

**CHARACTERIZATION OF VITAMIN E ON POLYVINYL ALCOHOL-
STARCH BLENDS**

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**A project report submitted in partial fulfilment of the
requirements for the award of the degree of
Bachelor (Hons.) of Chemical Engineering**

**Faculty of Engineering and Science
Universiti Tunku Abdul Rahman**

April 2012

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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Specially dedicated to
my beloved Swami and Babaji, mother and father

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CHARACTERIZATION OF VITAMIN E ON POLYVINYL ALCOHOL- STARCH BLENDS

ABSTRACT

Vitamin E has been proposed in this study to enhance the properties of Polyvinyl Alcohol-Starch blend such as mechanical, physical and enthalpy of melting. Specimens in the form of rectangular shape were prepared for each formulation to determine the tensile strength, elongation at break and modulus of elasticity. This was done using INSTRON 5848 MicroTester whereby the extension rate was 12.5 mm/min. Furthermore, Scanning Electron Microscopy test was conducted to determine the morphology of the compound using S-3400N Scanning Electron Microscope. Differential Scanning Calorimetry was conducted to investigate the enthalpy of melting. Specimen was heated from 50 °C to 250 °C at a heating rate of 10 °C min⁻¹ under dry nitrogen at a purge rate of 20 ± 5 mL min⁻¹. Lastly, the fourier transform infrared was conducted to determine the chemical interactions and bonding of the film. From this research, the tensile strength of the 50/50 wt % PVOH-starch blend films increased by 42 % after the addition of 0.3 g of Vitamin E. However, the percentage of elongation at break after the addition of both 0.1 and 0.3 g of Vitamin E decreased by 10 % and 20 % respectively. Besides that, addition of Vitamin E caused the PVOH-starch blend film to increase its modulus of elasticity. Furthermore, from the DSC and FTIR test, it was found that addition of Vitamin E caused stronger intermolecular bonds to be formed.

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LIST OF SYMBOLS / ABBREVIATIONS

| | |
|--------------|-----------------------------------|
| BHA | Butylated Hydroxyanisole |
| BHT | Butylated Hydroxytoluene |
| CSS | Cassava Starch |
| DSC | Differential Scanning Calorimetry |
| FTIR | Fourier Transform Infrared |
| HMMM | Hexamethoxymethylmelamine |
| HSPAN | hydrolyzed starch-g-acrylonitrile |
| LDPE | Low Density Polyethylene |
| MPa | Mega Pascal |
| PE | Polyethylene |
| PP | Polypropylene |
| PVC | Polyvinyl Chloride |
| PVOH | Polyvinyl Alcohol |
| SEM | Scanning Electron Microscopy |
| T_m | Melting Temperature |
| T_g | Glass Transition Temperature |
| ΔH_m | Enthalpy of Melting |

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CHAPTER 1

INTRODUCTION

1.1 Background

Polymers, which exist both ways naturally and synthetically, have wide prospective to be used for food and pharmaceutical packaging. Polymers are generally grouped along two scales which are their sources and biodegradability. Over the years, non-biodegradable polymers from fossil fuels have recorded the largest usage for food and pharmaceutical packaging due to the availability and excellent mechanical properties. In the beginning, low density polyethylene (LDPE) and polyvinyl chloride (PVC) were used in the production of the plastics processing. However, lately the usage of polyvinyl chloride (PVC) is being reduced merely for the reason that it's not biodegradable and it also causes severe ecological problems. Therefore, biodegradable polymers from fossil sources are now commonly used for packaging applications. An example of this type of polymer would be polyvinyl alcohol (PVOH).

Polyvinyl Alcohol (PVOH) is a synthetic, water soluble polymer formed by polymerization of vinyl acetate (PVAc). It is renowned as a biodegradable polymer whereby it can be decomposed naturally by microorganisms and enzymes when exposed to natural environment (Lee, Rahman, Rahmat, & Khan, 2009). PVOH has been used in wide range of industrial, commercial, food and pharmaceutical applications due to its biodegradability, gas and water vapour permeability, excellent chemical resistance, good film formation, high thermal stability, emulsifying and adhesive properties. Certainly, these key properties do not come all together for a

low price (Lee et al.). Thus, PVOH was blended with native starches to make it more economical to use.

The components of starch are amylose and amylopectin structures. These structures were originally formed from D-glucose unit with hydroxyl groups (-OH) whereby it is directed outside of the ring. Starch is a renewable and natural polymeric substance, which is growing its attention due to its natural biodegradability, ready availability and low cost. However, the poor mechanical properties and comparatively high hydrophilic nature of starch prevent its use in various applications (Mao, Imam, Gordon, Cinelli and Chiellini, 2000). Therefore, Vitamin E could be added into this PVOH- starch blend to improvise the characteristics.

