently integrated into the ecosystem.

Nowadays, combining natural and synthetic polymers has grown into a revolutionary technique for improving the cost-performance ratio of the films produced. Polyvinyl alcohol (PVA) is the most widely manufactured biodegradable synthetic polymer on a global scale due to its superior physical qualities, chemical resilience, and total biodegradability [3]. A renewable, ecologically friendly and biodegradable material, bioplastics derived from biopolymers such as starch, cellulose (including lignin and chitin) are being developed. Their usage will help to waste reduction and the development of a more sustainable ecosystem [4]. Biodegradable materials may be developed using agricultural products such as proteins, cellulose, starch and other comparable compounds. Starch is a biopolymer present in the seeds, roots, and tubers of a wide variety of plants, such as corn, potato, wheat and rice. It is also present in a variety of foods, including cereals, fruits and vegetables. In nature, starch serves as the primary source of energy for plants and it has received much research attention because to its availability, low cost and edible and biodegradable qualities [3]. Biopolymers are directly blended into coatings to improve their characteristics. Bio-composites, also known as biodegradable composite films are made up of two or more biopolymers. Starch and cellulose, its derivatives are examples of polysaccharides used in the packaging business. Carboxymethyl cellulose (CMC), a water-soluble cellulose derivative. It can produce flexible and robust films on its own and it is harmless and inexpensive [5]. CMC is a biodegradable and biocompatible anionic polymer synthesized through chemical derivatization of natural cellulose. Due to its great water-absorbing capability, CMC is used in bread products to preserve moisture and increase structural integrity. It is typically blended with other stabilizers and gums. When dissolved in water, a viscous suspension is formed. It is soluble in a mixture of solvents, in aqueous solution with an aqueous organic solvent and in organic solvents. Numerous studies in the literature have addressed this problem and used polymers such as CMC and PVA as film forming materials [6]. Citric acid (CA) has been shown to form strong hydrogen bond interactions with starch, which makes it more stable at high temperatures and in water and stops it from breaking down again. CA has been used to make packaging films made from biopolymers. CA has three carboxyl groups that can make ester bonds with hydroxyl groups in the polysaccharide, which improves strength and water resistance of the films. CA is a weak acid and use for food preservation. To make food taste sour and smell good. There are lots of ways you can use it because it has a lot of different qualities. It is used a lot in the food and drink industry as a flavoring agent in foods that have been made. CA is an acid that comes from raw materials, so it is a natural acid. CA is the acid that is closest to us because it is used in the food industry to keep fruit and vegetables fresh and keep their texture. On the other hand, CA considerably lowered the tensile stress of products produced under the specified conditions. CA was also utilized as an additives in starch/PVA films due to its antibacterial and acidic properties [7].

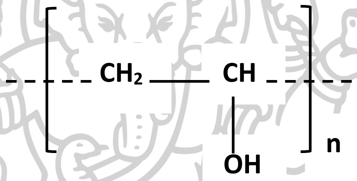
The food business is currently concerned about food quality and safety, since customers increasingly desire items that are fresher and less processed than previously. Most notably, foodborne bacterial contamination of ready-to-eat items is among the most significant health risks to the general public [1]. Attention to biodegradable plastics has arisen because of plastic problems because plastic is a difficult material to degrade. Hence, the idea was to use a material that has the same properties as plastics but is naturally biodegradable, which is the source of a material called biodegradable plastic. The biodegradable plastics may be prepared from natural polymers, synthetic polymers, or a combination of natural and synthetic polymers. Biomaterial was used to make packaging film and improve the mechanical properties of the PVA film, which PVA is the core material to develop active packaging biodegradable. PVA has high elasticity, high oxygen content, anti-odor and oil evaporation properties. Starch is considered a natural biodegradable polymer, which has attracted attention due to its good properties: high purity, low cost and high content. However, the starch film has low mechanical properties and high strength. In order to replace the poor mechanical properties of the starch-forming film, it was mixed with other biopolymers. CMC is a water-soluble biopolymer that is used as an additive in the food, cosmetic and pharmaceutical industries. Therefore, consumer desire for natural chemicals in all food applications has necessitated the employment of organic acids as crosslinkers. CA is the organic acid cross-linking used in this study, and it has the properties mentioned above. Because of their natural origin and physicochemical qualities, they are ideal for biopolymer food packaging films. This research also focuses on the development of bio-plastic films for active food packaging with primary qualities such as antioxidant and gas permeability, which will assist safeguard and maintain food quality. At the same time, when improving the film properties, it retains its strength and flexibility, making it suitable for food packaging and most significantly and biodegradable.

# CHAPTER 2

# THEORY

## 2.1 Polyvinyl alcohol (PVA)

Polyvinyl alcohol (PVA) is a synthetic polymer that is water soluble and has the qualities of being easy to prepare, having good biodegradability, being flammable, having no odor, having great chemical resistance and having strong mechanical properties. PVA possessed unique qualities that distinguished it from other thermoplastics. There have been several biomaterial uses for PVA [1]. PVA is a polymer with a solely carbon-based backbone. Both aerobic and anaerobic conditions are suitable for degrading PVA. Indeed, the physical properties of PVA are influenced by the method of hydrolysis or partial hydrolysis of polyvinyl acetate that is used to prepare it. Because of this, PVA may be categorized according to hydrolysis degree. Fully hydrolyzed and partially hydrolyzed PVA are known to be utilized in food. PVA may be utilized for film development because of its good film forming capability, full biodegradability, crystal modulus and wide range of crystallinity [8]. PVA is a semi-crystalline synthetic polymer with overhanging hydroxyl groups; it has excellent thermal stability, biocompatibility and mechanical qualities [9]. PVA is also frequently employed in the production of paper products, among other applications. PVA is a food additive that is used as a binder, thickener and stabilizer in the food business. PVA is used as a sizing and coating agent in the same way that it is in textiles [8]. PVA is a polymer with a linear structure that is nontoxic and noncarcinogenic. It is relatively insoluble in organic solvents and its solubility in aqueous solution is adaptable to its necessary application. PVA has outstanding compatibility with other materials, as well as excellent film forming capacity and strong emulsifying and adhesive capabilities, which have resulted in its widespread usage in industrial applications. PVA films have a reduced water adsorption capacity, but they also have a high tensile strength and are highly flexible. It also has excellent barrier characteristics against oxygen and aromatics. It has been demonstrated that the addition of PVA to biodegradable packaging improves the mechanical qualities and water resistance of the packaging [3]. PVA is valued for its excellent mechanical properties in the dry state, resistance to common solvents, barrier effect in dry environments and the ability to be used in food contact applications when the grade is appropriate. PVA is widely used not just in food packaging, but also in a variety of other applications such as the home and construction industries. Because of its superior qualities, including as mechanical performance, solvent resistance and biocompatibility, it is widely used in the construction industry. Furthermore, the low biodegradation rate and high moisture absorption of PVA are two of the most frequent characteristics that make it a good choice for food packaging applications. PVA is regularly blended with various biopolymers and/or biobased reinforcements in order to improve its performance and environmental qualities [6].



$$-\!\!\left[ CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} \right]_n\!\!-$$

Figure 1 Structure of PVA [10].

### 2.2 Carboxymethyl cellulose (CMC)

A chemical process called "derivatization" makes carboxymethyl cellulose (CMC), which is a biodegradable and biocompatible anionic polymer made from natural cellulose. CMC has no negative effects on human health. Carboxymethyl cellulose (CMC) is a biodegradable and biocompatible anionic polymer processed from natural cellulose by chemical derivatization. Moreover, CMC has no adverse impact on human health. CMC is a very effective addition used to enhance the quality and processing qualities of a wide variety of items ranging from meals, medicines, and cosmetics to textile and paper products [2]. CMC is a water-soluble cellulose derivative. It's harmless and it forms strong, flexible films on its own. Solubility in hot and cold water, high viscosity, capacity to induce viscosity in solution and the ability to create films make it a popular food additive. Preparation of films involves the use of plasticizers, which contain a variety of ingredients such as water, glycerol, fatty acids and acetone to improve mechanical strength and flexibility. It improves tensile strength of the films by altering their three-dimensional structure. Besides to their high efficiency, they should be also nontoxic and edible [5]. Due to its high water absorption capacity, CMC is used to retain moisture and improve the structural consistency of bekery products. It is typically blended with other stabilizers and gums [6].

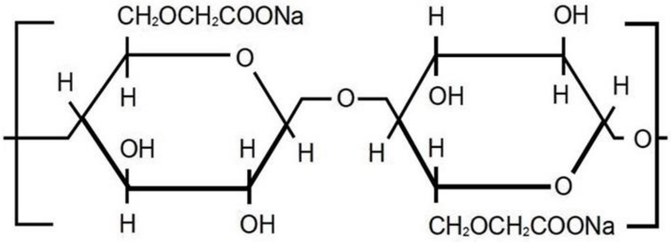


Figure 2 Molecular structure of CMC [11].

### 2.3 Starch

Renewable materials such as biodegradable polymers and polysaccharides, are often regarded as excellent candidates to replace synthetic polymers in a wide range of uses particularly in the food industry. Starch is the most major polysaccharide polymer employed in the development of biodegradable films and it is also the most abundant. Because it has the potential to build a continuous matrix and because it is a renewable and abundant resource, it is commonly used in construction [2]. Starch is a sustainable option for producing biodegradable materials for food packaging. Furthermore, because they are easily derived from renewable sources and are affordable, starch-based resins have enormous promise in packaging, medicines, cosmetics, paper and other sectors. Native starch exists as distinct and semi crystalline tiny granules held together by a long micellar network of related molecules, making it difficult to digest or melt. [12]. Despite this, starch-based films have poor mechanical characteristics and excessive stiffness, which restricts their use in material engineering applications because of this. Natural starches have water-resistant qualities that are altered by chemical modification, which is based on the reactivity of hydroxyl groups and the insertion of new functional groups into polysaccharide chains. To compensate for the poor mechanical qualities of starch-based films, the incorporation of additional biopolymers such as PVA, gelatin and chitosan has been investigated as a possible solution. The combination of two or more polymers allows for the creation of novel materials that have improved mechanical properties as well as gas barrier characteristics. Furthermore, it has the potential to be a viable alternative to synthetic food packaging materials in some instances [3].

### 2.4 Citric acid

Citric acid (CA) is a naturally occurring organic acid that may be found in citrus fruits and various berries, among other things. CA is a preservative and flavoring ingredient that is widely used in the food industry. For the creation of biopolymer-based packaging films, it has been employed as a crosslinker by researchers. CA has one hydroxyl and three carboxyl groups and is a naturally occurring organic acid that may form ester bonds with the hydroxyl groups of polysaccharide molecules, increasing the mechanical characteristics and water resistance of the films [13]. CA was chosen as the additive due to the possibility of esterification between the carboxyl groups of CA and the hydroxyl groups of PVA and starch. This interaction would increase the water resistance of starch by limiting the number of accessible OH groups. On the other hand, the carboxyl groups in CA can generate stronger hydrogen bonds with the hydroxyl groups in starch molecules, preventing retrograde and recrystallization. Additionally, due to the multi-carboxyl structure, CA may act as a cross-linking agent, enhancing the mechanical characteristics and water resistance. CA is nutritionally innocuous because it is a nontoxic metabolic product of the body and has previously been licensed for use in food formulations by the Food and Drug Administration (FDA) [2].

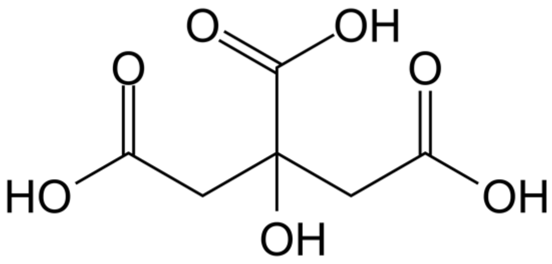


Figure 3 Structure of CA [14].

## 2.5 Polymer solution casting

The solution mixing system is a two- or multi-component polymer that is often applied by pouring a low viscosity material at room temperature and allowing it to interact in situ, occasionally with additional heat or by responding to the heat generated by the exothermic reaction to effect the cure. The two components are commonly referred to as component A and component B. Component A is the basic polymer, while component B is the enhancement additive. The requisite proportions for optimal stoichiometry are critical for the polymerized system to exhibit the desired chemical and physical characteristics. Generally, the needed proportions are expressed as percentages of weight. A typical solution casting method is shown in the figure [15].

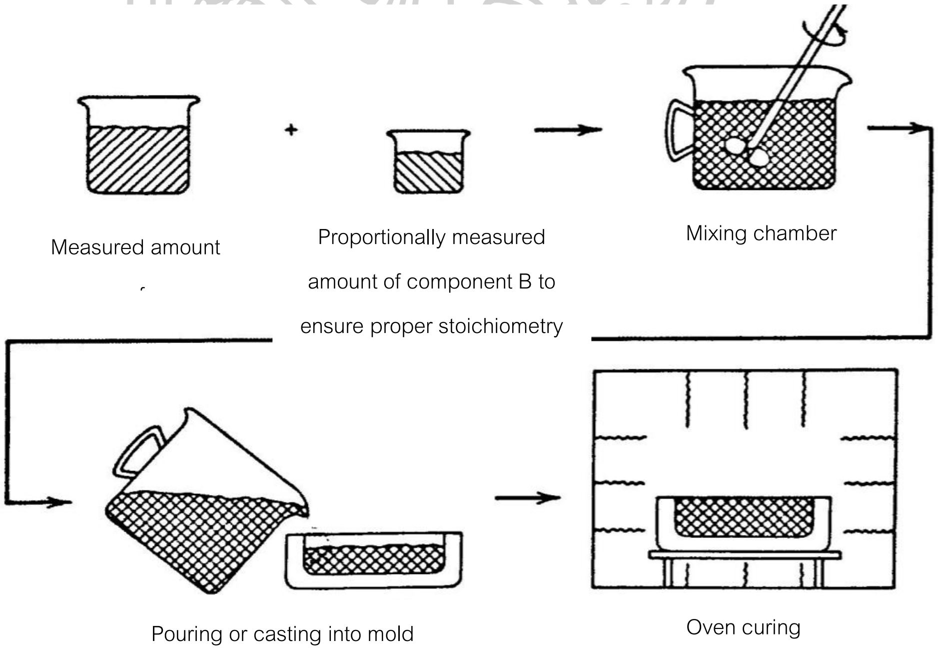


Figure 4 Hand mixing, proportioning, casting and curing of a two-component liquid reactive resin system [15].

