

**EFFECT OF CITRUS SINENSIS PEEL CHARACTERISTICS ON THE  
PROPERTIES OF POLYVINYL ALCOHOL FILM**

**By**

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## **ABSTRACT**

### **EFFECT OF CITRUS SINENSIS PEEL CHARACTERISTICS ON THE PROPERTIES OF POLYVINYL ALCOHOL FILM**

**TEOH KEAT YIN**

In this study, a new polymer blend was prepared by blending citrus peel waste flour (CPWF) and polyvinyl alcohol (PVA) using solution casting method. CPWF was characterized by Scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis, Fourier transform infrared spectroscopy (FTIR) and chemical composition analysis by AOAC standard methods prior to blending. PVA/CPWF films at different weight ratio of PVA and CPWF were formulated and developed successfully. The physical properties of the PVA/CPWF blended films at different composition were characterized by SEM, FTIR, tensile test, water absorption, solubility test, Differential scanning calorimetry (DSC), Thermogravimetric analysis (TGA), and degradability by natural weathering test. According to the basis of results, the tensile strength and elongation at break of the PVA/CPWF films decreased with the incorporation of the CPWF. The water absorption of the PVA/CPWF films also reduces with the increasing of the CPWF content when introduced into the PVA. Conversely, the water solubility of the PVA/CPWF films declines with the increasing of the CPWF content. Besides, the PVA/CPWF films shows an increment in the glass transition temperature ( $T_g$ ) when the concentration of

CPWF increases due to the increases in the rigidity of the blended film. Yet, the reduction of the crystalline phase temperature ( $T_c$ ) and melting temperature ( $T_m$ ) of the PVA/CPWF films with the increasing of the CPWF content owes to the decreases in the crystallinity of the structure of the blends. In addition, the thermal decomposition temperature of the PVA/CPWF films is shifted to higher values with the incorporation of CPWF indicates that the chemical interaction between PVA and CPWF plays an important role in the thermal stability of the blends. Apart from that, the degradability of the PVA/CPWF films is enhanced when the concentration of the CPWF increases. Since CPWF is more biodegradable than PVA, thus introducing of CPWF into the PVA shows improvement in the degradability of the films. The surface degradation of the PVA/CPWF films is supported by the SEM micrographs and disappearance and changing intensity of the absorption peaks that can be observed in the FTIR spectra of the weathered films.

**Keywords:** Polyvinyl alcohol (PVA), citrus peel waste flour (CPWF), tensile properties, water absorption and solubility, glass transition temperature ( $T_g$ ), thermal decomposition temperature, degradability

## **ABSTRAK**

### **KESAN SIFAT-SIFAT KULIT LIMAU MANIS DALAM CIRI-CIRI POLIVINIL ALKOHOL**

**TEOH KEAT YIN**

Dalam kajian ini, adunan polimer baru telah disediakan dengan mencampurkan tepung sisa kulit limau manis (CPWF) dan polivinil alkohol (PVA) melalui kaedah penuangan larutan. Sifat-sifat tepung sisa kulit limau manis telah disiasat dengan menggunakan mikroskop imbasan elektron (SEM) dengan serakan tenaga X-ray analisis, jelmaan Fourier spektroskopi infra merah (FTIR), dan komposisi kimia analisis dengan AOAC kaedah standard sebelum mengadun. Filem PVA/CPWF pada nisbah berat yang berbeza antara PVA and CPWF telah dirumuskan dan berjaya dihasilkan. Ciri-ciri fizikal filem PVA/CPWF pada nisbah berat yang berbeza telah disiasatkan dengan Mengimbas mikroskop elektron (SEM), jelmaan Fourier spektroskopi infra merah (FTIR), ujian tegangan, ujian penyerapan air and pembubaran, pengimbasan pembezaan kalorimeter (DSC), Analisis Termogravimetri (TGA), dan keterdegradasikan dengan ujian cuaca semula jadi. Mengikuti dasar keputusan, the kekuatan tegangan and pemanjangan pada takat putus bagi filems PVA/CPWF menurun dengan penambahan CPWF. Penyerapan air bagi filems PVA/CPWF juga menurun dengan penambahan kandungan CPWF dalam PVA. Sebaliknya, pembubaran filems PVA/CPWF dalam air semakin merosot

dengan peningkatan kandungan CPWF. Selain itu, filem PVA/CPWF menunjukkan peningkatan dalam suhu peralihan kaca ( $T_g$ ) apabila kepekatan CPWF meningkat disebabkan oleh peningkatan dalam ketegaran filem sebati. Namun, pengurangan kristal suhu fasa ( $T_c$ ) dan suhu lebur ( $T_m$ ) dalam filems PVA/CPWF dengan peningkatan kandungan CPWF disebabkan oleh kejatuhan dalam penghabluran struktur campuran. Di samping itu, suhu penguraian haba filems PVA/CPWF telah dipindahkan ke nilai yang lebih tinggi dengan penambahan CPWF menunjukkan bahawa interaksi kimia antara PVA dan CPWF memainkan peranan penting dalam kestabilan haba campuran. Selain daripada itu, keupayaan degradasi filems PVA/CPWF telah dipertingkatkan apabila kepekatan CPWF meningkat. Oleh kerana CPWF adalah lebih mesra alam daripada PVA, jadi memperkenalkan CPWF ke dalam PVA menunjukkan peningkatan dalam keupayaan degradasi dalam filems. Degradasi permukaan filems PVA/CPWF disokong oleh mikrograf SEM dan kehilangan dan intensiti perubahan puncak penyerapan yang boleh diperhatikan dalam spektrum FTIR filems degradasi.

**Keywords:** Polivinil alcohol (PVA), tepung sisa kulit limau manis (CPWF), kekuatan tegangan, penyerapan air dan pembubaran, suhu peralihan kaca ( $T_g$ ), suhu penguraian haba, keupayaan degradasi

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Last but not least, my thanks and appreciations also go to my friends and family for their endless support, love and all other unnamed who help me directly and indirectly in completing this project.

## **DECLARATION**

I hereby declare that the content presented in this project report has been composed solely by myself, except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted, in whole or in part, for any previous application of degree at UTAR or other institutions.

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TEOH KEAT YIN

## APPROVAL SHEET

This project report entitled **“EFFECT OF CITRUS SINENSIS PEEL CHARACTERISTICS ON THE PROPERTIES OF POLYVINYL ALCOHOL FILM”** was prepared by TEOH KEAT YIN and submitted as partial fulfilment of the requirements for the degree of Bachelor of Science (Hons) Chemistry at University Tunku Abdul Rahman.

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**PERMISSION SHEET**

It is hereby certified that TEOH KEAT YIN (ID No: 13ADB03799) has completed this final year project entitled “EFFECT OF CITRUS SINENSIS PEEL CHARACTERISTICS ON THE PROPERTIES OF POLYVINYL ALCOHOL FILM” under the supervision of DR OOI ZHONG XIAN (supervisor) from the Department of Chemical Science, Faculty of Science.

I hereby give permission to the University to upload the softcopy of my final year project in pdf format into the UTAR Institutional Repository, which may be made accessible to the UTAR community and public.

Yours truly,

\_\_\_\_\_

(TEOH KEAT YIN)

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## LIST OF SYMBOLS

<b>Symbol</b>	<b>Description</b>
$M_T$	Percentage of total moisture content in citrus peel waste flour (CPWF) (%)
$M_2$	Dried weight of CPWF (dried for 24 hours) (g)
$M_1$	Initial weight of CPWF (g)
$A_T$	Percentage of total ash content in CPWF (%)
$M_a$	Weight of empty crucible (g)
$M_b$	Weight of ash with the crucible (g)
$W$	Weight of the dried CPWF (dried for 1 hour) (g)
$F_T$	Percentage of total fat content in CPWF (%)
$M_3$	Weight of extraction beaker with boiling stones (g)
$M_4$	Weight of extraction beaker with the boiling stones and the fat extracted from CPWF (g)
$P_T$	Percentage of total crude protein in CPWF (%)
$V_s$	Volume of 0.1 M hydrochloric acid used for CPWF sample in titration (mL)
$V_b$	Volume of 0.1 M hydrochloric acid used for blank in titration (mL)
$N$	Normality of the 0.1 M hydrochloric acid (N)
$A_f$	Percentage of water absorption for PVA/CPWF blended film (%)
$W_f$	Weight of the PVA/CPWF blended film after water absorption (g)
$W_i$	Dried weight of PVA/CPWF blended film (g)
$S_f$	Percentage of water solubility of PVA/CPWF blended film (%)
$W_s$	Dried weight of the PVA/CPWF blended film after solubility test (g)
$D_f$	Percentage of degradability of the weathered PVA/CPWF film (%)
$W_a$	Initial weight of PVA/CPWF blended film(g)
$W_d$	Weight of the weathered PVA/CPWF blended films (g)

## LIST OF ABBREVIATIONS

<b>Abbreviation</b>	<b>Description</b>
PVA	Polyvinyl alcohol
CPWF	Citrus peel waste flour
PVAc	Polyvinyl acetate
CS	Corn starch
SF	Starch Fiber
CST	Cassava starch
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis
AOAC	Association of Official Analytical Chemists
ASTM	American Society for Testing and Materials
mm	Milimeter
MPa	Mega Pascal
EDX	Energy dispersive X-ray
μm	Micrometer
DrTGA	Derivative thermogravimetric analysis

# CHAPTER 1

## INTRODUCTION

### 1.1 Overview

Plastics are typically high molecular weight macromolecules that made up of multiple repeating units in which at least few thousands of monomer units are joined together through the process of polymerization. The consumption of plastics has been increased extensively in many fields of areas due to its desirable properties, such as simplicity of manufacture, light weight, low cost, good thermal and electrical insulation, water barrier and corrosion resistant. As a result, the utilization of many traditional resources, for instances wood, metal, ceramic, and glass, have been replaced by plastic due to its attractive properties. As reported by Prieto (2016), the total consumption of the plastic can grow from the existing 250 million tonnes per year to around 1000 million tonnes by the end of this century due to the demand for the plastic materials is growing globally. Some of the examples for the common used plastics are polyethylene (PE), polyester (PES), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyamide (PA) or nylon, polystyrene (PS), and polypropylene (PP).

The majority of plastics productions are derived from petroleum, owing to their non-biodegradable properties, they are resistant to natural processes of degradation (Prieto, 2016). The main reason that trigger to the bio-inert or non-

biodegradable properties of many plastics materials is due to their hydrophobicity and high molecular weight of the synthetic polymer that inhibit the process of phagocytosis. Subsequently, the decomposition of plastic by the action of certain microorganisms that capable of degrading plastic is very low (Eich et al., 2015).