In recent years, antioxidants and oxygen interceptors such as Vitamin E, also known as alpha- tocopherol, is being used in the plastic processing industry (Laermer, Young, & Zambetti, 1994). Vitamin E is being introduced to combat odours generated from the plastic. According to literature review, Vitamin E has been used in plastic packaging such as LDPE to put a stop to damage related to the effects of long term storage, heat and also exposure to air and atmospheric pollutants (Laermer et al.).

1.2 Problem Statement

PVOH is a biodegradable polymer used in extensive applications such as food and pharmaceutical packaging. However, this substance is available at a high cost. Therefore, starch was added to reduce the amount of consumption of PVOH. Unfortunately, addition of starch into the PVOH compound resulted in reduction of the vital properties. The PVOH- starch compound exhibited reduced mechanical properties such as tensile strength and elongation at break. Starch causes the compound to become very brittle. Besides that, reduced water resistance or increase in water absorption is also one of the most obvious shortcomings in confining this substance's applications. Drop off in the thermal stability also occurred when starch content was increased significantly. Thus, in order to bring a bright prospect for the

usage of PVOH, this research was done by adding Vitamin E as a stabilizer into the PVOH- starch compound. This was to evaluate whether there will be any betterment on the properties.

1.3 Aims and Objectives

This research mainly aimed to evaluate the properties of the PVOH- starch blend after addition of the Vitamin E compound. The sub- objectives were:

- i. To evaluate the mechanical properties of the PVOH- starch blend and Vitamin E compound;
- ii. To evaluate the physical properties of the PVOH- starch blend and Vitamin E compound;
- iii. To evaluate the enthalpy of melting of the PVOH- starch blend and Vitamin E compound;
- iv. To evaluate the chemical bonding and their interaction of the PVOH- starch blend and Vitamin E compound.

1.4 Scope of Study

The PVOH biopolymer had a broad applications and properties or characteristics to be studied on. However, only a number of properties were taken into account for this research. Therefore, the scopes of this study were as follows.

- **Mechanical Properties**

Tensile test was conducted to evaluate the tensile strength and elongation at break of the PVOH- Starch- Vitamin E blend compound. This tensile test was performed with accordance to the ASTM D882-10 standard.

- **Physical Properties**

Scanning Electron Microscopy (SEM) was conducted to evaluate the morphology of the PVOH- Starch- Vitamin E blend compound.

- **Enthalpy of Melting**

Differential Scanning Calorimetry (DSC) was conducted to investigate on the enthalpy of melting of the PVOH- Starch- Vitamin E blend compound.

- **Chemical Interactions and Bonding**

Fourier Transform and Infrared (FTIR) spectroscopy test was conducted to investigate the chemical interactions and bonding of the PVOH- Starch- Vitamin E blend compound.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Synthetic polymers such as polystyrene, polypropylene and polyethylene are widely used in our daily life. They are largely used in food and pharmaceutical industry, biomedical field and also in the agriculture. A heavy environmental pollution accompanies their uses as it takes over hundreds of years to degrade. Thus, the disposal of waste plastics has become a serious problem. Therefore, in the past two decades, biodegradable materials have been paid attention as alternatives to the petroleum based derived plastics.

2.1.1 Polyvinyl Alcohol (PVOH)

PVOH which is also known as Polyvinyl Alcohol is one of the fewest biodegradable synthetic polymers available today in the packaging market. PVOH is a hydrophilic polymer which is mainly composed of C-C bonds.

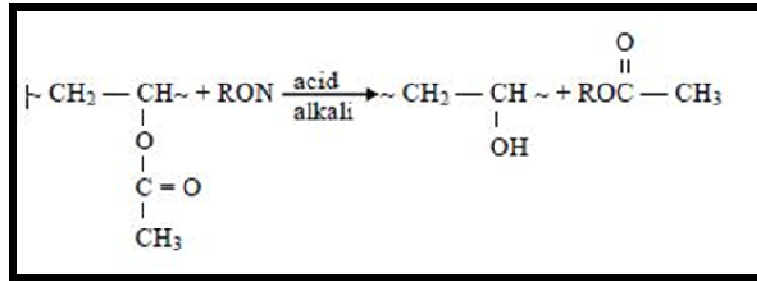


Figure 2.1: Synthesis of Polyvinyl Alcohol (Ganbold, 2010).

PVOH is naturally obtained in a fine white powder form which smells like vinegar. It's a substance with high prospective as melt processable or water processable polymer (Toh, Lai, & Rahman, 2006). This polymer is widely used in many applications such as food and pharmaceutical packaging and also in the biomedical field. The production of PVOH is shown in the figure below.