When opposed to melt methods, solution casting frequently provides superior quality and thinner films. Solution casting is the process of spreading a polymer solution (50-80% solvent) onto a thin layer and then removing the solvent. The dried film is significantly thinner than the initial solution film thickness and the drying process can also be employed to modify the final film properties [16]. Solvent cast technique is becoming more appealing for the creation of films with exceptionally high quality criteria. This method has several advantages, including consistent thickness distribution, optimum optical purity and exceptionally minimal haze. Many process techniques are employed to offer characteristics, such as co-solvent systems, overpressure dissolution, the use of polymers or co-polymers with unusual molecular weight distributions, as well as additives such as plasticizers and release agents and so on. Solution casting a polymer liquid in a solvent onto a temporary substrate provides several advantages, including more uniform thickness distribution, increased dimensional stability and optical purity. Furthermore, multi-layer coating technologies allow for the inclusion of functional coatings during the film casting process, hence minimizing the expense of later coating stages [17].

### 2.6 Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy can be used effectively in specialized areas such as microanalysis, where solid state samples require the use of special reflectance techniques, in investigations with a focus on quantitative evaluation, where high sensitivity is required, in the analysis of aqueous solutions or dark and in experiments where analysis time is a limiting factor, such as in process or quality control measurements [18].

A typical FTIR spectrometer is made up of a source, an interferometer, a sample compartment, a detector, an amplifier, an A/D converter and a computer. The source emits radiation, which goes through the interferometer and into the detector. The signal is then amplified and transformed to digital by the amplifier and analog-to-digital converter. Finally, the signal is sent to a computer, where the fourier transform is performed. Figure 5 depicts an FTIR spectrometer diagram [19].

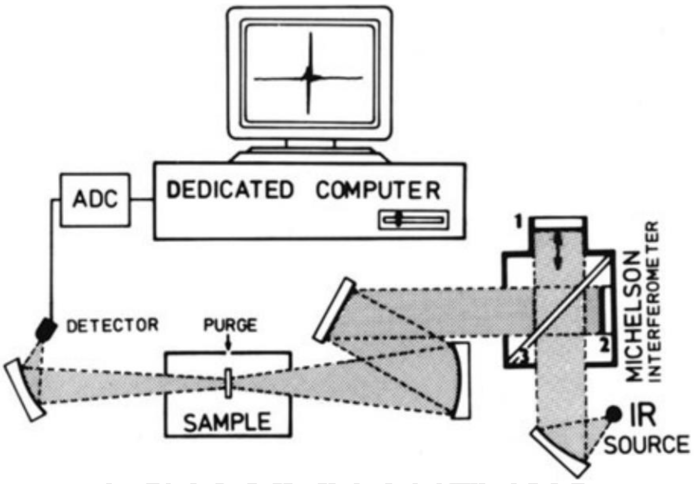


Figure 5 A FTIR instrument's schematic diagram: 1 moving mirror, 2 fixed mirrors, and 3 beam splitters built of KBr or CsI as the supporter and covered with a thin germanium layer, Analog-to-digital-converter (ADC) [18].

## 2.7 Scanning electron microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that scans the surfaces of microorganisms by focusing and scanning them with a stream of electrons traveling at a low intensity. The SEM operates on the idea of using kinetic energy to generate signals from electron interaction. The secondary electrons generated by the specimen are primarily used to identify of the specimen shape and topography, whilst the backscattered electrons reveal contrasts in the composition of the components of the specimen [20]. SEM analyzes the surfaces of materials, particles, and fibers in order to quantify and evaluate small features using image analysis. It can give a plethora of data to aid in the investigation of biological, chemical or material samples. Our specialists use SEM to investigate surfaces, materials, films, coatings, minerals, raw materials, metals, polymers, food, dust, catalysts, biological tissues, pollutants and unknown compounds. They generate high-resolution pictures, make important observations, and take measurements [21].

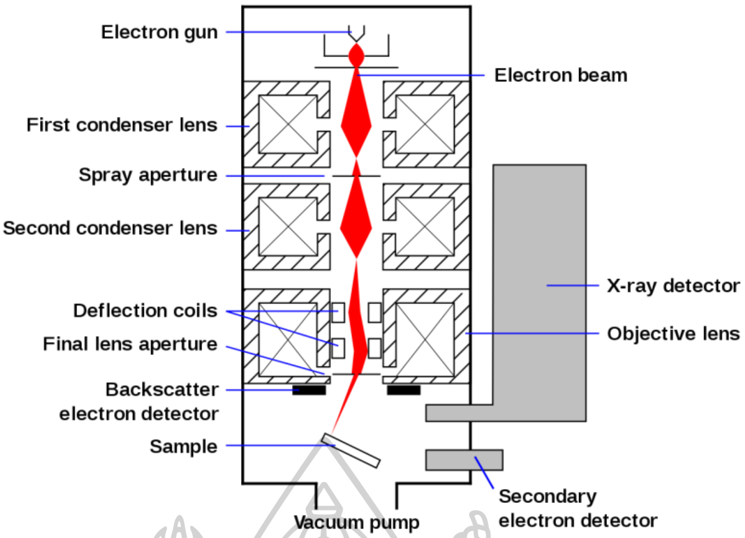


Figure 6 Operation of a Scanning electron microscope (SEM) [20].

### 2.8 Universal tensile testing

A tensile test is one of the most fundamental mechanical tests that can be done on a material. It involves subjecting the sample to a controlled tensile force until failure. The tensile force is immediately measured when the gauge length is increased. These values are transformed to engineering stress and strain, which results in a stress-strain curve identical to the force-elongation curve. The benefit of stress-strain management over load-elongation is that the stress-strain curve is nearly invariant with respect to specimen size [22]. This test technique is applicable for determining the tensile characteristics of plastics in the form of thin sheeting, including film with a thickness of less than 1.0 mm. Tensile characteristics may be utilized to aid in the creation of new products and processes, as well as quality and specification control. However, the results from such testing cannot be deemed meaningful for applications that operate at a load time scale that is significantly different from the load time scale employed in the tests. The tensile modulus of elasticity is a measure of the hardness of a thin plastic sheet. Reproducibility of test findings is excellent when precise control of all test circumstances is maintained. When evaluating the hardness of various materials, identical specimens of the same size are necessary. Tensile strength is determined by dividing the greatest weight by the original minimum cross-sectional area of the specimen. The result must be given in unit of area, often megapascals. This value must be reported to three significant.

## 2.9 Thermogravimetric analysis (TGA)

TGA is a method that determines the mass of a material as a function of temperature or time when the sample is submitted to a controlled temperature program in a controlled environment. The TGA is comprised of a sample tray and a precision balance. The pan was heated or cooled in the furnace during the experiment. Throughout the experiment, the mass of the sample is determined. The gas used to remove the sample regulates the sample environment. This gas can be either inert or reactive and flows over the sample before exiting via an exhaust. TGA analysis is commonly used to characterize and examine materials. The TGA is applicable to most industries. Thermogravimetric and evolved gas analyses are mostly used in the food science, environmental, pharmaceutical, and petrochemical industries [23].

Mass change occurs when a sample loses material in a different way or reacts to the surrounding atmosphere. This results in steps or peaks in the TGA or DTG curves. Numerous causes can result in sample loss, mass growth, or even gain, resulting in steps on the TGA curve. These devices can quantify water loss, plasticizer loss, solvent loss, weight percent filler, oxidation, pyrolysis and breakdown, as well as the quantity of metallic catalytic residue left on carbon nanotubes. TGA curves are often used to show the results of TGA measurements, in which mass or percentage is plotted versus temperature and/or time. A secondary and supplemental presentation is the first derivative of the TGA curve with respect to temperature or time. This graph depicts the rate of mass change and is referred to as the differential thermogravimetric or DTG curve [24].

## 2.10 Ultraviolet-visible spectroscopy (UV-Vis)

In analytical chemistry, ultraviolet and visible spectrometers are considered critical tools. Indeed, this is a frequently utilized approach in both clinical and chemical laboratories. This tool is used to identify compounds and do qualitative analysis. However, it is mostly used to quantify diverse chemical and inorganic substances in solutions. Spectroscopy in general is concerned with the interaction of light and matter. When light is absorbed by matter, the energy content of the atoms or molecules increases. Chemical compounds absorb visible or ultraviolet light in distinct ways, resulting in distinct spectra. Absorption of UV light results in the excitation of electrons from their ground state to a higher energy state. According to the theory behind this concept, the energy received from UV light is equal to the difference in energy between the higher energy level and the ground state. The principle of the UV spectrophotometer is based on Beer-Lambert's law. When a monochromatic light beam travels through a solution containing an absorbent, this rule is true. The rate at which the radiation intensity decreases and the thickness of the absorbent solution increases is related to the concentration of the solution and the incident radiation [25].

The transmission or reflection of a sample can be used to identify the shape of the absorption edge. The transmission measurement may be used to identify the absorption edge and energy band gap. When light emits from a thin film material with an energy equal to or higher than the frequency band gap, photons may be absorbed and electrons elevated in energy from the valence band to form electron-hole pairs and the conduction band. The capacity of a substance to absorb photons of a certain wavelength is quantified using the absorbance coefficient, which is expressed in mutual distance units [26].

## 2.11 Water vapor transmission rate (WVTR)

One of the most important functions of food packaging is to keep foodstuffs dry and wet. Without protective packaging, the product will quickly absorb or lose moisture until it achieves a state of balance with the relative humidity of its surroundings. Water vapor transmission rate (WVTR) is the steady-state rate at which water vapor penetrates a film under given temperature and relative humidity circumstances. WVTR is the industry standard for comparing the capacity of films to resist moisture transfer, with lower values indicating greater moisture protection. The water vapor transmission rate of flexible barrier materials used in packaging or industrial applications is determined by WVTR. The thickness of the material, as well as environmental parameters such as relative humidity and temperature, are important in understanding material permeation.

The MOCON Permatran equipment was used to assess water permeability where the film under examination divides the test cell into two chambers. Humidified nitrogen enters the cell and departs through an exhaust vent. To transport the water vapor that penetrated the film to the sensor, pre-dried, moisture-free nitrogen is continually supplied to the inner half of the test cell. Allowing the humidified nitrogen to flow until the WVTR achieved equilibrium [27].

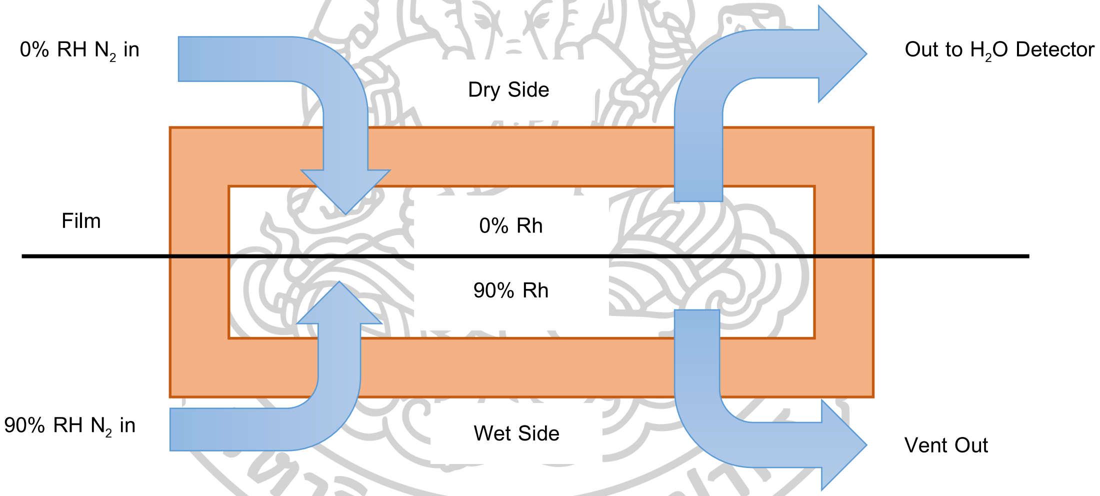


Figure 7 Cross-section of a WVTR test cell.

Exxon Mobil standardizes its reporting to 100°F (37.8°C) and 90% RH. A test cell is conceptually similar to Figure 7: dry nitrogen gas is swept through a chamber, with the test film acting as a membrane separating the dry nitrogen gas stream from a wet nitrogen stream on the opposite side. The difference in partial pressure works as a catalyst for water vapor to permeate the film and reach the low-pressure side. The barrier of the film determines how much water vapor can get through and an infrared detector in the outgoing stream of the dry side continuously records this transfer. The test is finished when the infrared sensor sees water molecules exiting the dry chamber at a consistent pace, which is when equilibrium or steady state is reached. This is the sample WVTR and it is measured in units of g/(m$^2$-day) at 100°F (37.8°C) and 90% RH [28].