Yet, the increasing of the production and consumption of the oil-based plastic products have been raised up the environmental problems from the discarding of non-degradable plastic materials. As the disposed plastic wastes are introduced into the marine environment, it can harm the marine species and destroy the ecosystem. According to Eich et al. (2015), the negative impacts of the plastic litter to the marine system include entanglement of animals, swallowed of plastics mistaken as food by marine species, accumulation of persistent organic pollutants, and the transportation of harmful algae and hostile species. Blue Ocean Society for Marine Conservation is one of the organization claimed that more than 1 million birds and 100,000 marine mammals and sea turtles die each year from eating or getting entangled in plastic waste (Mangu-Ward, 2015).

In addition, the disposal of non-degradable plastic wastes has created the shortage of the landfill. The plastic wastes are predicted to constitute for about 20-30 % of the total amount of municipal solid wastes landfill site among numerous wastes (Adamcová and Vaverkova, 2014). Plastics are resistant to the microbial degradation, hence they will remain in the landfill site semi-

permanently and will lead to the landfill depletion (Adamcová and Vaverkova, 2014).

There are several alternatives for plastic wastes management such as incineration, recycle, and reuse (Swift, 1993). However, the development of the environmental friendly biodegradable polymer is more likely a potential solution to solve these problems where the recovery of the conventional plastics for incineration requires high cost and is challenging (Swift, 1993). Besides, some problems may arise if the plastic wastes are disposed by incineration, such as releasing of the toxic gases or damaging of the incinerator (Tokiwa and Tsuchiya, 2003). Moreover, the non-degradable plastics are mostly hard to recycle or reuse might due to the plastic constitute the diverse types of contamination and complex composite (Davis and Song, 2006). Hence, development of biodegradable polymer is the most attractive solution for a number of environmental pollution issues resulting from non-degradable synthetic polymer materials. Biodegradable polymers tend to decompose completely into the carbon dioxide, methane, water, biomass, and inorganic compound through the microbial activities under the environmental condition (Adamcová and Vaverkova, 2014).

According to the Sedlařík et al. (2007), biodegradable polymer can be classified into three types:

- I. Biopolymer, the polymer that is derived from the natural resources such as plant-origin polysaccharide and animal-origin protein.

- II. Crude oil-based synthetic polymer with a hydrolyzable back-bone chain such as polyester and polyvinyl alcohol.
- III. Modified natural or synthetic polymer, polymer that undergoes several physical or chemical modifications to enhance certain polymeric properties, biodegradability, and cost.

The biodegradable polymers are suitable to be used in a wide range of applications such as packaging, surgical implant, controlled release, and drug delivery. Nevertheless, the high cost and low performance limit their utilization in such applications (Yun et al., 2008).

Polyvinyl alcohol (PVA) is technologically potential as a synthetic biodegradable polymer, and has been proven to be consumed by the microorganisms and enzymes when exposed to natural environment condition (Sin et al., 2010). As reported by Ozaki et al. (2005), PVA is the most widely produced water soluble and biodegradable synthetic polymer globally. It can be used in the preparation of the membrane or thin film because of its high water permeability and excellent film forming properties (Lang et al., 1996). Since PVA is water soluble, thus allowing the production of film by solution casting method (Ramaraj and Poomalai, 2006). It is slightly affected by grease, hydrocarbons, and animal or vegetable oils due to its chemical and physical stability against organic solvents (Lang et al., 1996). Hence, the good chemical resistance and physical properties have resulted it in wide spread used in the industrial area (Ramaraj, 2007). In the spite of advantages, the economic

reason of high cost for the PVA has become limiting factor for many applications and has to compete with the other low cost plastic materials such as polyethylene, polypropylene, and polyvinyl chloride especially in packing application (Ramaraj, 2007). Apart from that, PVA showed slow rate of degradation under natural aqueous and soil environment (Ozaki et al., 2005).

In order to enhance the biodegradability and reduce the cost, blend of PVA with the biomaterials was developed. Yet, there are concerns that the possible sources of the biomaterials have to compete with the food sources. Thus, finding a new resource of biomaterial that are not originate from food sources become more interested. Based on the previous study, PVA was blended with several natural biopolymers such as starch, chitin, chitosan, sugar cane bagasse and other lignocellulosic fillers (Ozaki et al., 2005). These natural macromolecules contain hydrolyzable linkages that are usually susceptible to biodegradation by the hydrolytic enzymes of microorganisms (Khemani, 2003). The newly composite film has greater hydrophilicity and biodegradability while reducing the production cost instantaneously (Ozaki et al., 2005). Successful blending of the PVA with the natural polymers like starch and lingo-cellulosic compounds can be developed by establishing the new bonding or interaction between the PVA and natural polymer while breaking the intermolecular or intramolecular hydrogen bonding within the PVA (Ramaraj and Poomalai, 2006). Good compatibility of PVA with the hetero-functional natural filler can be formed through the strong hydrogen bonding of the

hydroxyl and carboxyl groups among the molecules (Ramaraj and Poomalai, 2006).

According to Tang et al. (2008), blends of starch and PVA are typically one of the most popular biodegradable polymers and are broadly used in packaging and agriculture applications. Among all of the natural biopolymers, starches are certainly the most desirable to cooperate with the polyvinyl alcohol to produce the biodegradable composite film since they are cheap, abundant in nature and are completely biodegradable (Tang et al., 2008). Sources of starches can be obtained from the crops such as cassava, pea, rice, maize, and potatoes. As has been proven, the starch can be decomposed by microorganisms under natural environment because starch possesses similar functionality as PVA (Sin et al., 2010). When the PVA is blended with the starch compound, strong hydrogen bonds are formed between the molecules and consequently resulted in greater stability structure (Sin et al., 2010). However, the utilization of the crop yield as the source of starch is not economic, hence many attempts have been made to overcome this problem by using the wastes or the by-product of the harvests in the agriculture. The utilization of the wastes would be beneficially not only in the term of economic concern but also environmental consideration regarding to the disposal of large amount of the wastes. A number of studies have been focused on the uses of the organic agriculture wastes in the preparation of the low cost biodegradable polymers (Ooi et al., 2012; Ozaki, 2005; Ramaraj and Poomalai, 2006; Sedlařík, 2007).

To my best of knowledge, there is no previous study involving the citrus peel waste flour (CPWF) blend with the PVA in the preparation of the environmental friendly biodegradable polymer. As reported by M'hiri et al. (2015), the amount of the global industrial citrus waste is predicted at  $15 \times 10^6$  tons. The main industrial transformation of the citrus is on juice production and the citrus juice production has resulted in the accumulation of large amount of the by-products such as peel, seed, and pulp membrane residues which account approximately half of the fruit weight (M'hiri et al., 2015). Thus, the disposal of the citrus wastes has resulted to the environmental issues especially landfill problem. Among those of the citrus wastes, the peel contributes to the largest portion and it has been proven consist of predominantly starch content. Hence, the incorporation of the CPWF into the PVA to produce the biodegradable composite film is not only economic consideration but also environment concern where it can particularly reduce and solve the disposal of citrus wastes problem.

## **1.2 Problem Statement**

The plastic industries are growing gradually worldwide and the plastics are used in many applications due to its attractive properties such as light weight, high adaptability, and ease of manufacturing. The most widely used plastics are typically derived from the petroleum. Conversely, the consumption and the production of the petroleum-based plastics should be reduced, as the oil

resources are running out. Besides, the disposal of the non-degradable plastic wastes has resulted in the shortage of the landfill. Therefore, the reduction of the landfill available and increasing in the public environment awareness lead to the growing of the attention in the proper plastic waste management such as recycle and incineration as well as the development of the biodegradable plastic with the cooperate of the renewable biopolymer resources.

Nevertheless, some problems were encountered in the recycling of the plastic wastes like excessive contamination, difficulty in the separation, and poor polymer properties. In addition, the incineration of the plastic waste may lead to the releasing of the toxic gases to the environment. Hence, the development of the biodegradable polymers is the most compromising approach to solve the problem of the accumulation of the non-degradable plastic waste. Biodegradable polymers that are derived from the renewable sources such as starch provide an alternative to replace the petroleum-based polymers and thus can overcome the problem of the oil supply depletion.

Biodegradable plastic can be decomposed under the natural process of degradation without leaving any environmental impact. The blending of the starch and PVA is the most attractive method to be produced in term of environmental concern as reported by many researches (Ooi et al., 2012; Yun et al., 2008; Ramaraj, 2007; Wang et al., 2008; Sin et al., 2010; Elizondo, Sobral, and Menegalli, 2009). Starch can be decomposed completely by the action of microorganism and it is believed that the incorporation of the starch

with the PVA can enhance the biodegradability of the polymer. However, the utilization of the agriculture crops yields as the sources of the starch is not economic consideration, thus the agriculture organic wastes are suggested to be introduced into the PVA in order to produce the low cost and biodegradable composite film. Apart from that, the usage of the agriculture organic wastes can provide a solution to the problem of disposal of the huge amount of agriculture waste. In this research project, the citrus peel waste flour (CPWF) is selected to be used as the natural filler to blend with polyvinyl alcohol (PVA) in order to yield the newly biodegradable cast film by solution casting method.

### **1.3 Research Objectives**

The main goal for this research project is concerned with the biodegradability of the PVA films after incorporating the natural biopolymer, citrus peel waste flour (CPWF) as filler. There are few objectives for this research which including:

- I. To characterize the citrus peel waste flour.
- II. To prepare and formulate the environmental friendly and biodegradable citrus peel waste flour-filled polyvinyl alcohol composite films using solution casting method.
- III. To study the effect of citrus peel waste flour on the properties of the prepared films in terms of the surface morphology, tensile properties, water absorption and solubility, thermal properties, and degradability by natural weathering.

## 1.4 Research Hypothesis

In this research work, the polymer blend of polyvinyl alcohol (PVA) with citrus peel waste flour (CPWF) was being synthesized by solution casting method. Different weight ratio of the CPWF and PVA are used to prepare the cast film as to determine which composition has the superior properties in terms of the thermal properties, tensile properties, water resistance, and degradability for the uses of packaging application. The hypothesis for this research project are:

- I. The tensile strength of the blended film will be improved when the amount of the CPWF added into the PVA matrix increased.
- II. The higher the amount of the CPWF incorporated into the polymer blend will cause to the significant increase in the thermal stability of the blended film.
- III. The water absorption and solubility of the PVA and CPWF blended film was predicted to be increased as the CPWF incorporated increased.
- IV. The increasing of the concentration of CPWF in the polymer blend will enhance the degradability of the blended film.