## 2.12 Gas transmission rate (GTR)

Oxygen, an essential ingredient for humans is a key source of the reactions related with food deterioration. Coffee, tea, chocolate, nuts, meat, gourmet snacks and retorted goods can all be affected by oxidative deterioration because to their sensitive color, taste and microbiological stability. The two basic ways to avoiding undesired oxygen-induced reactions throughout shelf life are vacuum packing, which removes air from a package and modified atmosphere packaging (MAP), which replaces the air in a container with nitrogen or carbon dioxide. Maintaining product quality with either strategy is dependent on packaging of the film capacity to operate as a barrier, countering the natural drive caused by the difference in oxygen partial pressures inside the package (0-2%) and outside the package (21%). The oxygen transmission rate (OTR) is the rate at which oxygen gas permeates a film in a steady state. A good oxygen barrier is obtained by combining functional layers to form a film that possesses the needed barrier qualities as well as those necessary for the production of a serviceable package. Another part, the carbon dioxide ($CO_2$) contained in the packaging is produced by fermentation by yeast or certain microorganisms released during growth through respiration of plants such as fresh fruits and vegetables, or by chemical reactions in food. Carbon dioxide is required to be extracted from the product to protect the packaging. The carbon dioxide released combines with the water in the food. It becomes carbonic acid, causing the pH on the surface of the food to decrease, which can inhibit the growth of bacteria, especially pathogenic bacteria. A gas permeability tester was used to determine the gas transmission rate, GTR (carbon dioxide transmission rate and oxygen transmission rate). The gas permeability tester was developed for the purpose of determining the permeability of films. It features an exterior water bath circulator that allows for a wider temperature range.

## 2.13 Antioxidant

Antioxidants have received a lot of attention for their ability to improve the stability of food products susceptible to oxidation. A wide range of synthetic and natural antioxidant chemicals have been identified as having antioxidant action in active packaging systems. As a result, a careful selection should be made, taking into account dietary features as well as health and safety concerns. Antioxidants are thus used in food packaging systems to inhibit oxidation processes and to improve the shelf life of food goods [29]. The DPPH method will be used in this research. DPPH is a common abbreviation for the organic chemical compound 2,2-diphenyl-1-picrylhydrazyl. It is a dark-colored crystalline powder composed of stable free radical molecules. DPPH is a chemical reaction monitor that detects chemical processes involving radicals; it is most commonly used as an antioxidant test. This characteristic enables visual monitoring of the reaction and the counting of the initial radicals. The antioxidants reduce the DPPH radicals to diphenyl picrylhydrazine, a yellow-colored compound and the reaction extent relies on the hydrogen-donating ability of the antioxidants [30]. DPPH is a well-known extremist who serves as a snare ("scavenger") for other radicals. As a result, the rate decrease of a chemical reaction caused by the addition of DPPH is used to determine the radical character of that reaction. Due to the strong absorbance band centered around 514-520 nm, DPPH radial is dark purple in solution and becomes colorless or pale yellow when neutralized.

## 2.14 Soil burial test (SBT)

Bioplastics or biodegradable plastics refer to plastics made from natural materials. Most of them are derived from plants and are biodegradable in nature, helping to reduce environmental pollution problems. Biodegradable plastics contain at least one active ingredient that is a biopolymer. Most of the raw materials used in production are new or renewable raw materials. It can be divided into 5 main types of degradation: photodegradation, mechanical degradation, oxidative degradation, hydrolytic degradation and biodegradation. In order for the efficient and rapid degradation of polymers or bioplastics, there are important factors to consider: the polymer's chemical structure, microbial type and environmental conditions [31]. SBT method is a common method for quantitatively identifying bioplastic breakdown. The biodegradability of starch-based bioplastic was assessed by analyzing physical changes in the bioplastic, such as color changes and weight loss [32]. Bioplastic samples were immersed in compost soil before being incubated at room temperature. After that, the buried samples were cleaned and weighed.

# CHAPTER 3

# LITERATURE REVIEWS

**Carlos Alberto Gomez-Aldapa et al.** [3] prepared film from different blends of potato starch and PVA. They demonstrated superior mechanical, water adsorption and permeability capabilities when compared to pure starch films, owing to the fact that combining two or more polymers results in the formation of novel materials with improved functional qualities. The addition of PVA enhanced the functional characteristics, gas permeability and mechanical properties of potato starch films substantially. PVA produced potato starch films with adequate qualities for use in food packaging and as a biodegradable substitute for synthetic packaging materials.

**Carolina Medina-Jaramillo et al.** [33] investigated the possibility of using biodegradable thermoplastic films derived from cassava starch and natural compounds such as green tea and basil as smart and active food packaging. Furthermore, it was noted that the films degrade rapidly in soil (less than two weeks), resulting in ecologically beneficial materials. The addition of tea and basil extracts to films decreased their water vapor permeability in comparison to conventional thermoplastic starch-based polymers while maintaining their flexibility for easy handling.

**Bushra H. Musa et al.** [34] investigated the properties of PVA and corn starch for application in drug delivery. The cast process was used to make PVA and corn starch blend films. The results showed that adding starch to PVA reduced elongation and tensile strength while increased Young's modulus. An optical microscope gave a great depiction of the starch particle dispersion in mix films containing up to 30 wt% starch. Agglomeration and voids in the film occur when starch concentration is increased to 35, 40, or 50 wt%.

**Hanna Christophliemk et al.** [35] studied the effects of corn starch coatings using an ethylene modified PVA grade. When compared to a regular PVA grade, an ethylene modified PVA grade provided lower oxygen transfer rates at high relative humidity. The creation of an intelligent starch/PVA film capable of detecting pH changes and suppressing undesired microbial growth in meals was accomplished.

**Bin Liu et al.** [36] studied starch/PVA film, which were doubly cross-linked to improve their water-resistance and mechanical strength. On pasteurized milk, the resultant film showed good color indication and antibacterial activity. The results indicate that the intelligent film is capable of both alerting and suppressing food deterioration.

**Daranee Khunphet et al.** [37] studied the mechanical characteristics of PVA/Sodium carboxymethyl cellulose (Na-CMC) thin films intended in order to be used as active food packaging. The thin films were enhanced by combining them with starch (0–40 wt%) and glycerol (0–15 wt%) and casting them from solution using hot water as solvent. The mechanical and thermal characteristics, as well as the surface morphology of thin films of PVA/Na-CMC/starch were examined. It was discovered that adding less than 40 wt% starch and utilizing glycerol as a plasticizer boosted the flexibility and miscibility of polymer blend films and thin films PVA/Na-CMC/starch, as confirmed by tensile tests, SEM pictures and thermal analysis.

**Mahsa Tabari** [5] studied cold water fish gelatin and CMC composite films. When compared to the fish gelatin film, increasing the concentration of CMC lowered the equilibrium moisture and enhanced the mechanical characteristics of composite films. It also raised the tensile stress and hardness of the film while decreasing its elongation. The results showed composite films had better physical and mechanical properties than the fish gelatin film. In addition, cold water containing CMC can be used as an alternate packaging material for several natural and manufactured items.

**Hye-Ryoung Park et al.** [38] prepared glycerol (GL), sorbitol (SO) and CA to create the starch/PVA blend films. GL contains three hydroxyl groups, SO has six hydroxyl groups, while CA has one hydroxyl group and three carboxyl groups structurally. The effect of mixing time, extra components and drying temperature on film characteristics was examined. The starch/PVA mix film with CA outperformed the others in terms of tensile strength and elongation (%). Except for degree of swelling, the film containing CA performed better than GL or SO in all measurements because hydrogen bonding between the hydroxyl and carboxyl groups in the presence of CA improved the inter/intramolecular interaction between starch, PVA and additives.

**Narendra Reddy et al.** [7] studied the potential of strength and stability by cross-linking starch films with CA. CA cross-linked starch films have a greater strength than non-cross-linked starch films and are stronger than the majority of previously produced cross-linked starch and synthetic polymer blended films.

**Babak Ghanbarzadeh et al.** [2] studied the impact of CA and CMC on the barrier and mechanical characteristics of starch films. The inclusion of CMC increased moisture resistance of the composites. Moreover, expanding the CA content most likely resulted in an increase in chain mobility, interchain spaces and voids because the incorporation of residual-free CA molecules between the polymer chains, which promotes water vapor transmission and strain at break (SB) values while decreasing ultimate tensile strength (UTS) values.

**Zhijun Wu et al.** [39] studied starch and PVA composite and modified them to obtain films with improved antibacterial, mechanical and thermal characteristics by developing biodegradable antimicrobial films based on PVA/starch. Solvent casting was used to produce practical food packaging films composed of a starch/PVA ternary combination. Several composite films were created utilizing varying quantities of CA, drying durations and primary component proportions. The composite film was discovered to have a high water retention capacity as well as a high-water resistance. Because of their excellent antibacterial properties, the starch/PVA/CA composites have a great potential for packaging highly breathable fresh agricultural items as antifogging packaging films and active food packaging systems.

**Sweetie R. Kanatt et al.** [13] investigated the functional and water-resistant film made of CMC/PVA as polymers, which might improve the safety and shelf life of minced chicken meat during chilled storage. The films were created using the casting method. The addition of CA increased the mechanical properties of the CMC/PVA film while decreasing its water solubility, moisture content, water vapor permeability and physicochemical properties. As a consequence, the findings of this study suggested that a composite film made of CMC/PVA with CA as the cross linker and aloe-vera as the active component has potential applications in the food industry.

# CHAPTER 4

# EXPERIMENTAL PROCEDURE

The methodology of the research, including the chemicals utilized in the experiment, sample preparation and sample characterization of PVA/CMC/starch composite films is described in this chapter.

## 4.1 Material

### 4.1.1 Polyvinyl alcohol (PVA)

PVA (a molecular weight range of 115,000; viscosity 25-32 cP and degree of hydrolysis 98-99 mole%) was produced by LOBA chemie pvt.ltd (Mumbai, India).

### 4.1.2 Carboxymethyl cellulose (CMC)

Carboxymethyl cellulose (CMC) having viscosity of 1,700-2,200 mPa.s and was produced by SHANDONG HEAD (China).

### 4.1.3 Starch

Tapioca starch was purchased from Thai wah food products public co., ltd. (Thailand).

### 4.1.4 Citric acid

Citric acid monohydrate (CA) of food grade quality was sourced from China. CA has colorless crystals or white crystalline powder.

## 4.2 Sample preparation

PVA/CMC/starch films without and with CA (15 phr) were made in the following ratios: 45:45:10, 40:40:20 and 35:35:30 are shown in Table 1. CMC were disseminated in DI water over an overnight period at room temperature. In DI water, the starch mixture was stirred and heated to 80°C, then PVA was added and stirred constantly for 30 minutes at 80°C. Once the PVA and starch have dissolved, the dissolved CMC was added and stirred for another 30 minutes. When all three mixtures were dissolved, glycerol was added to make the solution more compatible. After that, the solution was stirred at room temperature, when the substance cooled down, CA 15 phr was added and continued stirring without heat for another 2 hours. A compatible solution was obtained and the solution was casting onto an acrylic tray. The solution was vaporized in an oven at 60°C. Afterwards, dried composite films with thicknesses ranging from 0.02-0.03 mm were collected and examined for characteristics.

Table 1 The composition of PVA/CMC/starch films without and with CA.

| **Film** | **PVA** (wt%) | **CMC** (wt%) | **Starch** (wt%) | **Citric acid** (phr) |
|---|---|---|---|---|
| P01 | 45 | 45 | 10 | - |
| P02 | 40 | 40 | 20 | - |
| P03 | 35 | 35 | 30 | - |
| PCS1 | 45 | 45 | 10 | 15 |
| PCS2 | 40 | 40 | 20 | 15 |
| PCS3 | 35 | 35 | 30 | 15 |

### 4.3 Sample characterization

#### 4.3.1 Fourier transform infrared spectroscopy (FTIR)

The surface functional groups of film samples were measured using an FTIR (Nicolet 6700, Thermo Scientific, USA) in the wavenumber range 400 to 4000 cm$^{-1}$, as shown in Figure 8.

Figure 8 Fourier-transform infrared spectroscopy (Nicolet 6700, Thermo scientific, USA).

### 4.3.2 Degree of swelling and water solubility

The dry films were soaked in distilled water for 24 hours at room temperature. Excess water was removed and the weight of the wet and swollen films was calculated. The following formula was used to estimate the proportion of swelling in films:

$$\text{Degree of swelling} = (W_e - W_0) / W_0 \times 100 \quad (1)$$

The films were then dried once more until they reached a consistent weight, and the percentage solubility in water was measured as follows:

$$\text{Solubility of the films (\%)} = (W_0 - W_d) / W_0 \times 100 \quad (2)$$

Where, $W_e$ is the weight of the film at absorbing equilibrium, $W_0$ is the initial dry weight of the film and Wd is the dry weight of the film following the final drying process.

### 4.3.3 Scanning electron microscopy (SEM)

The morphology and dispersion of starch, CMC and CA in the PVA matrix of the composite films were observed using a scanning electron microscope (MIRA3, TESCAN, Czech), as shown in Figure 9. All samples were gold-coated and detected using backscattered electrons (BSE) at a 5 kV accelerating voltage.

Figure 9 Scanning electron microscopy (MIRA3, TESCAN).

### 4.3.4 Universal tensile testing

The mechanical characteristics of the films were examined by universal tensile testing (EZ-LX model, Shimadzu, Japan), as shown in Figure 10. The specimen dimensions were 120 x 15 mm and the gage length was 100 mm. Tensile testing was carried out at a crosshead speed of 50 mm/min. The acquired findings were the average of the results of five samples.

Figure 10 Universal tensile testing (EZ-LX model, Shimadzu, Japan).

### 4.3.5 Thermogravimetric analysis (TGA)

TGA (SDT Q600, TA Instruments, UK) was used to analyze the thermal stability of the composite films, as shown in Figure 11. The composite films produced by the solution casting process were split into small pieces weighing about 10-15 mg. The experiment was conducted out in a nitrogen environment at temperatures ranging from 50 to 600 ˚C at a heating rate of 10 ˚C/min.