## **1.5 Scope of Study**

The overarching aim of this research project is to synthesis the degradable plastic materials resulted from the economic and environmental concern. Numerous researches regarding to the current practices in the production of the environmental friendly packaging polymeric material by blending PVA and the agriculture crops or its wastes have been studied (Ooi et al., 2012; Yun et al., 2008; Ozaki et al., 2005; Imam, 2005; Ramaraj, 2007; Wang et al., 2008; Sin et al., 2010; Elizondo, Sobral, and Menegalli, 2009; Ramaraj and Poomalai, 2006). In this project, the polymer blends of different weight ratio of PVA and citrus peel waste flour (CPWF) are synthesized by solution casting method and the several tests are conducted on the cast films in order to study the tensile strength, thermal properties, water absorption and solubility, and degradability by natural weathering. The introducing of the CPWF into the PVA has subjected to improve certain properties of the blended film. The cast film with specific composition of the PVA and the CPWF with the superior properties in the view of packaging application can be used to replace the massive utilization non-degradable plastic packaging materials in the industries area.

## **1.6 Significance of Study**

This study will focus on the development of the biodegradable plastic materials as to improve the environment condition not only in Malaysia but also in the view of global. I hope that this research can introduce an effective strategy to

the efficiently utilization of the agriculture wastes and to reduce the negative impact to the environment from the disposal of the non-degradable plastic materials.

The outcomes to be considered from this research project are shown as the following:

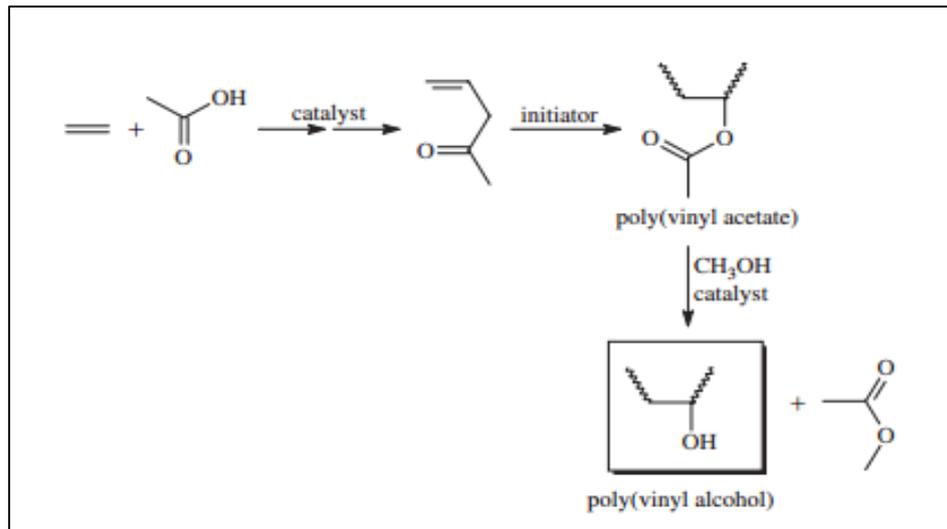
- I. Resolve the critical landfill shortage problem for plastic wastes.
- II. Reduce the amount of non-degradable plastic wastes as to improve the sanitation of the environment as well as marine system.
- III. Decrease the negative impacts from the accumulation of the non-degradable plastic wastes to the living organisms.
- IV. Introduce an effective approach for the plastic wastes management in the view of environment and economic concern.
- V. Efficiently use or manage the agriculture wastes.
- VI. Create low cost and biodegradable plastic materials for packaging application that is beneficial for both consumers and environment.

## CHAPTER 2

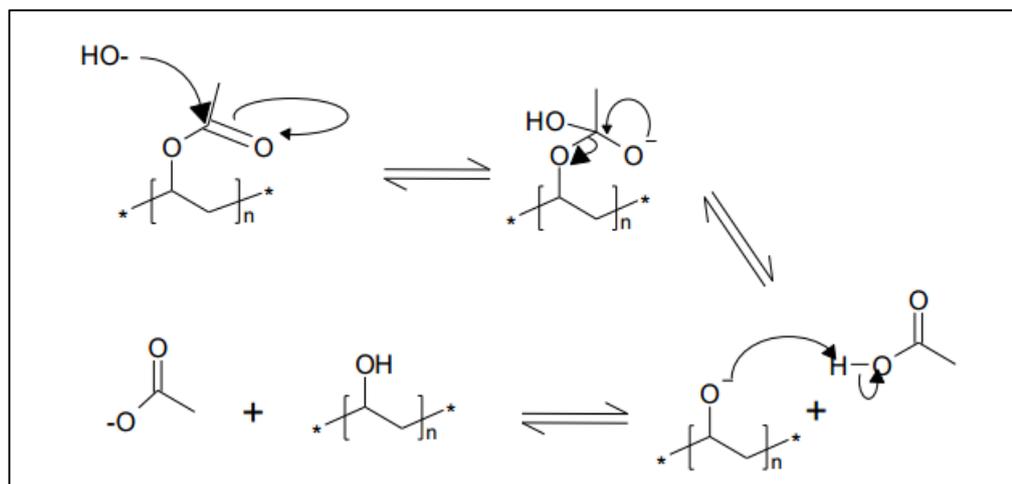
### LITERATURE REVIEW

#### 2.1 Polyvinyl alcohol (PVA)

According to Saxena (2004), polyvinyl alcohol (PVA) is synthesized commercially by the radical polymerization of the vinyl acetate monomers followed by partial hydrolysis of polyvinyl acetate (PVAc), in which the process of hydrolysis is dependent on the partial replacement of the ester group in the vinyl acetate with the hydroxyl groups and the process is completed in the presence of aqueous sodium hydroxide. PVA can ultimately be obtained through a saponification process from PVAc or via alcoholysis (hydrolysis) reaction of PVAc with methanol (Tan et al., 2015). Methanolysis is the most conservative way to hydrolyze PVAc in which PVAc is dissolved in methanol and afterward a base or acid catalyst is added into the solution in order to hydrolyze the acetate groups into hydroxyl groups (Illanes, 2010). The hydrolysis reaction does not always go to completion, hence PVA often exists as a copolymer of PVA and PVAc (Hassan and Peppas, 2000). High degree of hydrolysis of PVA (99 %) is commercially available. Different degrees of hydrolysis of PVA can be gained by regulating the time, temperature and pH strength of the methanolysis (Illanes, 2010).



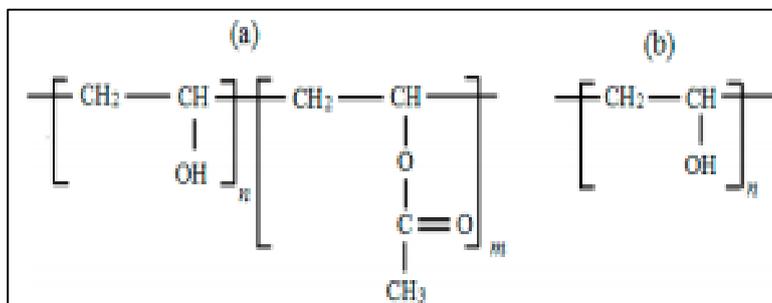
**Figure 2.1:** Manufacturing pathway for PVA (Rudnik, 2008).



**Figure 2.2:** Schematic pictures for the synthesis of the PVA through the methanolysis of PVAc (Illanes, 2010).

The physical properties and its practical uses or applications depend on the degree of polymerization and degree of hydrolysis. PVA can be classified into two different grades depend on the extent or degree of hydrolysis which are fully hydrolyzed and partially hydrolyzed (Saxena, 2004). The degree of polymerization represents the number of remaining acetate groups that are

present in the polymer chain where the saponification and alcoholysis (hydrolysis) has not taken place (Tan et al., 2015).



**Figure 2.3 :** Structural formula of polyvinyl alcohol (a) Partially hydrolyzed (b) Fully hydrolyzed (Gaaz et al, 2015).

PVA is odorless, tasteless, translucent, and presence as white or cream color granular powder. It is soluble in water and slightly soluble in ethanol, but insoluble in any other organic solvent (Saxena, 2004). Moreover, it is non-toxic, high oxygen and aroma barrier properties, consists of considerable tensile strength, and satisfactory flexibility (Gaaz et al., 2015). PVA is a synthetic polymer that has been used during the first half of the 20<sup>th</sup> century worldwide (Gaaz et al., 2015). Apart from that, PVA is one of the largest amount of the synthetic resin production globally owing to its excellent chemical resistance, physical properties, biocompatibility, and completely biodegradability under natural environment (Ballén, 2012). Since PVA is water soluble, its films can be prepared by casting evaporation technique from the aqueous polymer solutions, hence can reduce the production cost and more environmental friendly by preventing the use of the organic solvent (Ballén, 2012). A clear, homogenous film with tear resistance property can be produced by this method.

In addition, PVA is the petroleum-based synthetic polymer that can degrade naturally in the environment under aerobic (composting) and anaerobic (landfill) conditions (Pajak, Ziemski, and Nowak, 2010). Unlike other vinyl polymer that resist to the degradation under natural environment, PVA is known to be one of the few vinyl polymer with higher biodegradation rate. PVA is the exception to the rule in which polymer with single carbon-carbon single bonds are resistant to the degradation (Stevens, 2002). The regular occurrence of hydroxyl groups on alternate carbon atoms of the polymer chain results in the formation of the strong interactions with the water molecules by great extent of hydrogen bonds (Stevens, 2002). Therefore, PVA is hydrophilic and water soluble that can help to enhance the degradation via hydrolysis mechanism. The degradation of PVA will result in the releasing of water molecules from the polymer matrix, followed by the formation of volatile degradation products, such as acetic acid in partially acetylated samples (Rudnik, 2008). Yet, the degradation of the PVA is particularly slow owing to its aliphatic backbone and the carbon-carbon bond required high energy to breakdown (Illanes, 2010).

PVA has been proven can be degrade under microbial environment, it can be enzymatic degraded by secondary alcohol peroxidases isolated from soil bacteria of the *Pseudomonas* strain (Chandra and Rustgi, 1998). Hence, it can be concluded that the early biodegradation of the PVA involved the enzymatic oxidation of the secondary alcohol groups into the ketone functional groups and further hydrolysis of ketone groups will lead to the chain cleavage into the small fragments (Chandra and Rustgi, 1998). Other than *Pseudomonas*, the

bacteria such as *Flavobacterium* and *Acinetobacter* have been proven to degrade PVA efficiently (Chandra and Rustgi, 1998).