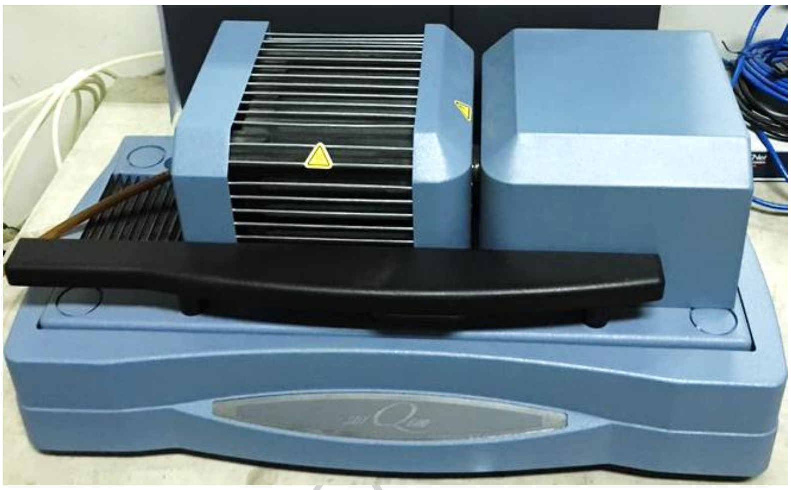


Figure 11 TA Instruments (SDT-Q600, UK).

### 4.3.6 Ultraviolet visible spectroscopy (UV-Vis)

As illustrated in Figure 12, a UV-Vis spectrophotometer (Cary 5000, Varian, USA) was used to assess UV absorption of the composite films in the wavelength range of 200-800 nm. As depicted in Fig 13, a UV-Vis spectrophotometer (T92+, PG Instruments, UK) was used to detect UV absorbance at 518 nm to assess the DPPH scavenging activity of the composite films.

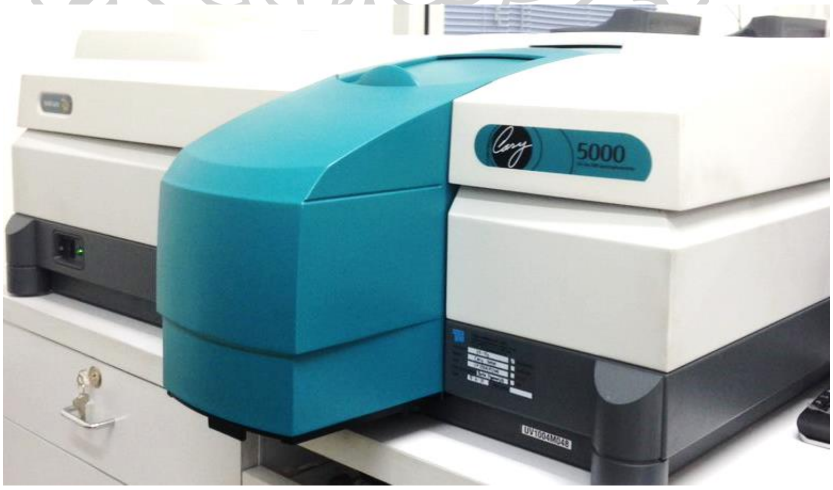


Figure 12 UV-Vis spectrophotometer (Cary 5000, Varian, USA).

Figure 13 UV-Vis spectrophotometer (T92+, PG Instruments, UK).

### 4.3.7 Water vapor transmission rate (WVTR)

The MOCON Permatran W® instrument, as shown in Figure 14, was used to measurement water vapor transmission rate (WVTR) and instrument use method comply with ASTM F1249.

Figure 14 The MOCON Permatran W® instrument.

### 4.3.8 Gas permeability tester

Gas permeability tester (Brugger, Munich, Germany), as shown in Figure 15, was used to determine the permeability of dry gases for packing materials using the manometric method. It is used to measure oxygen transmission rate (OTR) and carbon dioxide transmission rate ($CO_2TR$) for food packaging films.

Figure 15 Gas permeability tester (Brugger Feinmechanik, Munich, Germany).

### 4.3.9 Antioxidant

The stable radical DPPH assay was used to assess the antioxidant activity of film samples in terms of radical scavenging activity. 5 mL of methanol was used to extract the film samples, which were kept at room temperature. In the following step, 2 mL of the methanol extract were added to recently made DPPH solution (0.05 mM in methanol). The associated solution was vigorously mixed and then kept in the dark for 30 min before measuring the absorbance spectrophotometrically at 518 nm and calculating the radical scavenging activity (RSA) using equation (3):

$$\% \text{ radical scavenging activity } (\%RSA) = [(A_{control} - A_{sample}) / A_{control}] \times 100 \qquad (3)$$

where $A_{control}$ and $A_{sample}$ are defined as the absorbance readings of the DPPH solution without and with the sample solutions present.

### 4.3.10 Soil burial test (SBT)

Film samples (5x5 cm) were buried at 7.5 cm deep in compost soil and cultured at room temperature for 12 weeks. Following the test, the blend samples were removed, cleaned with distilled water, dried in an oven and stored in a desiccator. Equation was used to compute the weight loss of the bioplastics (3);

$$\% \text{ Weight loss} = (W_0 - W_f) / W_0 \times 100 \qquad (4)$$

The weight loss of the sample was measured by weighing samples before inoculation as initial sample weight ($W_0$) and after the test ($W_f$).

# CHAPTER 5

# RESULTS AND DISCUSSION

## 5.1 FTIR spectroscopy

FTIR is a qualitative spectroscopic approach for determining chemical functionalities that has been widely used to define interactions occurring during polymer mixing and modification. FTIR spectroscopy was recorded in the range of 4000-400 cm$^{-1}$. Figure 16 shows the FTIR spectra of PVA, PVA/CMC and PVA/starch. PVA has a peak at 3260.1 cm$^{−1}$, defined as OH stretching and a peak corresponding to C–H asymmetric stretching vibrations occurs at 2935.9 cm$^{−1}$. The presence of C=O of the carboxyl groups was confirmed for peaks of 1587.6 cm$^{−1}$ these peaks were present only in the PVA/CMC composite films and no peak in the PVA films. The FTIR spectrum of PVA/CMC/starch films (P01, P02 and P03) are depicted in Figure 17. The FTIR spectra of PVA/CMC/starch/CA films (PCS1, PCS2 and PCS3) are shown in Figure 18. The effect of CA on absorbance of PVA/CMC/starch films revealed that at high CA concentration resulted in a significant reduction in bandwidth. The composite films of PCS1, PCS2 and PCS3 showed peak at 1720-1725 cm$^{-1}$ which corresponds to ester C=O stretching vibration and confirmed the presence of C=O stretching of the carboxyl group. A sharp absorption in the 1690-1750 cm$^{-1}$ region was characteristic of C=O group in CA. This was due to the small peak in the PVA/CMC/starch films that did not contain CA (P01, P02 and P03) and the peak height increased depending on CA concentration. This result indicates the interaction of crosslinking between the polymer chain. CA is widely regarded as a safe substance (GRAS), very inexpensive, readily available and induces crosslinking of many biopolymers at low doses. As a result, they are frequently chosen over synthetic crosslinks.

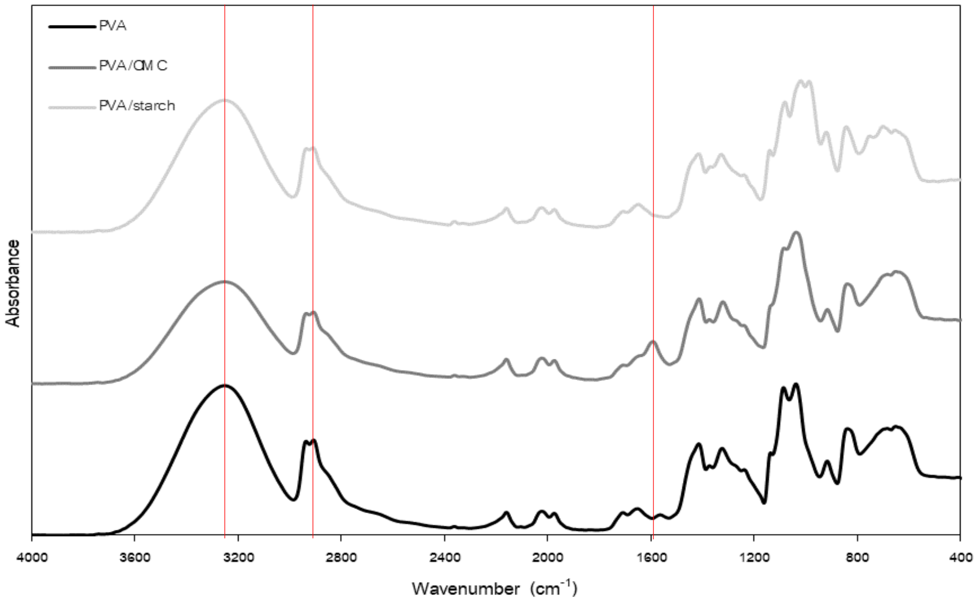


Figure 16 FTIR spectra of PVA, PVA/CMC and PVA/starch films.

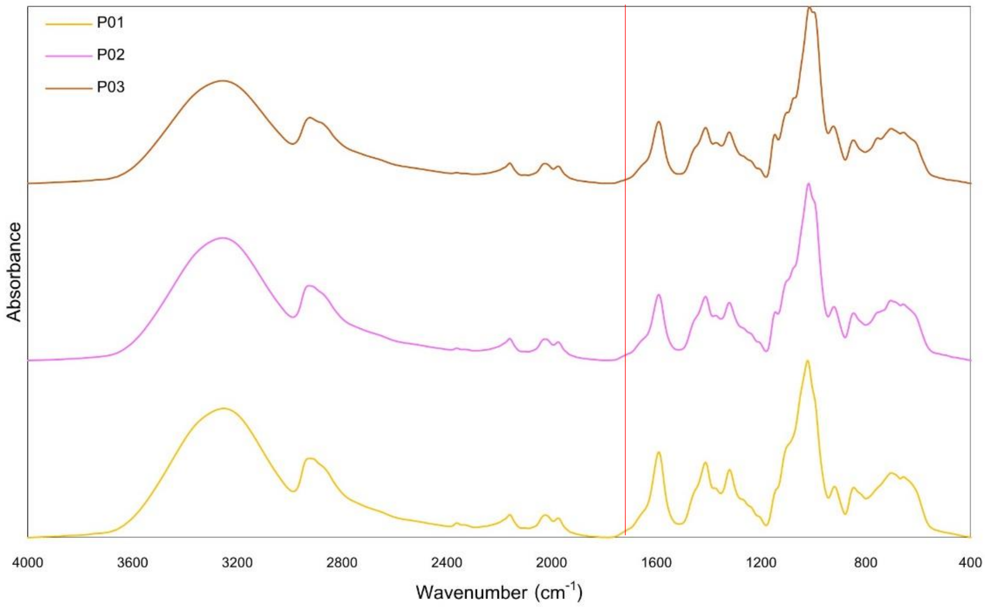


Figure 17 FTIR spectra of PVA/CMC/starch films (P01, P02 and P03).

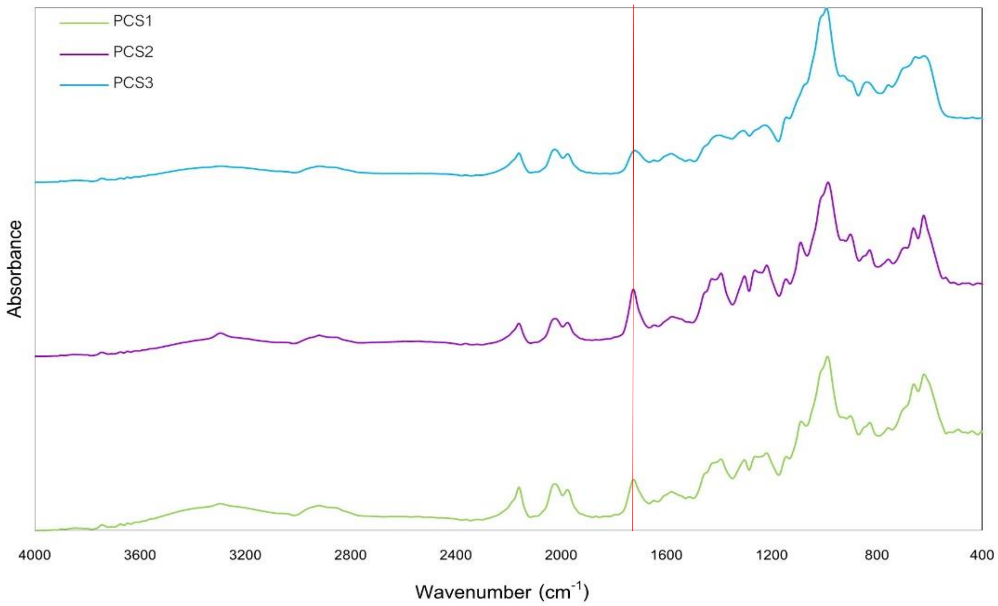


Figure 18 FTIR spectra of PVA/CMC/starch films with 15 phr of CA (PCS1, PCS2 and PCS3).

### 5.2 Degree of swelling and solubility

Packaging films with low water solubility aid in the preservation of their integrity. The solubility of the films is a significant component in determining their water resistance. PVA/CMC/starch films without CA were completely dissolved within 1 hour. Even after 24 hours of immersion in water, all films containing CA were determined to be in good condition. Previous tests have shown that with more CA content added, the film has a lower degree of swelling value which is good for food packaging films. Initially, a CA greater than 10 phr was chosen because when a CA less than 10 phr was added, the film would swell and expand. It can be observed from cutting the test specimen 3x3 cm. dissolved in DI water. After 24 hours, it will show that the film expands to 3.5x3.5 cm and 4x4 cm. If more CA content was added, even with better degree of swelling, the film was phased and not as smooth, as shown in Figure 19 and 20, respectively.

The degree of swelling of the films that were immersed in DI water for one day is shown in Figure 21 and solubility (%) of the films is shown in Figure 22. From the Figure 19 shows the degree of swelling ability of PCS1 was slightly higher than that PCS2 and then PCS2 was lower than PCS3. Because the amount of starch was higher than the PCS1 and PCS2 films. Figure 22 displays that the solubility of PCS1, PCS2 and PCS3 films are similar. The solubility of PCS1 was lower than that PCS2 and PCS2 was higher than that PCS3. Since it comes to swelling capability, the ability of a film to trap water molecules is the determining factor. When CA is added to a polysaccharide, it forms ester linkages, resulting in a denser structure and better water solubility. It is postulated that the degree of swelling is linked to the extent of the crosslink and that as the degree of crosslinking increases, the degree of swelling generally decreases.

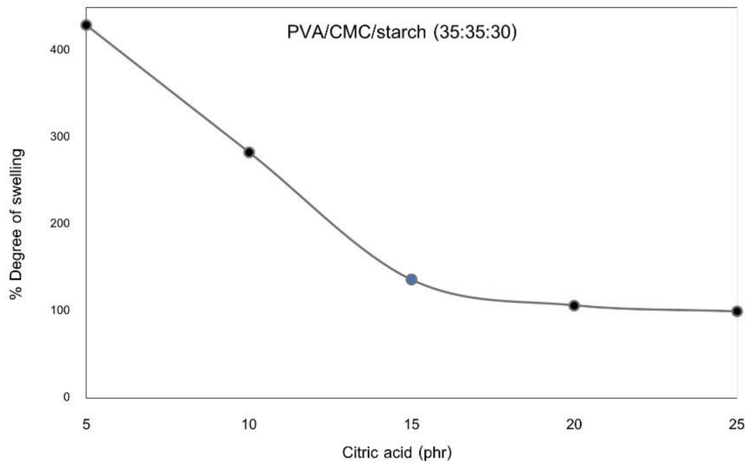


Figure 19 Degree of swelling of PVA/CMC/starch with CA (5, 10, 15, 20 and 25 phr) films.

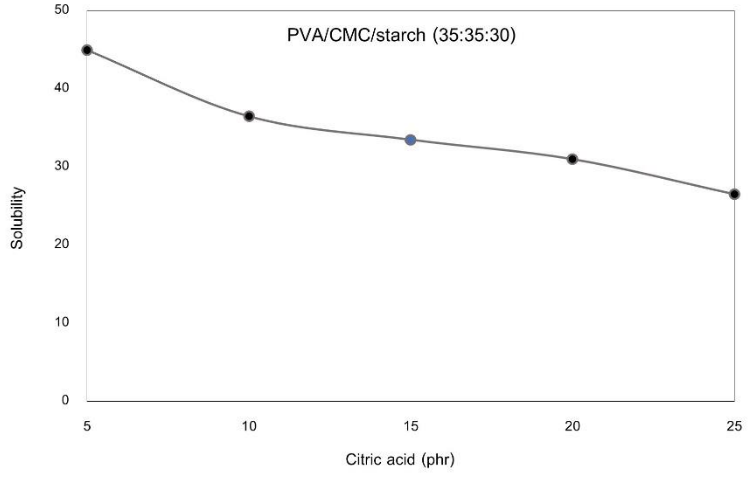


Figure 20 Solubility of PVA/CMC/starch with CA (5, 10, 15, 20 and 25 phr) films.

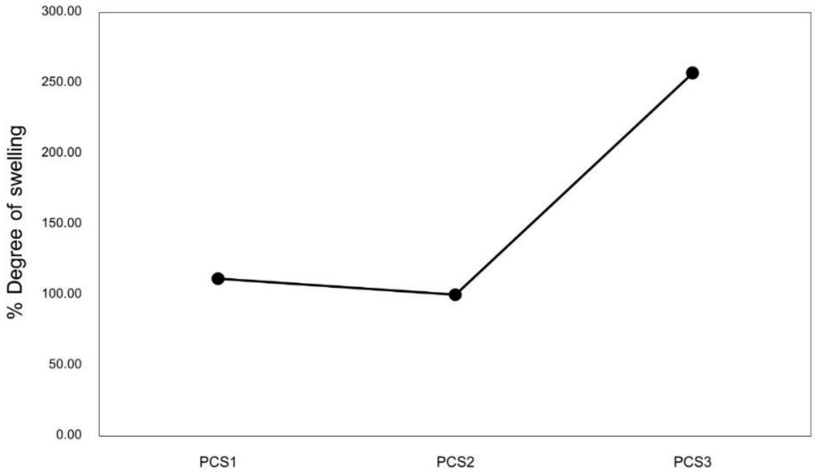


Figure 21 Degree of swelling of PVA/CMC/starch/CA (PCS1, PCS2 and PCS3) films.

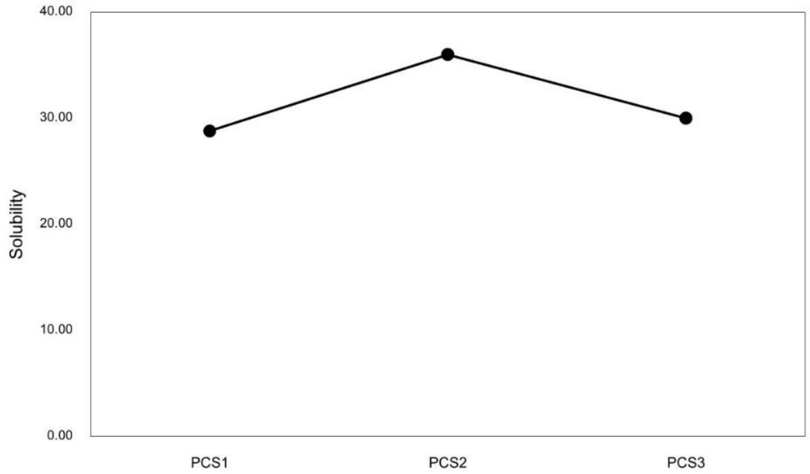


Figure 22 Solubility of PVA/CMC/starch/CA (PCS1, PCS2 and PCS3) films.

### 5.3 Morphology

Figure 23 shows SEM images of the bottom surface of PVA, PVA/CMC (50:50) and PVA/starch (50:50) films. The surface of PVA film was smoother than surface of PVA/CMC and PVA/starch films, while PVA/CMC film was smooth than surface of PVA/starch film. The poor dispersion of starch in the PVA/starch film was clearly observed when the starch amount was greater than 40-50 wt% [37]. Figure 24 shows SEM micrographs of the bottom surface of PVA/CMC/starch (P01, P02 and P03) films. It can be seen that the films of PVA/starch were two phases with irregular domain sizes and shapes while the films of PVA/CMC/starch films had homogeneous morphology. PVA, CMC and starch three-component polymer film was prepared with glycerol as an elastic agent by solution casting method. At a concentration of 10 phr glycerol could form a smooth film with reduced phase separation. Glycerol was a small molecule with a -OH functional group that may form hydrogen bonds with PVA and CMC, indicating that polymer films are compatible. Because of the hydrophilic nature of PVA, it increases hydrogen bonding and adhesion between starch chains.

SEM micrographs of PVA/CMC/starch/CA film various ratios based on PCS1, PCS2 and PCS3 film samples with 15 phr of CA are shown in Figure 25. The PCS1 film is extremely homogeneous. Although the PCS2 film is less homogeneous, but it is considered that the film does not deteriorate. The surface of PCS3 film was more turbidity than surface of PCS1 and PCS2 because the starch was added more 30 wt% to the films.

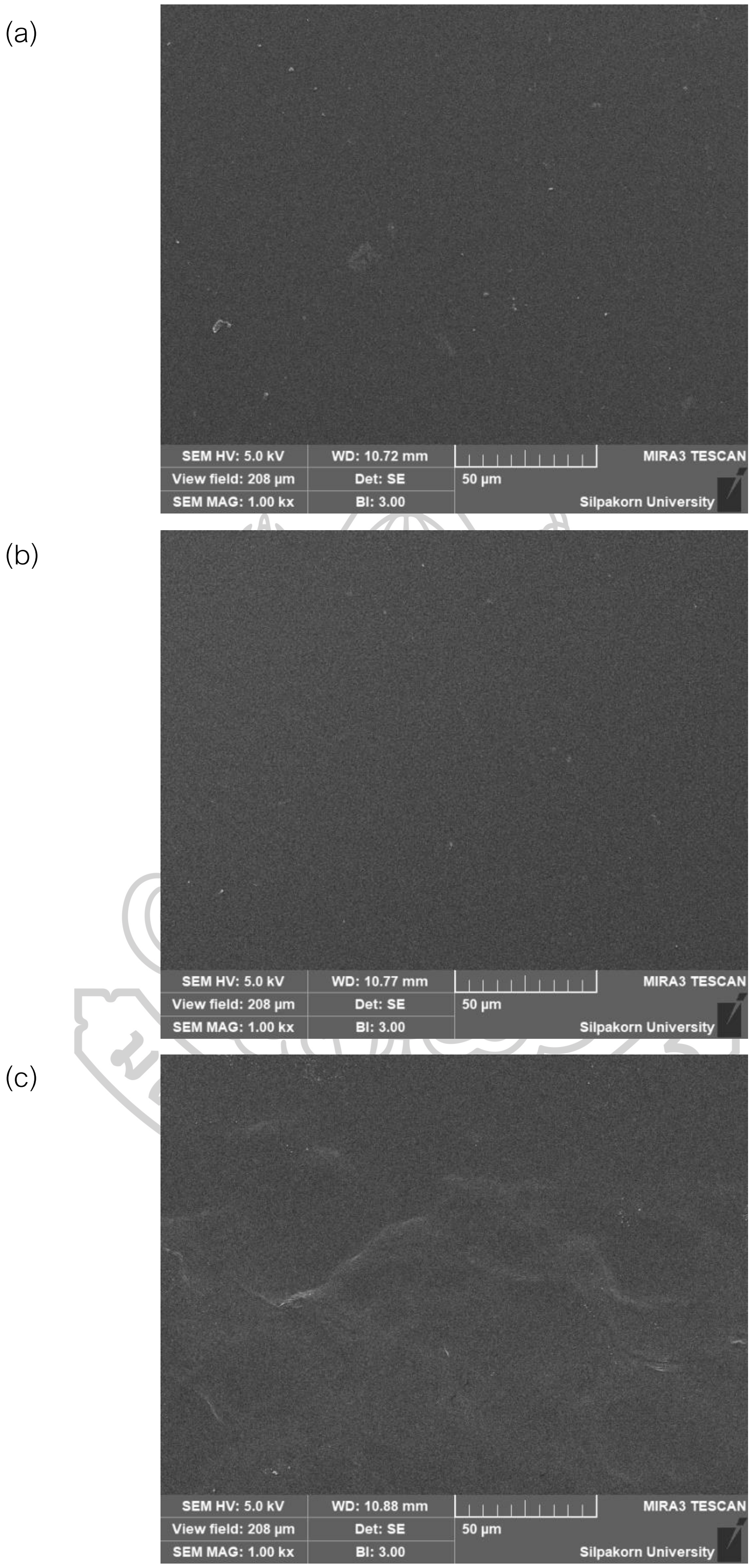


Figure 23 SEM images of films (a) PVA, (b) PVA/CMC and (c) PVA/starch at magnitude 1000X.

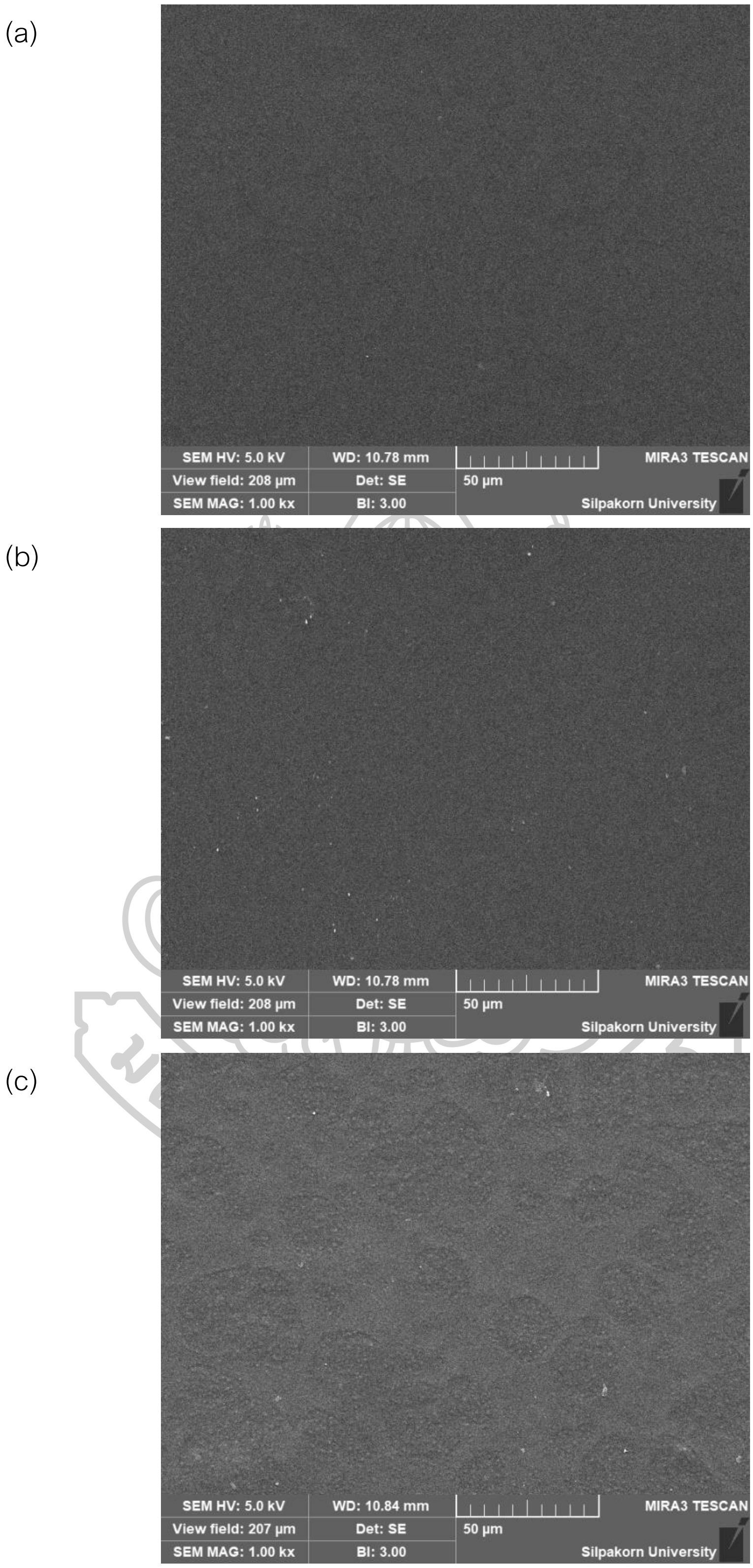


Figure 24 SEM micrographs of PVA/CMC/starch films (a) P01, (b) P02 and (c) P03 at magnitude 1000X.