PVA is often used in blends or composites with other polymers components, like biopolymers and other polymers with hydrophilic properties. The polymer blends are used in many industrial applications to improve the mechanical properties of the films due to its compatibility structure and hydrophilic properties. (Gaaz et al., 2015). Renewable polymers such as chitosan, nanocellulose, starch or lignocellulosic fillers have been blended with PVA to produce polymer blends and composites (Tan et al., 2015). The polymer blends can be processed by conventional plastic technology show good balance of barrier and strength properties, low moisture absorptivity, and combinations of toughness and modulus suitable for packaging applications (Jelinska et al., 2010). For the consideration of many inventive and environmentally conscious manufacturers, the composites of PVA and biopolymers like natural fibers will improve the biodegradability and physical properties of the newly produced polymer, consider as a good choice of eco-sustainable materials (Tan et al., 2015).

## **2.2 Citrus Fruit and Citrus Wastes Generation**

Citrus is a big genre that consists of various major cultivated types, including *citrus sinensis* (sweet orange), *citrus reticulata* (tangerine and mandarin), *citrus limon* (lemon), *citrus grandis* (pummelo) and *citrus paradisi* (grapefruit) (Xu et

al., 2013). Citrus sinensis or sweet orange are originated from south East Asia, it is the excellent source for vitamin C and consumed all over the world (Etebu and Nwauzoma, 2014). Sweet orange was accounted for nearly 60 % of the citrus production mainly for both fresh food and processed juice consumption among the 10.9 million tons (valued at \$9.3 billion) of citrus products transacted in 2009 (Xu et al., 2013).

Yet, the problem arising due to the citrus processing industry will produce tons of the residues annually, consisting of peels and segment membranes resulting from the production of citrus juice in the industrial plant (Torrado et al., 2011). As reported by Ma, Cervara, and Sánchez (1993), huge amount of solid wastes resulted from the industrial extraction of the citrus juice mainly constitute by citrus peel, which is about 45 to 50 % of the original weight of Mexican citrus. The management of the citrus wastes will generate unpleasant odor and lead to soil pollution and imply a main problem in the food industry (Torrado et al., 2011).

According to Rivas et al. (2008), citrus peel contains several important components, including soluble sugars (16.9 %), cellulose (9.21 %), hemicellulose (10.5 %), and pectin (42.5 %). As reported by Torrado et al. (2011), the citrus peel is composed of several components as shown in the following table:

**Table 2.1:** Chemical compositions in the citrus peel and their proportions (Torrado et al., 2011).

<b>Components</b>	<b>Percentage (% wt)</b>
Soluble Sugars	16.90
Starch	3.75
Fiber (cellulose, hemicelluloses, lignin and pectins)	63.05
Ashes	3.50
Fats	1.95
Protein	6.50

### **2.3 PVA-Starch Blend Film**

Polymer blending is a conservative way for the production of new polymeric compounds with superior properties than individual components (He, Zhu, and Inoue, 2004). The concept of combining two or more different polymers to generate a new compound with desirable properties is not new (Paul and Barlow, 2008). In the spite of advantages, polymer blending consumed relatively low cost and less time required for the generation of polymeric compounds with desirable properties than the development of newly polymer or by new polymerization paths (He, Zhu, and Inoue, 2004). Besides, the properties of the polymer produced can be adjusted for specific application via combination of different polymer types and altering the composition of the blends.

Nowadays, the production and consumption of non-degradable synthetic plastic materials have been created serious environmental pollutions. Hence, the development of environmental friendly and biodegradable polymeric materials can discover a short term application to replace the petroleum-based

synthetic polymer to preserve the petroleum resources and to reduce the negative impact from the non-degradable polymer materials. Among the natural polymers, starch is the most attractive candidate to be used because it is totally biodegradable, low cost and potential for mass production in renewable resources. Starch can be found widely in the plant crops such as potatoes, corn, and rice. Besides, several desirable properties of the starch make it suitable to be used widely in the plastic industry, such as comparable mechanical properties, useful particulate form, providing materials with low energy demands from renewable resources (Chandra and Rustgi, 1998). However, the brittleness, poor resistance to water, and easily loss of strength at low humidity are also the factors that limit the use of most starch in the application of biopolymer materials (Wittaya, 2012). Therefore, blending of starch with PVA is a popular method as to increase the mechanical properties and reduce the water sensitivity of starch (Hejri et al., 2012). To add to that, the flexibility and strength of starch can be improved accordingly with the incorporation of PVA (Wittaya, 2012). Starch-PVA blend films are now extensively used in packaging application.

Several attempts have been made to blend the starch such as potato starch, rich starch, corn starch, fruit waste, cassava starch with PVA and these blends have demonstrated excellent compatibility. Characterizations of starch-filled PVA films in the terms of morphology studies, tensile strength, elongation, water absorption and solubility and degradation have been studied by many researches (Azahari, Othman and Ismail, 2011; Ooi et al., 2012; Yun et al., 2008; Imam et al., 2005; Ramaraj, 2007; Wang et al., 2008; Sin et al., 2010;

Elizondo, Sobral and Menegalli, 2009). Based on the previous study, it was found that the tensile properties, elongation at break of PVA were improved with the addition of PVA. This can be explained by both starch and PVA are polar compounds that consist of hydroxyl group in their chemical structure, which are able to form intermolecular and intramolecular hydrogen bonds that enhance the integrity of the PVA-starch films (Lani et al., 2014).

Next, the solubility parameter of starch and PVA are close to each other, this indicates that the starch and PVA are compatible blend (Wittaya, 2012). Apart from that, the vibration frequency analysis of starch-PVA blend show that the hydroxyl group was shifted to lower wavenumber due to the formation of hydrogen bond between starch and PVA.

## **2.4 Solution casting method**

Starch-based film can be formulated by several methods, one of the popular method is solution casting. Solution casting method is a relatively easy and adaptable technique to produce laboratory scale composite thin films (Oksman et al., 2014).

In this technique, polymer is dissolved in an appropriate solvent to obtain a viscous polymer solution, the solution is then poured onto a level and non-adhesive surface. Next, the solvent is allowed to evaporate or remove and thus

the dry film can be stripped or peeled off from the flat surface. The solvent used in this method must be adequately volatile as to evaporate the solvent at room temperature or slightly higher. However, the solvent must not vaporize too rapidly because the bubbles or semi-crystalline precipitate will form (Kumbar, Laurencin, and Deng, 2014). Moreover, the process of rapid volatilization of the solvent will also cause cooling of the film, which will further caused the occurrence of crazing or condensation of water from the atmosphere (Kumbar, Laurencin, and Deng, 2014).

Several parameters have to control in order to produce the thin film that is adhere well to the substrate, uniform to thickness, and are free from imperfections (Taylor and Schultz, 1996). Such parameters including polymer concentration, solvent composition, amount of solution deposited, and the rate of solvent evaporation (Taylor and Schultz, 1996). Solution casting method is typically carry out at low temperature and produce the films with uniform thickness, optical purity, low haze, and isotropy (Oksman et al, 2014).

## **2.5 Characterizations of PVA-Starch Blend Film**

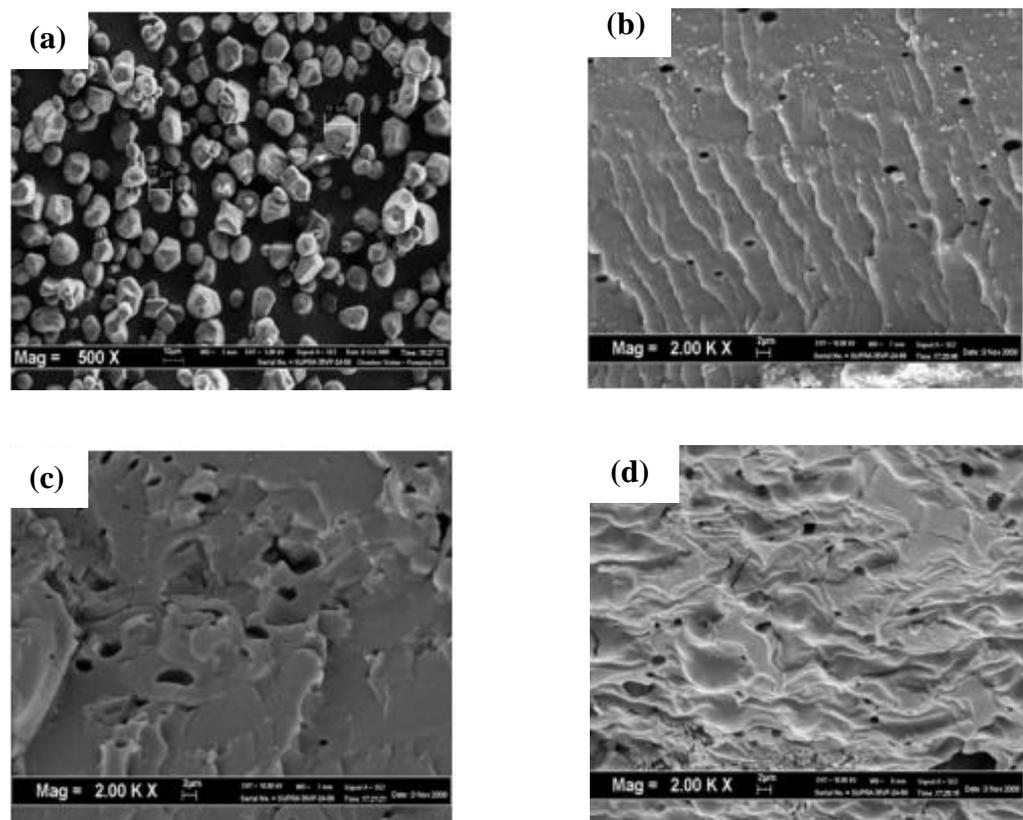
### **2.5.1 Morphologies Studies- Scanning Electron Microscope (SEM)**

#### **Analysis**

Today, the polymeric materials used are usually not homopolymer, but consist of more than one type of polymer, which may result in morphologies of different length scales and shapes (Hassander, 2004). Since the characteristics and properties of the polymer vary depending on its structure, thus it is essential to determine the surface morphologies. The polymer morphologies can be studied by Scanning Electron Microscopy (SEM) in order to make a precise interpretation of the results.

According to Azahari, Othman and Ismail (2011), polyvinyl alcohol (PVA)/corn starch (CS) blends were prepared by solution casting method and the surface morphology of the blended films was characterized by scanning electron microscopy (SEM). The morphological structures of CS, pure PVA film, and PVA/CS blended films are shown in Figure 2.4. According to SEM micrographs of CS and pure PVA film as revealed in Figure 2.4 (a) and Figure 2.4 (b) respectively, the CS granules are present as elliptical in shape while the pure PVA film contains voids which may be due to the trapping of bubbles during the casting of film. With the increasing of the CS introduced in the PVA matrix, the CS phase changes from the dispersed phase, it represents that the amorphous starch is partially miscible with PVA. From Figure 2.4 (c), we can observe that the CS granules are well dispersed in PVA/CS blend with the weight ratio of 70/30. However, the cryo-fractured surface becomes

coarser and more brittle when the CS content added into the PVA matrix up to 70 %. It may due to the PVA is finely dispersed in the CS but the starch granules coalesce instantaneously. The well dispersion of the corn starch in the PVA matrix can improve the mechanical properties of the blended film. This is in agreement with the tensile properties of the PVA/CS blended film that shows reduction when the CS concentration increased from 30 % to 70 %.

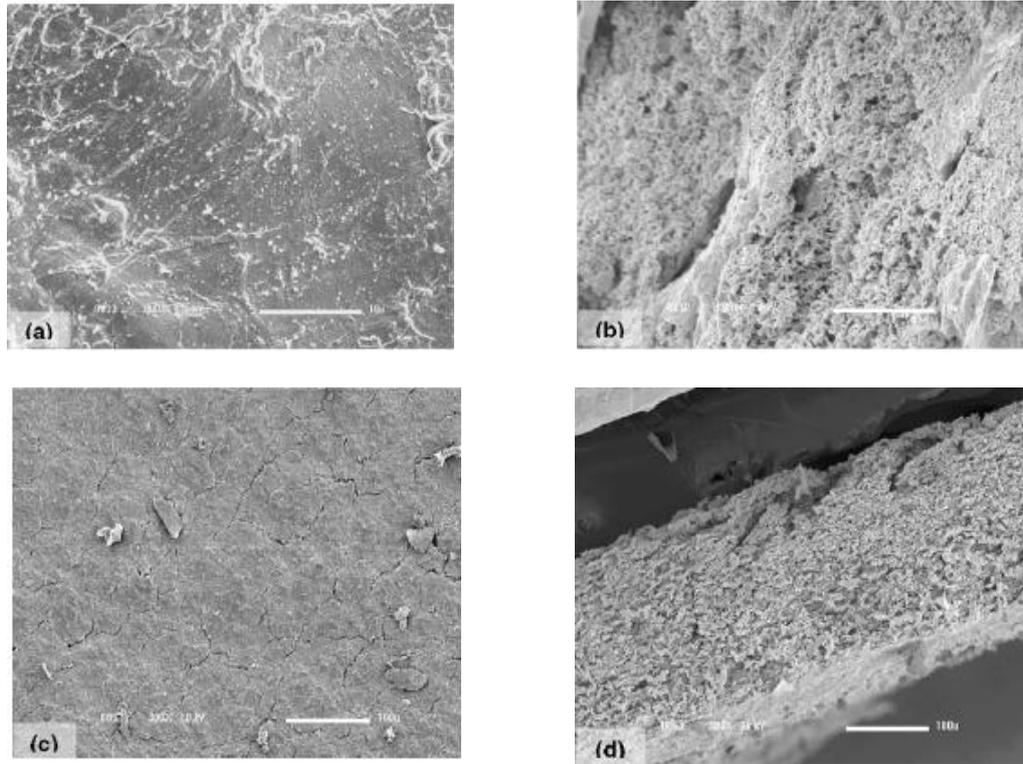


**Figure 2.4:** SEM micrographs of (a) corn starch (CS) granules, (b) pure PVA film, (c) PVA/CS (70/30) film, (d) PVA/CS (30/70) film (Azahari, Othman and Ismail, 2011).

As reported by Elizondo, Sobral and Menegalli (2009), polyvinyl alcohol (PVA) with different degree of hydrolysis were blended with amaranth flour in the film production. The surface morphologies of the *Amaranthus cruentus* flour and PVA-325 (98-98.8 % degree of hydrolysis) blends and pure

amaranthus cruentus flour film were study by scanning electron microscopy (SEM). The SEM micrographs of Amaranthus cruentus flour/PVA-325 blended film and pure amaranthus cruentus flour film are illustrated in Figure 2.5. Based on Figure 2.5 (a), it can be observed that the surface amaranthus cruentus flour/PVA-325 is compact and shows some uneven distribution along the surface but without any fractured as compared to surface of pure amaranthus cruentus flour film. It is due to incorporation of PVA into the starch triggers changes in the biopolymer structure at both molecular and morphological levels, reducing its rigidity simultaneously.

According to the Figure 2.5 (b), the cross-section of the Amaranthus cruentus flour/PVA-325 blended film shows a significant amount of well-distributed micro-pores which is similar in the emulsion, possibly because of the homogenization process in the preparation of the blended film used to increase the miscibility between the PVA and amaranth flour starch and proteins. Besides, the surface of pure amaranthus flour film is denser due to the amaranthus cruentus granules are distributed evenly in the film along but with the present of some cracks. Besides, the cross sectional micro-structure of the pure amaranthus cruentus film is denser and compact compared with the Amaranthus cruentus flour/PVA-325 blended film, which shows agreement with typical starch and protein films.



**Figure 2.5:** Scanning electron micrographs of (a) the surface and (b) the cross section of amaranthus cruentus flour/PVA-325 film blended in equal proportions at the magnification of 3,000 x, and (c) the surface and (d) the cross-section of pure Amaranthus cruentus flour film at the magnification of 300 x (Elizondo, Sobral and Menegalli, 2009).

### 2.5.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FTIR) is a technique that is widely used to characterize the properties polymer blends both quantitatively and qualitatively as well as to their compatibility via intermolecular bonding. FTIR spectroscopy are potentially used in the polymer blend studies because the physical properties of the polymer blends are depending on their structure of the molecular chains and types of interactions and configuration exhibited. Hence, FTIR spectroscopy is useful for predicting the physical and mechanical properties of the polymer blends.

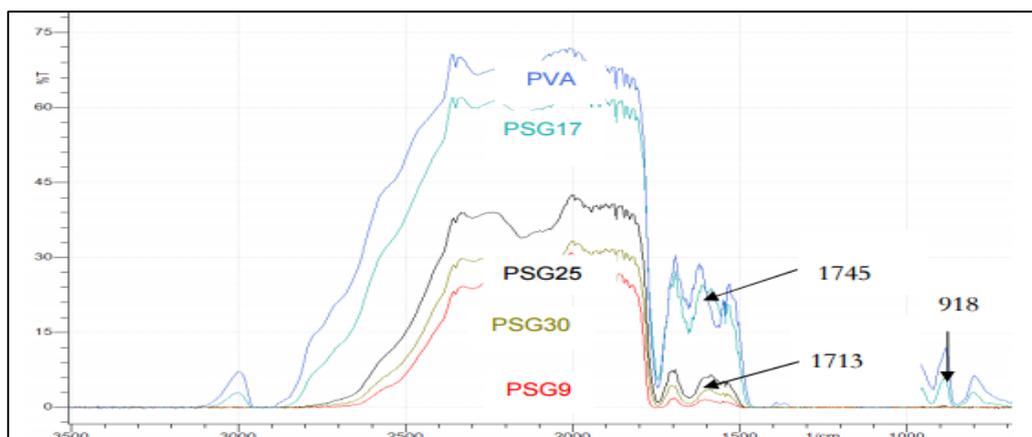
As reported by Răpă et al. (2014), the polyvinyl alcohol (PVA)/starch blends films were prepared by using the melting method. The formulation used to prepare the PVA/starch blended films is shown in the Table 2.2. The FTIR spectra of the PVA and PVA/starch films are revealed in Figure 2.6 while Table 2.3 summarizes the absorption peaks assigned in FTIR spectra of PVA and PVA/starch blends. The stretching and the bending vibration of the hydrogen bonding –OH group for both PVA and PVA/starch blends are located at wavenumber 3500-3200  $\text{cm}^{-1}$  and 1653  $\text{cm}^{-1}$ , respectively. Next, the absorption peak signals at 790-775  $\text{cm}^{-1}$  may arise from the stretching vibration of C-O bonding in C-O-C group in anhydrous glucose ring. Besides, the absorption peaks occur at 1745  $\text{cm}^{-1}$  and 1713  $\text{cm}^{-1}$  in the pure PVA film are attributed to the present of residual acetate group due to the manufacture of the PVA from the hydrolysis of polyvinyl acetate was incomplete. All of the PVA/starch blends exhibit absorption bands characterized by pure PVA, including 3500-3200  $\text{cm}^{-1}$ , 2955  $\text{cm}^{-1}$ , 1745  $\text{cm}^{-1}$ , 1456  $\text{cm}^{-1}$ , 1430-1275  $\text{cm}^{-1}$  which are corresponding to O-H stretching, C-H stretching, C=O stretching, C-H bend of  $\text{CH}_2$ , and C-H wagging. This represents the successful blending of PVA with starch. In addition, absorption peak appears at 918  $\text{cm}^{-1}$  in FTIR spectra of PVA is C-H rocking mode and is slightly shifted in PVA/starch blends.