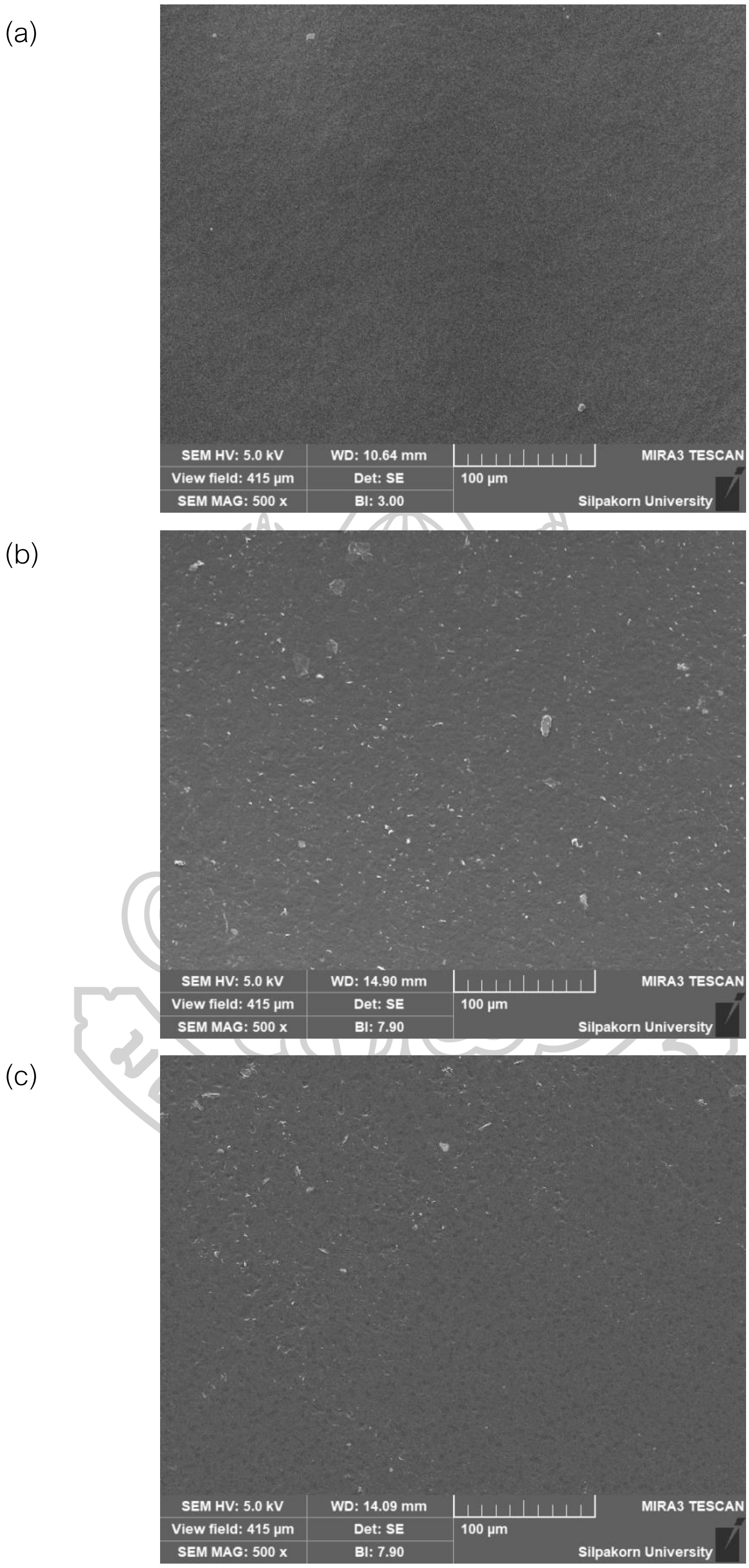


Figure 25 SEM micrographs of PVA/CMC/starch/CA films (a) PCS1, (b) PCS2 and (c) PCS3.

### 5.4 Mechanical properties

The mechanical behaviour of composite films were tested with the tensile test. Other research has found that when CA is used as a crosslinking agent, the water solubility of film is decreased but at the same time its tensile strength is lowered. As shown in Figure 26, it can be seen that when testing the mechanical properties and the tensile strength of film decreases with increasing CA content. As a result of degree of swelling and mechanical properties of films, 15 phr of CA added to the film was selected suitable for this research.

The tensile strength and Young's modulus of PVA, PVA/CMC, PVA/starch, PVA/CMC/starch (P01, P02 and P03) and PVA/CMC/starch/CA (PCS1, PCS2 and PCS3) films are showed in Figures 27 and 28, respectively. The tensile strength of the PVA/CMC film was increased when CMC was added to PVA pure film. The tensile strength increased with the increase of CMC contents in composite films. The tensile strength of PVA/starch film was lower than the tensile strength of PVA pure film. The tensile strength of PVA/CMC/starch and PVA/CMC/starch with 15 phr of CA films were greater than those of PVA, PVA/CMC and PVA/starch films and PCS2 film has the highest tensile strength, as shown in Figure 27. The interfacial interaction could be caused by the polymer matrix PVA and starch being able to create strong networks by hydrogen bonding with the hydroxyl and carboxyl groups of CMC macromolecules. Additionally, CA can hydrolyse the branched chains of starch molecules that catalyze the formation of highly linear structures, which allows for the formation of more hydrogen bonds between the starch chains, resulting in improved tensile strength in the resultant films [2].

Young's modulus of the composite films is illustrated in Figure 28. Young’s modulus of PVA increased when added CMC and starch. Young’s modulus of PVA/CMC/starch films was higher than that of PVA, PVA/CMC and PVA/starch films. Obviously, The PVA/CMC/starch/CA film was higher than PVA, PVA/CMC, PVA/starch and PVA/CMC/starch (P01, P02 and P03) films. The Young’s modulus of PCS2 was 1865.57 MPa, which was the maximum value when compared with the other polymer films. This implied that the addition of CA to the PVA/CMC/starch film improved Young’s modulus. However, there is an optimal amount of CA that is necessary to obtain an increase in the tensile strength and Young’s modulus of the films.

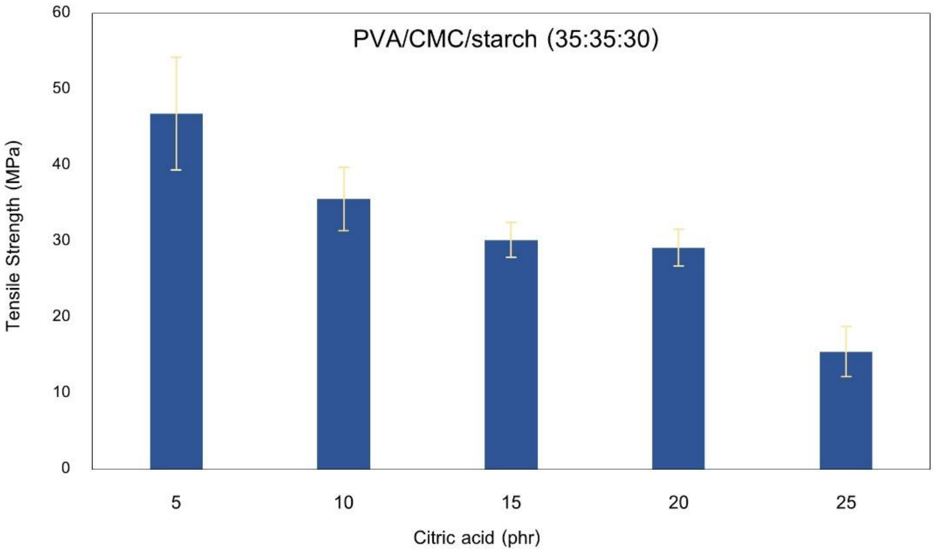


Figure 26 Tensile strength of PVA/CMC/starch (35:35:30) with CA (5, 10, 15, 20 and 25 phr) films.

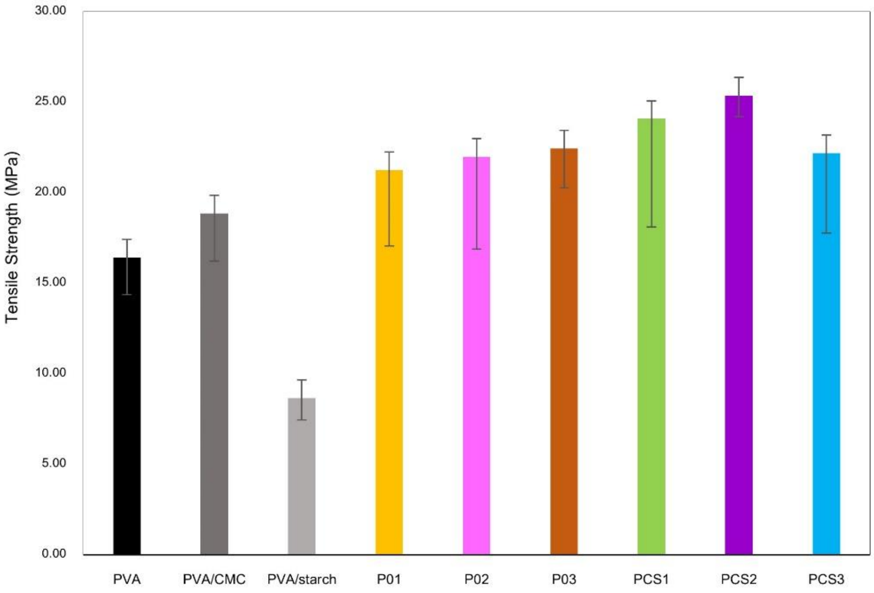


Figure 27 Tensile strength of PVA, PVA/CMC, PVA/starch, PVA/CMC/starch (P01, P02 and P03) and PVA/CMC/starch/CA (PCS1, PCS2 and PCS3) films.

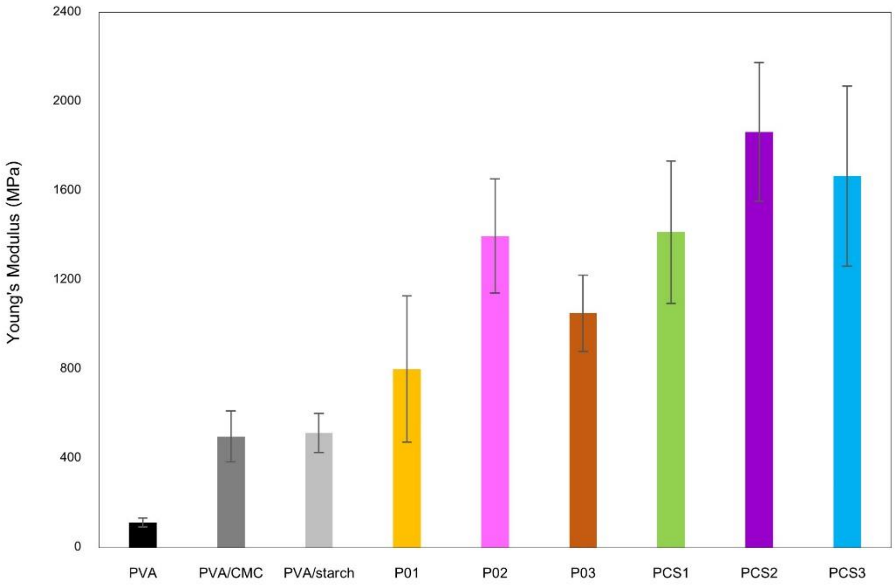


Figure 28 Young's modulus of PVA, PVA/CMC, PVA/starch, PVA/CMC/starch (P01, P02 and P03) and PVA/CMC/starch/CA (PCS1, PCS2 and PCS3) films.

### 5.5 Thermogravimetric analysis (TGA)

The thermal characteristics of polymers may be determined via TGA measurements. The thermal degradation of PVA, PVA/CMC, PVA/starch and PVA/CMC/starch/CA films are shown in Figure 29. The composite films degraded at the same rate as the PVA film, which went through three stages of deterioration. The evaporation of water caused the first stage at temperatures between 80 and 200°C. The second stage, which occurred at 250-400°C, resulted in a significant weight loss owing to chain scission for PVA breakdown. This is followed by an additional broken polymer chain in the third step approximately 420-490°C. Obviously, the addition of PVA to the composite film would likely increase the thermal stability of the film by reducing the degradation rate in the second step, an outstanding degradation process caused by starch and PVA molecules hydrogen bonding generated by the new thermal breakdown structure. As a result of the addition of CA to the PVA/CMC/starch films, the cross-linking between the modified PVA with the CMC and starch becomes more compact and the stability of the films is improved. The results were confirmed by determination the decomposition temperature at 5% weight loss ($T_{d5}$), 10% weight loss ($T_{d10}$) and 50%

weight loss ($T_{d50}$) as presented in Table 2. The result was that $T_{d50}$ increased with increasing starch content as did $T_{d5}$ and $T_{d10}$. Residue after final thermal destruction at temperature 550°C were also shown in Table 2.