**Table 2.2:** Formulation used to prepare the PVA/starch blends (Răpă et al., 2014).

<b>Sample code</b>	<b>PVA, wt.%</b>	<b>Starch, wt.%</b>	<b>Glycerol wt.%</b>	<b>PVA/Starch wt./wt.</b>	<b>Dry substances/Plasticizer, wt./wt.</b>
PSG 9	62	9	29	6.88	2.44
PSG 17	37	17	46	2.17	1.17

**Table 2.2:** Continued.

Sample Code	PVA, wt.%	Starch, wt.%	Glycerol wt.%	PVA/Starch wt./wt.	Dry substances/Plasticizer, wt./wt.
PSG 25	29	25	46	1.16	1.17
PSG 30	30	30	40	1.00	1.50



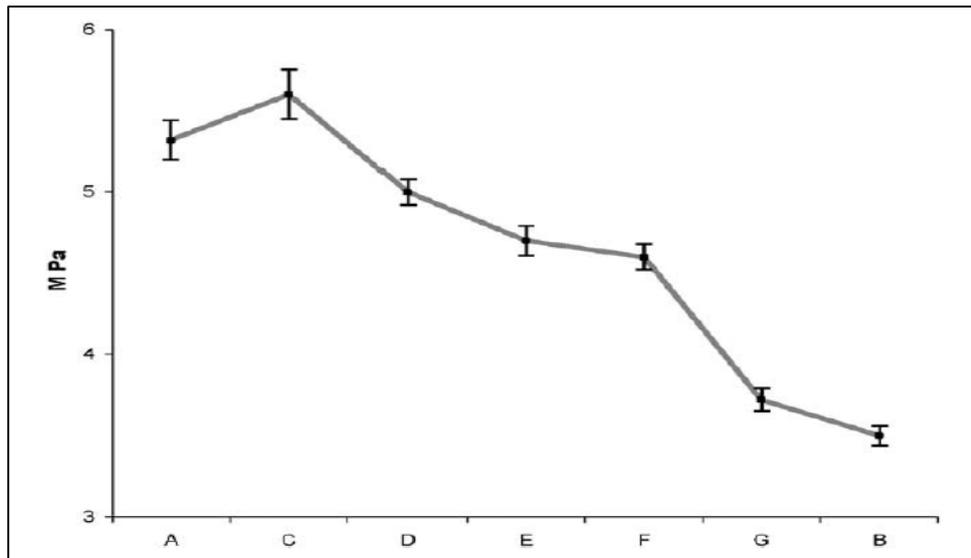
**Figure 2.6:** FTIR spectra of PVA and PVA/starch blends (Râpă et al., 2014).

**Table 2.3:** Absorption peak assigned in FTIR spectra of PVA and PVA/starch blends (Râpă et al., 2014).

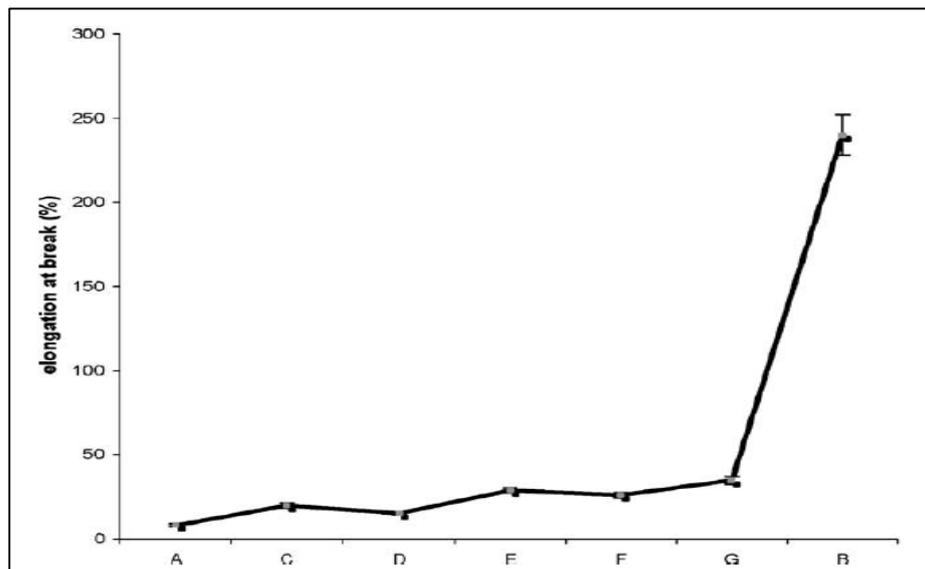
Absorption peak assigned	PVA	PSG 9	PSG 17	PSG 25	PSG 30
C-O bending in C-O-C ring due to starch	-	790-775	758	789-775	789-775
C-H rocking	918	916	926	916	943
C-O stretching in C-O-C	1055	1013	1022	1043	1022
C-O stretching in C-O-H	-	1143	1146	1148	1149
C-H wagging	1430-1275	1433-1205	1433-1205	1433-1205	1433-1205
C-H bending of CH <sub>2</sub>	1456	1460	1460	1460	1458
O-H bending	1653	1653	1656	1653	1653
C=O stretching (carbonyl vibration in the residual acetate in PVA)	1745	1742	1744	1742	1745
C-H stretching	2955	2850	2964	2964	2947
-OH stretching	3500-3200	3500-3200	3500-3200	3500-3200	3500-3200

### 2.5.3 Tensile Properties

Tensile test is typically used to study the tensile properties of the polymeric materials. The ability of the polymeric materials, such as film to resist the tensile stress plays an important in identifying the mechanical properties of the film in structural applications. As reported by Sudhamani, Prasad and Sankar (2003), the tensile properties of pure gellan, pure PVA and gellan/PVA blends at different weight ratio were studied. The tensile strength and elongation at break of the pure components of gellan and PVA and their blended films are revealed in Figure 2.7 and Figure 2.8 respectively. Based on Figure 2.7, the tensile strength tends to decrease with the increasing amount of PVA in the blended films. Gellan/PVA blends with the weight ratio of (3:1) has highest tensile strength, the notable increase in the tensile strength in the blended film indicates the molecular interaction between PVA and gellan. According to the Figure 2.8, the elongation behaviour of the films is similar with the tensile strength, except pure PVA film consists of highest percentage of elongation. The resulting mechanical properties is due to the molecular interaction between gellan, PVA, water, and glycerol in the blended films. The blending can improve the mechanical strength of the gellan is principally due to the formation of hydrogen bonding between PVA and Gellan.



**Figure 2.7:** Tensile strength of A-pure gellan, B-pure PVA, gellan and PVA blends at weight ratio of C) 3:1 D) 3:2 E) 1:1 F) 2:3 G) 1:3 (Sudhamani, Prasad and Sankar, 2003).

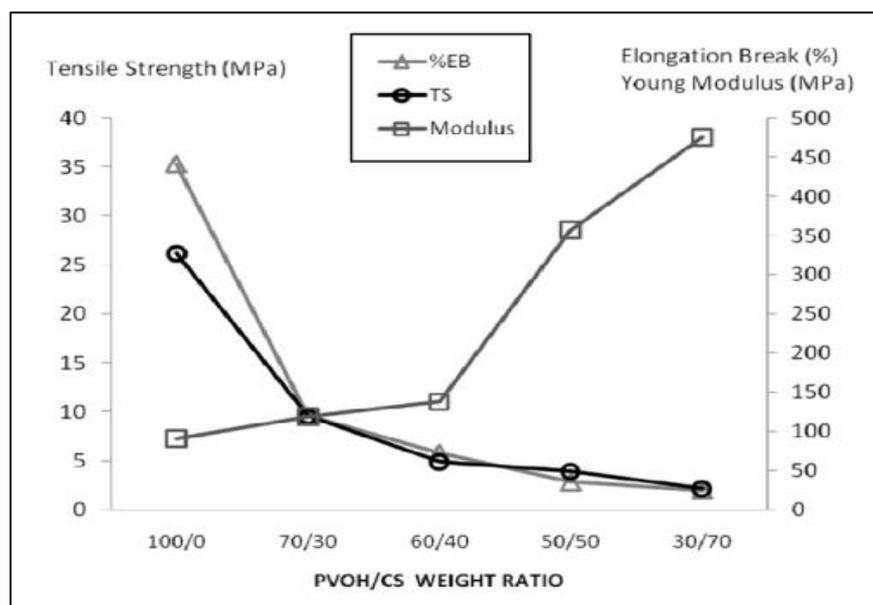


**Figure 2.8:** Percentage of elongation of A-pure gellan, B-pure PVA, gellan and PVA blends at weight ratio of C) 3:1 D) 3:2 E) 1:1 F) 2:3 G) 1:3 (Sudhamani, Prasad and Sankar, 2003).

According to Azahari, Othman and Ismail (2011), the effect of the blend ratio of the PVA and corn starch (CS) to the tensile properties of the PVA/CS films

was studied. Figure 2.9 illustrates the tensile strength of the PVA/CS films at different blend ratio. According to the Figure 2.9, the tensile strength of the PVA/CS blended film decreases with the increasing of the amount of CS. The reduction in the tensile strength is due to the amorphous nature of starch. The pure PVA film shows highest tensile strength (35.35 MPa) whereas the tensile strength of PVA/CS blended film at weight ratio of 70/30 is the highest compared to other blended films (9.58 MPa). Tensile strength is decreased with the incorporation of the starch is mainly due to filler-filler interaction. Filler-filler interaction become more obvious than filler-matrix interaction in higher starch introducing.

Similar trend can be observed in the elongation at break of the PVA/CS blended film. According to the Figure 2.9, the percentage of the elongation at break for the PVA/CS blended films decreases as the amount of the CS introduced into the matrix increases. To illustrate, pure PVA film shows highest elongation at break (327.2 %) while the PVA/CS (70/30) films shows highest percentage elongation at break (119.1 %) among all the the PVA/CS blended films. It indicates that the lowest weight percentage of PVA in the PVA/CS blended film will result in the lowest percentage of elongation at break. Conversely, the pattern of modulus for the film samples shows different trend with the tensile strength and elongation at break. The modulus of the blended films increases with the increasing of the CS content.



**Figure 2.9:** The tensile strength, elongation at break and modulus for PVA/corn starch (CS) blended film at different weight ratio (Azahari, Othman and Ismail, 2011).

#### 2.5.4 Water Absorption and Water Solubility

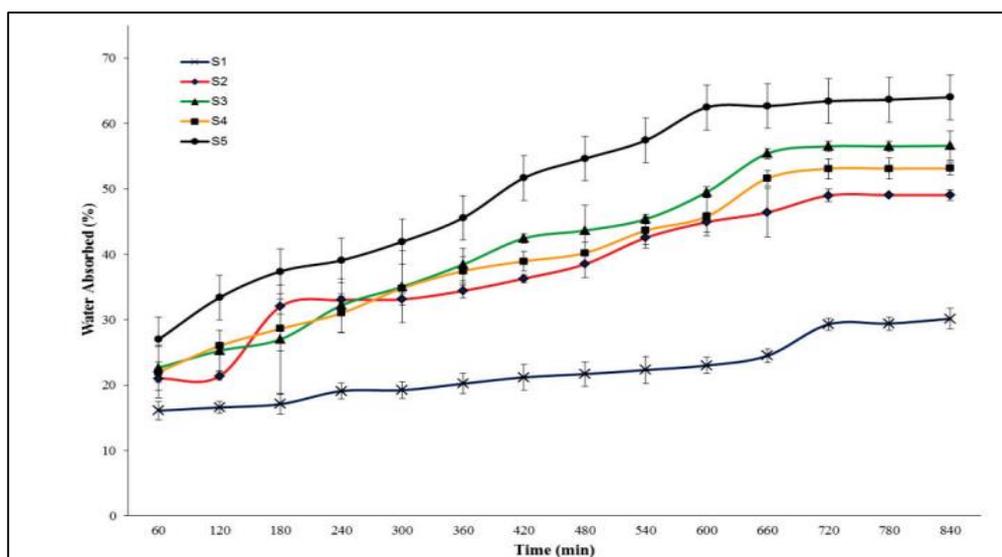
High water absorption and solubility are the limitations of the polymeric materials to prevent its widely used in many application. Hence, water resistance of the polymeric films should be improved to increase its utilization in various application.