Table 2 The decomposition temperature of 5%, 10% and 50% weight loss ($T_{d5}$, $T_{d10}$ and $T_{d50}$) and %char yield at 550 °C of PVA, PVA/CMC, PVA/starch and PVA/CMC/starch/CA (PCS1, PCS2 and PCS3) films.

| Sample | $T_{d5}$ (°C) | $T_{d10}$ (°C) | $T_{d50}$ (°C) | Char yield at 550°C (%) |
|---|---|---|---|---|
| PVA | 114.5 | 197.3 | 288.9 | 6.4 |
| PVA/CMC | 92.3 | 185.3 | 294.4 | 19.4 |
| PVA/starch | 156.5 | 228.3 | 330.5 | 10.2 |
| PCS1 | 87.4 | 178.7 | 296.2 | 26.4 |
| PCS2 | 100.0 | 179.6 | 301.8 | 24.4 |
| PCS3 | 112.0 | 181.9 | 300.6 | 23.9 |

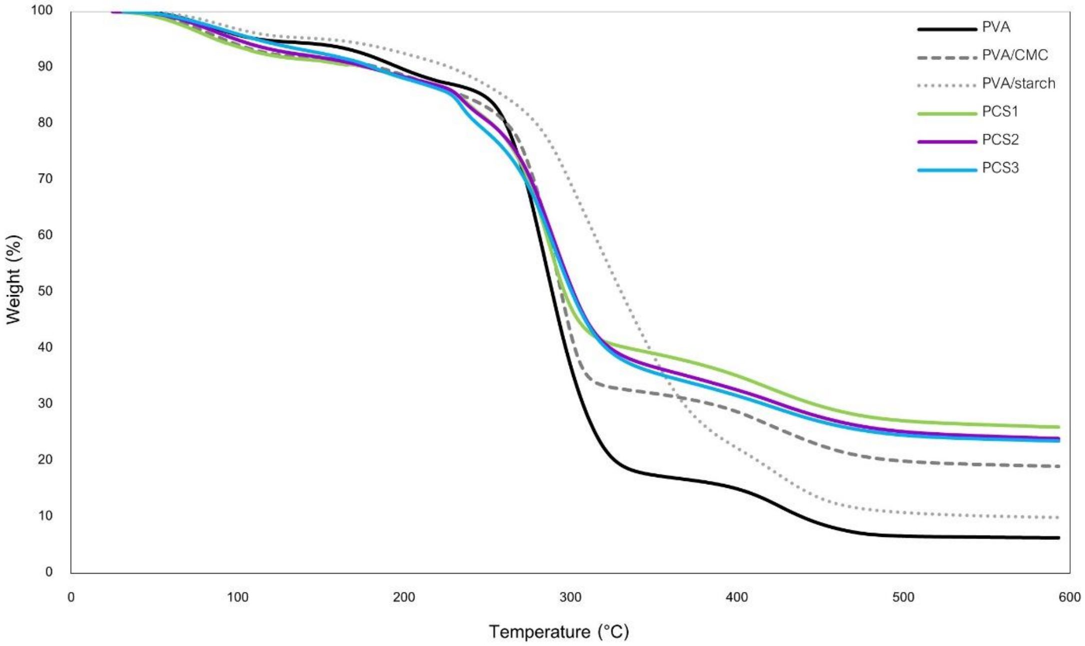


Figure 29 TGA analyses of PVA, PVA/CMC, PVA/starch and PVA/CMC/starch/CA (PCS1, PCS2 and PCS3) films.

### 5.6 Optical properties

UV light resistance is a critical factor to consider when considering polymeric films for packaging, particularly when it comes to light-sensitive food products. Whereas PVA is commonly used as a packaging material, its weak UV resistance should be enhanced to expand its application sector [30]. The effects of UV absorption spectra are shown in Figures 30, 31 and 32 and opacity on films are shown in Figure 33. CA of PVA/CMC/starch films has shown UV protective properties even in low quantities. On the other hand, PVA film was most transparent. The film opacity slightly increased as the CMC or starch content were increased. At the same time, the PVA/CMC/starch films with CA had higher film transparency than the PVA/CMC/starch without CA films. Additionally, the transmittance of previously researched composite films containing CA in the UV region may establish their suitability for usage in specific fields requiring UV protection.

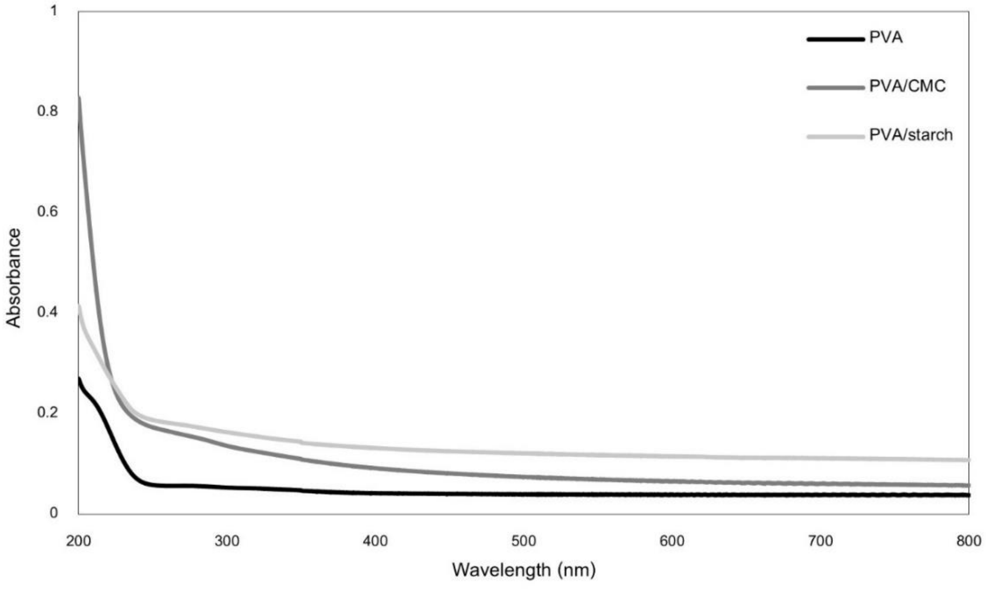


Figure 30 UV-Vis absorption spectra for PVA, PVA/CMC and PVA/starch films.

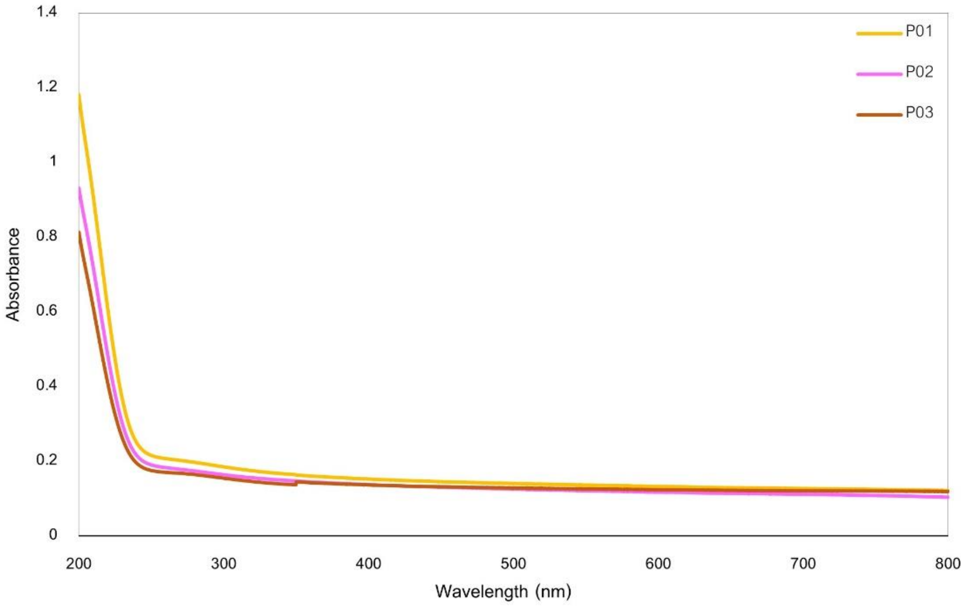


Figure 31 UV-Vis absorption spectra for PVA/CMC/starch (P01, P02 and P03) films.

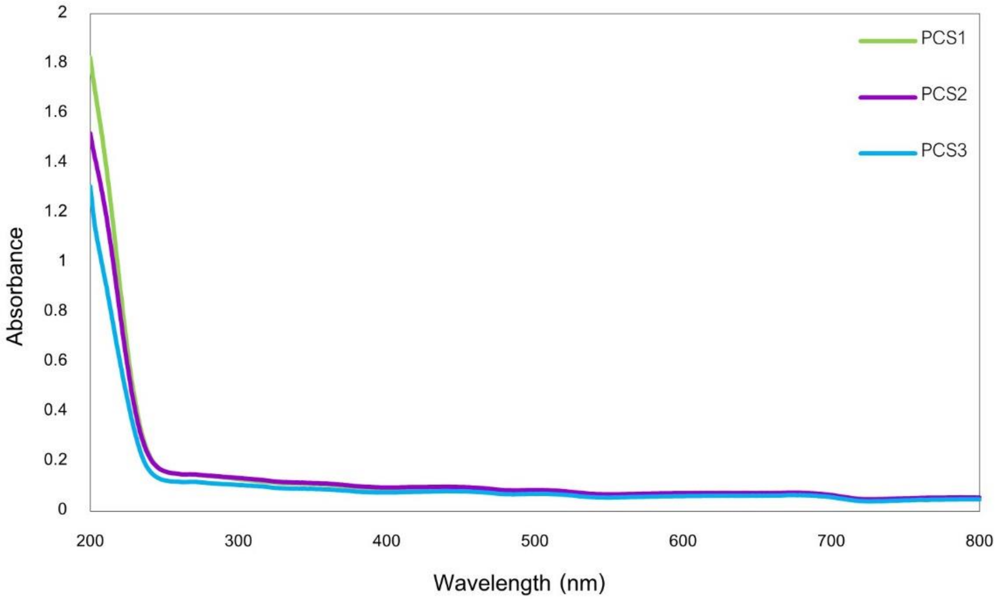


Figure 32 UV-Vis absorption spectra for PVA/CMC/starch/CA (PCS1, PCS2 and PCS3) films.

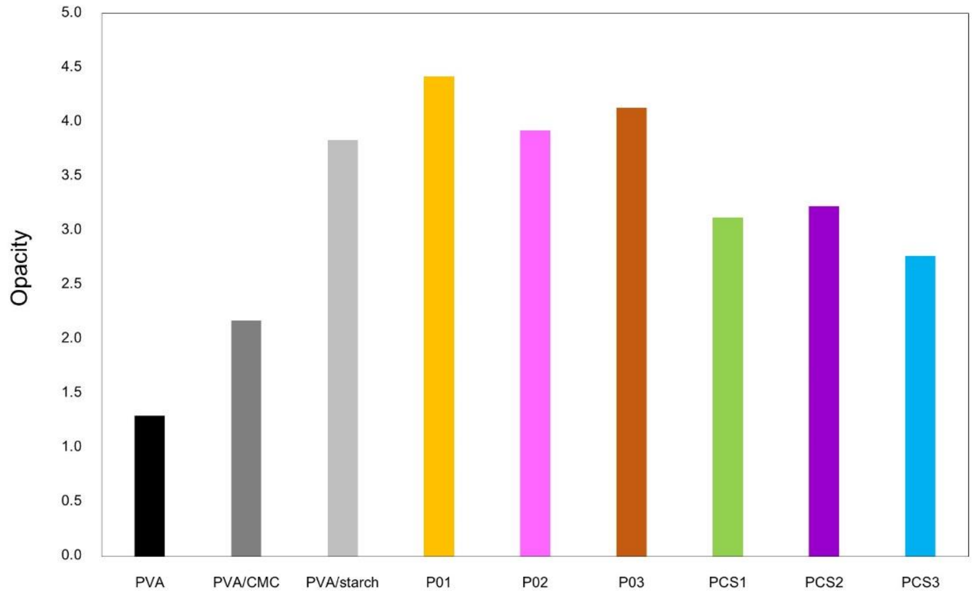


Figure 33 Opacity for PVA, PVA/CMC, PVA/starch, PVA/CMC/starch (P01, P02 and P03) and PVA/CMC/starch/CA (PCS1, PCS2 and PCS3) films.

## 5.7 Barrier properties of film

### 5.7.1 Water vapor transmission rate (WVTR)

The ease with which moisture can infiltrate a food packaging film can have an impact on the shelf life and quality of the product. Due to the degree of swelling and solubility of the films, the PVA/CMC/starch without CA films completely dissolved within 1 hour. For the results obtained, only PVA/CMC/starch containing CA films were tested. WVTR of the test PVA and PVA/CMC/starch/CA (PCS1, PCS2 and PCS3) films are shown in Table 3. The PVA film had the lowest WVTR was 2380.4 g/($m^2$-d). The WVTR of PCS1, PCS2 and PCS3 films was 2572.8 g/($m^2$-d), 2513.1 g/($m^2$-d) and 3414.9 g/($m^2$-d), respectively, making this biodegradable packaging film acceptable. The WVTR of films containing starch increased significantly with decrease of PVA concentration. It has been concluded that increased concentrations of CA resulted in it performing as a plasticizer, which resulted in lower in the water vapour transmission ratio. Alteration in the composition of the biopolymer matrix, solution casting film technique and CA concentration all have the potential to affect the degree of WVTR. Previous investigations supported similar findings and ascribed them to the creation of ester linkages between the CA and the polysaccharide, which resulted in a denser structure [13].