According to the Salleh et al. (2017), the polyvinyl alcohol (PVA)/starch fiber (SF) films were prepared by using the melt mixing method and the water absorptivity of these films was investigated. Table 2.4 reveals the formulation used to prepared the PVA/SF blended films. The percentage of the water absorptivity of the SF-filled PVA blends at different composition is illustrated

in Figure 2.10. According to the Figure 2.10, the percentage of the water absorptivity of the PVA/SF blends increases with the incorporation of the SF content. This is due to the hydrophilic nature of the starch fiber that is easily to be influenced by the effect of water absorption. The PVA/SF blends of S1, S2 and S3 display similar trend of water absorption capacity but the percentage of water absorptivity increases with the increasing of SF content. All of the PVA/SF blends tend to absorb water after being immersed in water until 780 minutes or 13 hours. After 780 minutes, these blends are saturated with the water molecules inside the blended films and lost their water absorption ability. Besides, the PVA/SF film consists of lowest content of PVA (S5) has highest percentage of water absorptivity among all the blends films, due to the SF blend is not fully enclosed by the continuous PVA matrix and attributes to more freely available of hydroxyl groups expose to water binding sites. In addition, the amount of the SF into the PVA exceed 80 wt % will cause the decomposition of the components inside the blends. It may be attributed by higher hydrophilic nature matter inside the blends interrupted the PVA continuously phase and nearly all hydroxyl groups were bonded with water molecules. Eventually, the PVA/SF blends are gradually fragmented and loss their original structure prior to immerse in water.

**Table 2.4:** The formulation used to prepare the starch fiber (SF)-filled PVA blends (Salleh et al., 2017).

Sample code	PVA (wt %)	SF (wt %)	Glycerol (phr)
S1	50	50	20
S2	40	60	20
S3	30	70	20
S4	20	80	20
S5	10	90	20



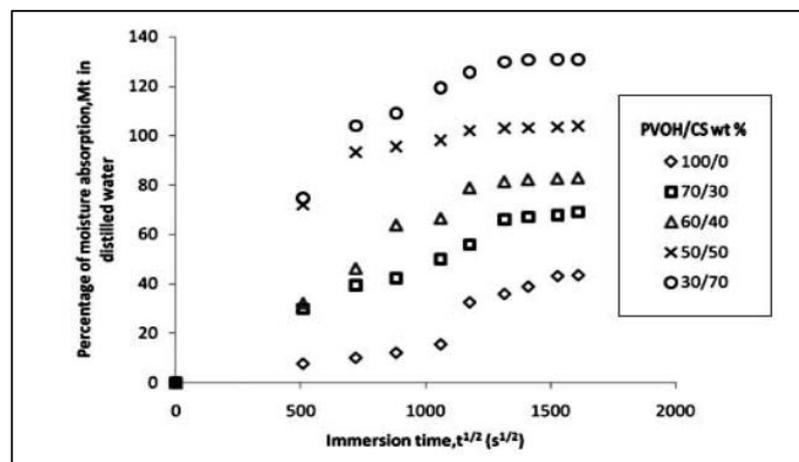
**Figure 2.10:** The percentage water absorptivity of the PVA/starch fiber (SF) blends at different composition (Salleh et al., 2017).

According to the Azahari, Othman and Ismail (2011), the water absorptivity of the corn starch (CS)-filled PVA film is higher than the unfilled PVA film and the water absorptivity increases with the increasing of immersion time and starch content. This fact may due to the hydrophilic nature of starch that shows significant water absorption characteristic in the composites. The diffusion constant ( $D$ ) and the moisture content ( $M_m$ ) for the PVA/CS blends at different weight ratio is illustrated in Table 2.5. According to the Table 2.5, the  $M_m$  and  $D$  values are higher in PVA/CS blended films than in pure PVA film and these values show increment with increasing of the CS content. This is due to the hydrophilic nature of the PVA and CS in which the presence of hydroxyl groups in PVA and CS are available for hydrogen bonding. However, the water absorption of the PVA/CS blended films is slightly decreased with the increasing of the immersion time due to some starch particles are leached out from the film samples. It indicates that starch absorbs moisture more rapid than pure PVA.

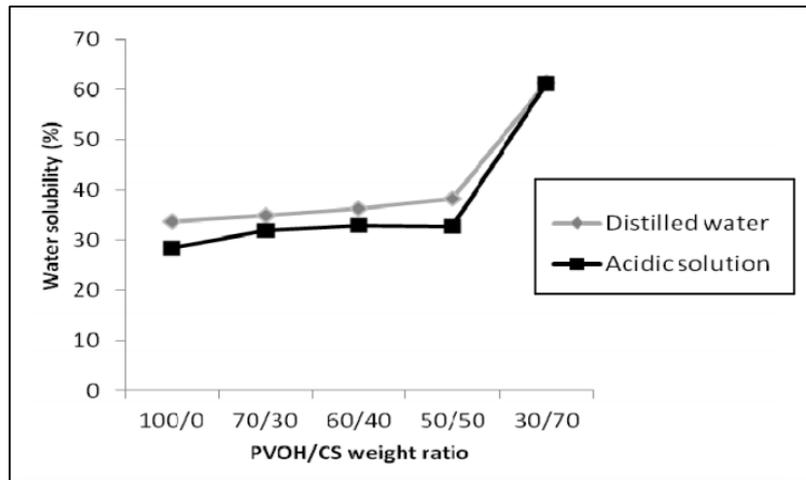
The water solubility of the PVA/CS blends at different weight ratio in water and acidic solution is shown in the Figure 2.12. The water solubility of the PVA/CS blends in distilled water and acidic solution shows similar trend with its water absorption. According to the Figure 2.12, the percentage of water solubility increases with the increasing of the CS content. To illustrate, PVA/CS blend in the weight ratio of (30/70) characterizes highest percentage of water solubility in both distilled water and acid solution due to the amylopectin branch structure of starch. Besides, the percentage of water solubility of PVA/CS blends in distilled water is higher than in acidic solution, because the blended films are capable to dissolve in distilled water than more concentrated acidic solution.

**Table 2.5:** The diffusion constant (D) and the maximum moisture content ( $M_m$ ) of PVA/corn starch (CS) in distilled water (Azahari, Othman and Ismail, 2011).

PVA/CS	100/0	70/30	60/40	50/50	30/70
D ( $\times 10^{-9} \text{ m}^2/\text{s}$ )	0.2310	1.4846	1.9291	6.1599	14.1995
$M_m$ (%)	43.503	67.012	83.002	103.256	130.76



**Figure 2.11:** The water absorptivity of PVA/corn starch (CS) blended films at different weight ratio with increasing immersion time (Azahari, Othman and Ismail, 2011).



**Figure 2.12:** The water solubility of PVA/CS blended films at different weight ratio (Azahari, Othman and Ismail, 2011).

## 2.5.5 Thermal Characterizations

The thermal behavior of the structurally complex materials such as polymer blend can be investigated by thermogravimetric (TGA) analysis and differential scanning calorimetry (DSC). Differential scanning calorimetry is used to determine the onset and end-point melting temperature of the polymer blends. Thermogravimetric analysis studies the thermal stability of the material and its fraction of volatile components by determining the weight change of the components as a function of increasing temperature (Salleh et al., 2017).

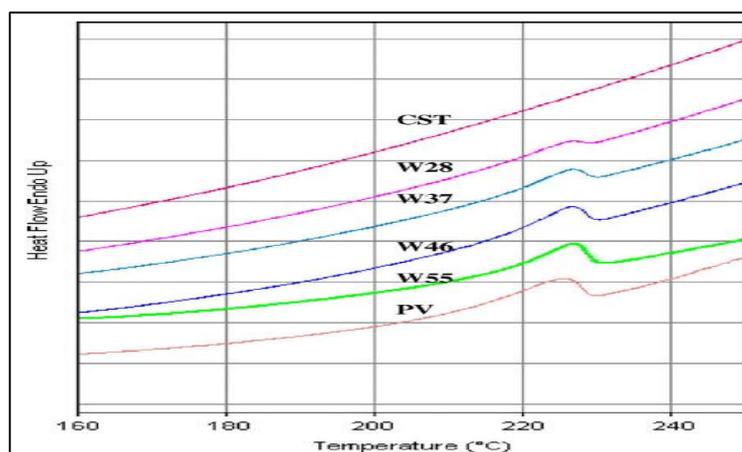
### 2.5.5.1 Differential Scanning Calorimetry (DSC)

As reported by Sin et al. (2010), the pure components of polyvinyl alcohol (PVA) and cassava starch (CST) and their blends at different weight ratio were

prepared by solution casting method. The thermal characteristic of these blended films was then studied by differential scanning calorimetry (DSC). Table 2.6 reveals the onset and end-point melting temperature of the PVA/CST blends at different weight ratio. Onset temperature is the temperature where the sample started to melt whereas the end-point temperature is the temperature where the melting process is completed. According to the Table 2.6, the onset and end-point temperature are shifted to lower temperature when the PVA content in the blends increased from 20 to 50 wt.%. This fact is due to when the PVA begins to pre-dominate the blends, the film samples perform towards PVA thermal behaviour. Based on the DSC thermograms of the PVA/CST blends, the CST does not show any melting stage, however the introducing of 20 wt.% of the PVA into the neat cassava starch (W28 sample) will cause the significant change in the onset and end-point melting temperature. In addition, the endothermic peak and onset and end-point temperature of PVA/CST blends are higher than the pure PVA (symbolized by PV), it is due to the unique helical structure of starch with the presence of many hydroxyl groups directed outside of the rings have interacted with the open-chain hydroxyl groups of PVA. The strong interaction between PVA and CST will produce synergistic effect towards higher thermal stability hierarchy.

**Table 2.6:** Onset and end-point melting temperature of PVA/cassava starch (CST) blends at different weight ratio (Sin et al., 2010).

<b>Sample code</b>	<b>W28</b>	<b>W37</b>	<b>W46</b>	<b>W55</b>	<b>PV</b>	<b>CST</b>
<b>PVA:cassava starch (wt.%)</b>	20:80	30:70	40:60	50:50	100:0	0:100
<b>Onset temperature (°C)</b>	218.04	216.39	216.22	215.70	214.03	-
<b>Standard deviation (SD)</b>	2.08	0.35	0.31	0.16	1.53	-
<b>End-point temperature (°C)</b>	230.99	229.43	229.71	229.50	229.47	-
<b>Standard deviation</b>	1.65	0.41	0.22	0.37	0.39	-



**Figure 2.13:** DSC thermograms of PVA/cassava starch (CST) blends at different weight ratio (Sin et al., 2010).

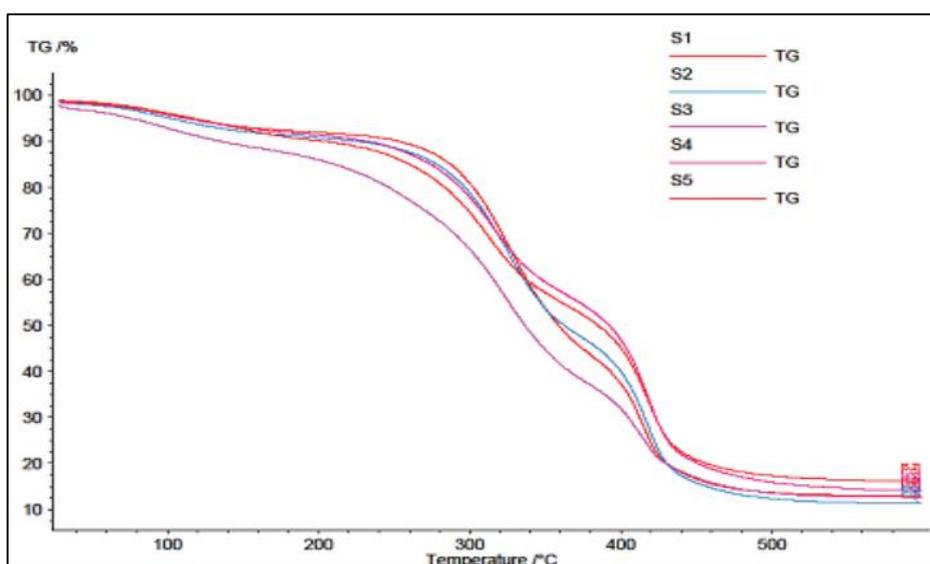
### 2.5.5.2 Thermogravimetric (TGA) analysis

According to Salleh et al. (2017), the thermal stability of the polyvinyl alcohol (PVA)/starch fiber (SF) blends at different composition was studied by thermogravimetric analysis (TGA). The percentage of weight loss at onset degradation temperature for PVA/SF blends at different weight ratio is illustrated in Table 2.7 whereas Figure 2.14 reveals the TGA thermogram of PVA/SF. Based on Table 2.7, the onset degradation temperature ( $T_{dg}$ ) of PVA/SF blends increases with the incorporation of the SF into the blends. To illustrate, the PVA/SF blend with 90 wt.% of SF shows highest  $T_{dg}$  value. This fact can be explained by the starch molecule is formerly built up of cyclic hemiacetal that consists of stable five- or six- membered rings in its structure. This cyclic hemiacetal sheltered the components of the blends to prevent the disorder arrangement and thus the interruption of the structure at low temperature can be avoided. Hence, this phenomenon also explains that the

PVA/SF blends are synergistically compatible and therefore attribute towards higher energy stability. To add to that, the amount of carbonaceous and char residue of S1 blends are higher than S5, owing to the insufficient of the cyclic hemiacetal supplied by the S1 blend film to withstand the thermal attack.

**Table 2.7:** Percentage of weight loss at onset degradation temperature for PVA/starch fiber (SF) blends at different weight ratio (Salleh et al., 2017).

PVA/starch fiber (wt.%)	Sample code	Percentage of weight loss at onset degradation temperature (%)	Onset degradation temperature (°C)
50:50	S1	55.60	301.01
40:60	S2	63.21	320.78
30:70	S3	65.66	338.10
20:80	S4	66.93	340.23
10:90	S5	81.02	356.40



**Figure 2.14:** TGA thermogram of PVA/starch fiber (SF) at different weight ratio (Salleh et al., 2017).

## 2.6 Concluding Remarks

According to the previous studies, the incorporation of the different types of starches into the PVA showed enhancement in certain properties in the final blended film products. Nevertheless, the utilization of gigantic amount of crops yields as the starch resources to produce the polymer blends is competitive with the food sources. Despite of the environmental and consumer concerns, the use of agriculture crop wastes to synthesize the low cost and environmental friendly polymeric materials are more desirable. Citrus peel is very common national fruit waste that are easily to be found because it is a non-seasonal fruit. Interestingly, it has inspired me to incorporate the citrus peel waste flour (CPWF) into the polyvinyl alcohol (PVA) to produce the biodegradable blended films. In this research project, different weight ratio of PVA and CPWF were formulated and the PVA/CPWF blends were prepared by solution casting method. The effect of the CPWF on the properties of the PVA in the terms of tensile strength, elongation at break, water absorption and solubility, thermal stability and degradation by natural weathering have been studied.

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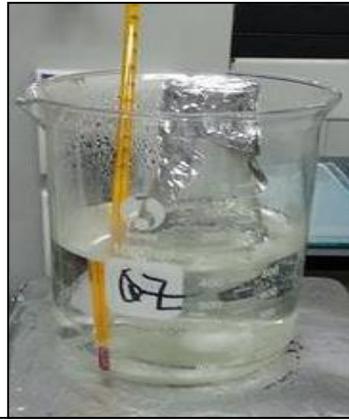
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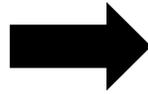
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## APPENDICES

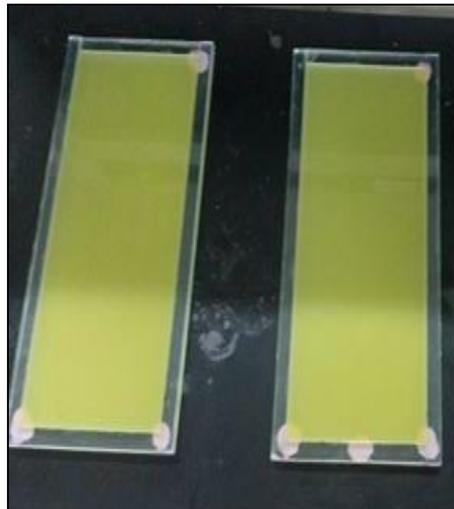
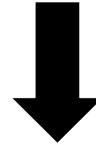
### APPENDIX A



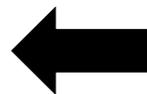
Different weight ratio of PVA powder was dissolved in 200 mL deionized water in a hot water bath at 80-90 °C with mild stirring



Different weight ratio of CPWF was added to the clear PVA solution with continuously stirring for about one and a half hour.



The mixture was casted on the glass plate and dried it overnight to promote film formation.



The glass plate was ensured to be flat by using the water level ruler.

**Figure A:** Flow chart for preparation of PVA/CPWF blended film.

## APPENDIX B

The records of daily mean temperature, daily mean relative humidity, and daily rainfall amount for November and December 2016 were collected by the Department of Meteorology Malaysia based on Hospital Kampar station with latitude, longitude, and elevation of 4°18'42"N, 101°09'23"E and 37.5 m respectively. The daily mean temperature, daily mean relative humidity, and daily rainfall amount for November and December 2016 are summarized in the following table:

**Table B1:** Records of 24 hours daily mean temperature for November and December 2016 in Kampar area, Perak.

Date	Temperature (°C)	
	November	December
1	27.1	25.8
2	28.2	24.9
3	26.9	26.3
4	26.5	27.7
5	27.2	29.4
6	28.0	29.6
7	27.8	29.7
8	29.1	28.8
9	25.5	28.0
10	26.0	25.9
11	25.8	25.1
12	25.9	26.1
13	27.2	27.6
14	26.1	27.4
15	27.5	27.6
16	26.9	-
17	26.6	-
18	26.4	-
19	27.3	-
20	26.4	-
21	28.2	-
22	26.9	-
23	27.1	-
24	26.1	-
25	26.5	-
26	26.7	-
27	26.1	-
28	26.5	-
29	24.3	-
30	26.6	-
<b>Mean Temperature (°C)</b>	<b>26.8</b>	<b>27.3</b>

**Table B2:** Records of 24 hours daily mean relative humidity for November and December 2016 in Kampar area, Perak.

Date	Relative Humidity (%)	
	November	December
1	80.3	87.5
2	75.4	93.8
3	Def.	87.7
4	81.7	78.0
5	79.9	67.1
6	80.6	67.8
7	80.0	69.0
8	72.3	78.2
9	88.8	81.1
10	86.1	88.8
11	89.8	87.6
12	89.1	80.8
13	83.3	70.5
14	89.1	75.0
15	80.5	71.5
16	85.9	-
17	86.0	-
18	86.2	-
19	85.0	-
20	86.9	-
21	78.1	-
22	86.9	-
23	84.7	-
24	89.1	-
25	86.8	-
26	88.8	-
27	91.9	-
28	87.0	-
29	94.2	-
30	78.9	-
<b>Mean Relative Humidity (%)</b>	<b>84.6</b>	<b>79.0</b>

**Table B3:** Records of daily rainfall amount for November and December 2016 in Kampar area, Perak.

Date	Rainfall amount (mm)	
	November	December
1	0.2	7.2
2	0.0	0.8
3	6.2	0.0
4	0.0	0.0
5	0.2	0.0
6	0.0	0.0
7	0.0	0.0
8	0.8	8.6
9	16.2	0.2
10	7.0	16.8
11	3.0	17.8
12	9.4	0.0
13	1.0	0.0
14	21.0	0.0
15	1.0	0.0
16	40.6	-
17	0.8	-
18	6.4	-
19	6.4	-
20	4.2	-
21	0.0	-
22	1.0	-
23	0.6	-
24	0.6	-
25	0.2	-
26	0.0	-
27	0.0	-
28	0.2	-
29	0.4	-
30	13.0	-
<b>Total Rainfall Amount (mm)</b>	<b>140.4</b>	<b>3.4</b>
<b>Amount of raindays</b>	<b>23</b>	<b>-</b>