Table 3 Water vapor transmission rate (WVTR) of PVA and PVA/CMC/starch with CA (PCS1, PCS2 and PCS3) films.

| Sample | PVA | PCS1 | PCS2 | PCS3 |
|---|---|---|---|---|
| WVTR [g/($m^2$-day)] | 2380.4 | 2572.8 | 2513.1 | 3414.9 |

### 5.7.2 Gas barrier properties

#### 1) Carbon dioxide gas transmission rate ($CO_2TR$)

Part of the active food packaging is the $CO_2$ emission. $CO_2$ dissolves in the products and the proliferation of some bacteria (Gram negative) is reduced leading to improved product quality and increased shelf life. Table 3 shows the gas transmission rate of the films. PVA film had the highest $CO_2TR$ of 25.9 $cm^3/m^2$-d-bar. The $CO_2TR$ of PCS2 was lower than PCS1 and PCS3. As a result, PCS2 film is the greatest because it has the lowest $CO_2TR$. The values of PVA/CMC/starch/CA (PCS1, PCS2 and PCS3) films tended to increase as expected due to the reduction of the PVA content and increased CA content of the base film and the values were still considered excellent. Other studies have reported that CA is used in $CO_2$ emission systems. Laboratory-type emitters have been found to be used CA in a ratio adjusted to product pH. The carbon dioxide gas transmission rate of the test gas is measured by the gas permeability tester.

#### 2) Oxygen gas transmission rate (OTR)

Oxygen scavengers can be used to remove the oxygen remaining in the headspace of packaging and therefore can prevent oxidation of food or growth of microorganisms in food and to improve food safety and maintain food quality. The OTR through the film was obtained by complying with the standard. This is useful for determining the barrier properties of the film to oxygen gas under specific test conditions. The experimental design of the investigation of OTR was based on the degree of swelling and WVTR and on $CO_2TR$ results in the parallel study. The target OTR at 23°C and 50% RH was 0-20 $cm^3/m^2$-d-bar to match requirements for a variety of food packaging purposes. The OTR values obtained from the test are shown in Table 4. The results were assumed to be in line with expectations as the increase in OTR was a consequence of the decrease in the PVA content. Overall, the test values are considered good for food packaging. An oxygen absorber is a substance that can absorb oxygen by itself reacting with oxygen. This reduces the amount of oxygen used in food packaging to prevent oxidation that is a major cause of food deterioration.

Table 4 Gas transmission rate (GTR) of PVA and PVA/CMC/starch with CA (PCS1, PCS2 and PCS3) films.

| Sample | $CO_2$TR ($cm^3/m^2$-d-bar) | OTR ($cm^3/m^2$-d-bar) |
|---|---|---|
| PVA | 25.9 | 11.9 |
| PCS1 | 9.8 | 14.7 |
| PCS2 | 8.7 | 19.6 |
| PCS3 | 12.6 | 27.3 |

### 5.8 Antioxidant activity

The concepts of active packaging and minimally processed produce are aligned with biodegradable films in this study. The DPPH assay is a simple approach for measuring radical scavenging activity in polymeric films. The antioxidant activity was determined for several composite films that were straight stirred into a methanol solution for 24 hours at room temperature. The antioxidant activity of the extract was determined using a calibration curve (0, 5, 10, 20, 40, 100 ppm) established with BHT ($R^2$=0.9897) (Figure 34). The antioxidant activity (%RSA) of the active film was measured using the DPPH assay in Figure 35. The film of PVA/CMC/starch with CA 15 phr showed the absorbance value at 518 nm decreased. The PVA/CMC/starch/CA (PCS1, PCS2 and PCS3) films showed better radical scavenging activity and had higher antioxidant activity compared to PVA, PVA/CMC and PVA/starch films in this research, this could be attributed to the presence of CA in the films.

The herein developed PVA/CMC/starch/CA films were confirmed to have antioxidant activity through their methanolic extracts even at low concentrations. That is, active function can be obtained with natural antioxidant compounds such as CA. The radical scavenging action of CA was aided by the presence of phenolic compounds. Because of their hydrogen-donating ability and ability to scavenge free radicals, phenolic compounds perform as antioxidants.

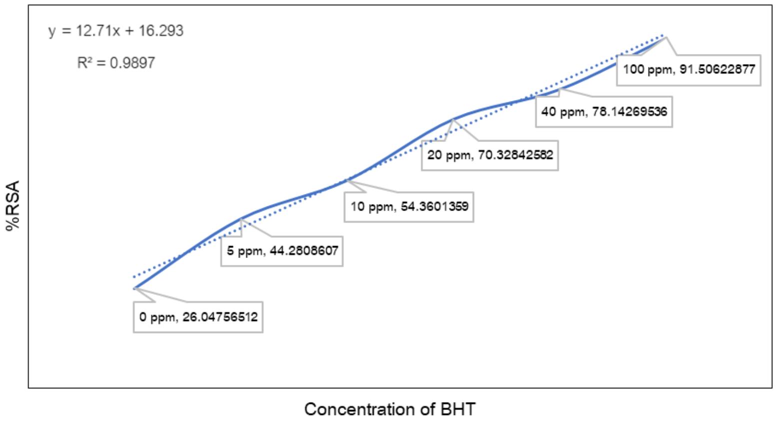


Figure 34 Calibration curve of antioxidant activity with 0, 5, 10, 20, 40 and 100 ppm of BHT.

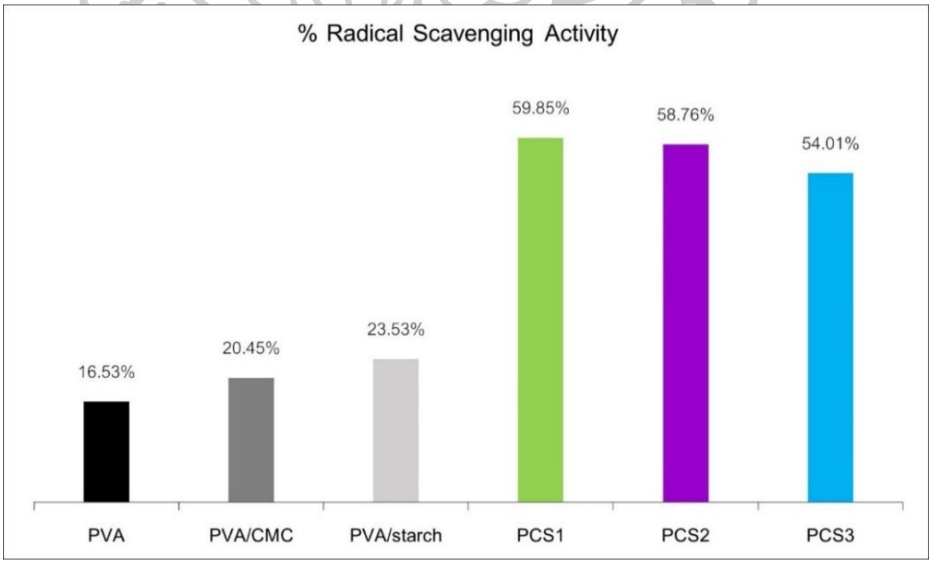


Figure 35 Antioxidant activity (radical scavenging activity, %RSA) of PVA, PVA/CMC, PVA/starch and PVA/CMC/starch/CA (PCS1, PCS2 and PCS3) films by DPPH assay.

### 5.9 Soil biodegradability

Biodegradability of bioplastics as determined by soil burial test (SBT). This test was used to measure the biodegradability of composites by examining the weight loss (%) of samples for 12-week period owing to moisture and microbial activity. Figures 36 and 37 illustrate the results of the biodegradability test conducted using the SBT method. As can be demonstrated, the longer the burial period and the greater the weight loss of film bioplastic, the more degradation happened. Each day, the percentage of weight lost increased until week 10-12. Among all the PVA, PVA/CMC, PVA/starch films and PVA/CMC/starch without CA, found that the film with the addition of CA demonstrated the highest biodegradation resistance.

This could be due to the fact that PCS1, PCS2 and PCS3 had strong crosslinking and adhesion, which made it difficult for these samples to disintegrate and resulting in their high tensile strength. In linear polymers, chemical degradation reactions lead to the decrease in molecular weight or a shortening of the chain length chain. Starch has acetal bonds which are very easy to degrade. The bioplastic component was a natural material that is easily digested by bacteria, which explains of the mass reduction. The presence of a hydroxyl group (-OH) in a natural polymer was the most important component in a polymer that might be degraded spontaneously and this group was easily degraded by bacteria [32].

(a)

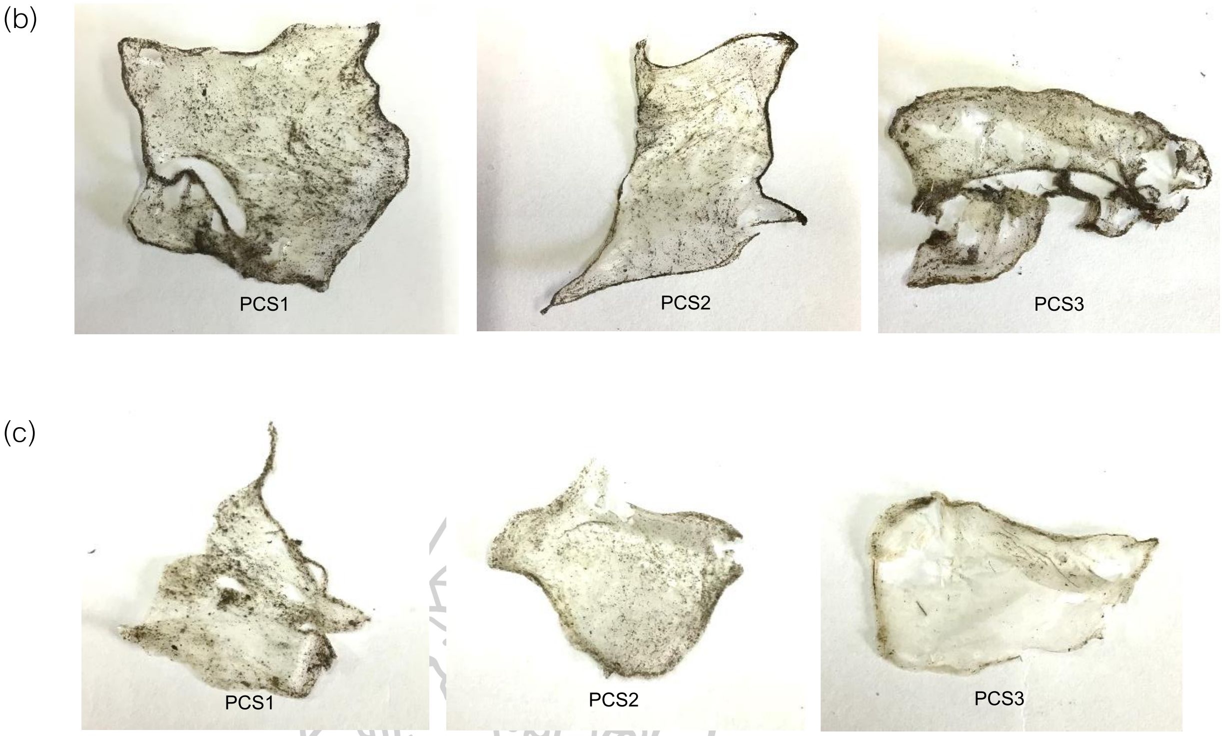


Figure 36 Soil burial Test. (a) PVA, (b) On week 8, more soil water and soil itself enter the bioplastic pores and (c) On week 12, the cracking region on the bioplastic sample was larger.

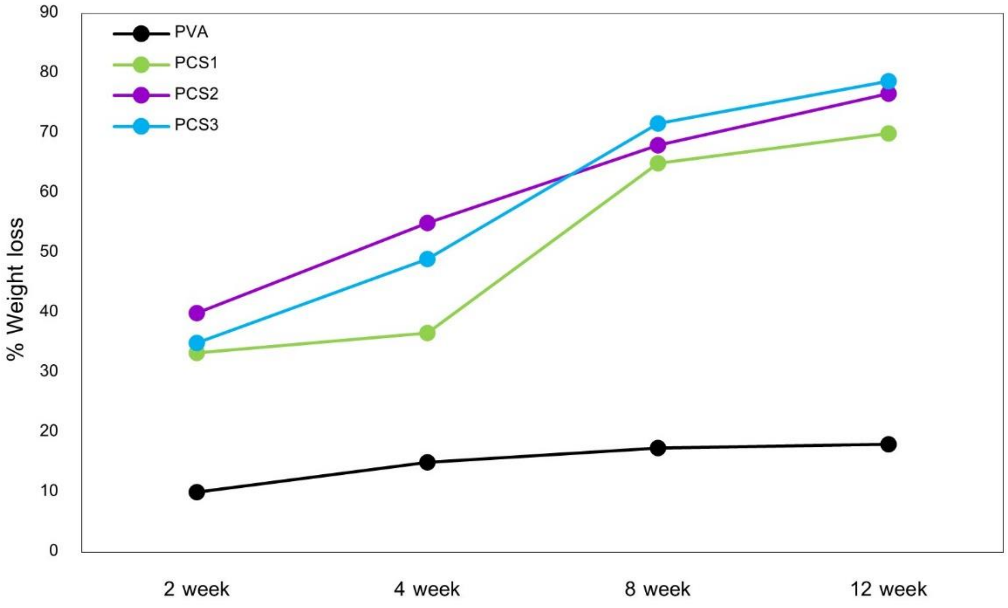


Figure 37 Weight loss of biodegradable films after 12 weeks test with SBT method.

# CHAPTER 6

## Conclusion

This work investigated the structure, degree of swelling, water solubility, mechanical, thermal and morphological properties of PVA/CMC/starch films without and with CA. It also tested the film barrier properties of PVA/CMC/starch/CA films. The addition of CMC was found to improve film strength and clarity and when glycerol was added as a plasticizer, the polymer composite film became more flexible and film compatibility increased. The results establish that formulations based on crosslinked PVA/CMC/starch films reinforced with CA could be considered as interesting biodegradable film. Another intriguing test result is the gas transmission rate, which in the film under test is regarded to be excellent. The film of PVA/CMC/starch (40:40:20) with 15 phr CA showed the best values of tensile strength, Young's modulus and homogeneity. Furthermore, solution casting film was produced using a simple and sparing technique provided films with outstanding physical properties and the potential to be used in food packaging applications. In conclusion, the results of this study indicate that biodegradable films can be developed for active food packaging films.

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