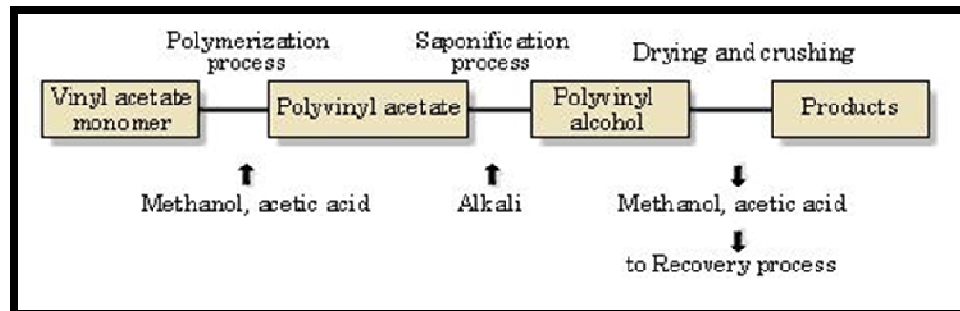


Figure 2.2: Chemical Synthesis of PVOH (Ganbold, 2010).

2.1.2 Starch

Due to the high cost of PVOH, starch is normally introduced to reduce the cost. Starch has been considered as suitable source material because of its inherent biodegradability, ready availability and also relatively low in cost (Russo et al., 2009). There are various types of starch such as cassava starch, corn starch, potato starch and also wheat starch. Starch has been used in wide applications. For instance,

it is used as food additive. Besides that, it's also used in papermaking industry, for corrugated paperboard adhesives and the most common is for the clothing laundry.

2.1.3 Vitamin E

Vitamin E exists in eight different types of isomers, whereby four of them are called tocopherols and other four are called tocotrienol. Tocopherols types of isomers are made up of alpha, beta, gamma and delta tocopherol whereas tocotrienol made up of alpha, beta, gamma and delta tocotrienol. Tocotrienols are less widely distributed in nature and are found mainly in palm oil. Figure 2.3 below shows the molecular structure of tocopherol and tocotrienol.

The form of vitamin E which is most active is Alpha-tocopherol, a type of biological antioxidant. In human body, vitamin E is mainly present as alpha tocopherols. This Vitamin E can be secluded from natural supplies for instance plants, vegetables, meats or it can also be prepared in the laboratory. Naturally occurring alpha tocopherol is referred as RRR-alpha tocopherol whereas the synthetic alpha tocopherol is referred as all-rac-alpha tocopherol.

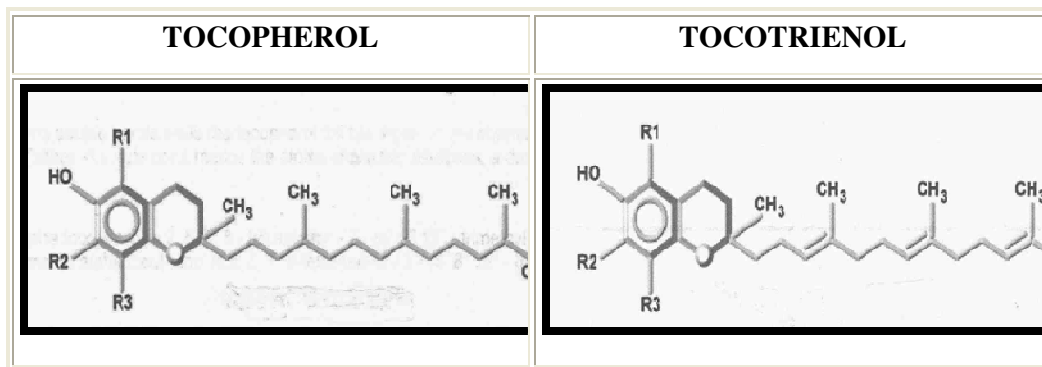


Figure 2.3: Molecular Structure of Tocopherol and Tocotrienol (Moussa, Peter, Silvia, & Leontino, 2007).

Generally, vitamin E exists in many types and it can be obtained from many sources. Two types of tocotrienols named desmethyl- and didesmethyl- tocotrienol

can be derived from stabilized and heated rice bran. Besides that, homologues of γ -tocotrienol, named plastochromanol, can be found in vegetal tissues, such as leaves and seeds. The first species was discovered in the leaves of *Hevea Brasiliensis* in 1965 by thin layer chromatography and chemical identification. It can be found at the highest amounts in flax and rape seed oils, as well as in minor amounts in seed oils of camelina, maize, hemp, many Vietnamese plants and also black pine. In addition, γ -tocotrienol-9 was identified in lipid extracts of yam tuber. A new Vitamin E element, α -tocomonoenol, was then revealed in palm oil. In 2009, another form was isolated from *Actinidia chinensis* (kiwi) fruits and its structure elucidated as δ -tocomonoenol.

Vitamin E has been used far and wide over the years. It has been contributing in sectors such as health, cosmeceutical and also in the plastic or polymer industry.

2.2 Studies on Polyvinyl Alcohol (PVOH) and PVOH - Starch Blend

Countless literature studies have been done on this PVOH. There are heaps of advantages and disadvantage of this polymer. There are two groupings for PVOH, named fully hydrolyzed and partially hydrolyzed as shown in Figure 2.4. The distribution of acetyl group in the partially hydrolyzed PVOH is dependent on the condition of the reactions. The acetyl group in this PVOH has an overall effect on its chemical properties, solubility and crystallinity of PVOH.

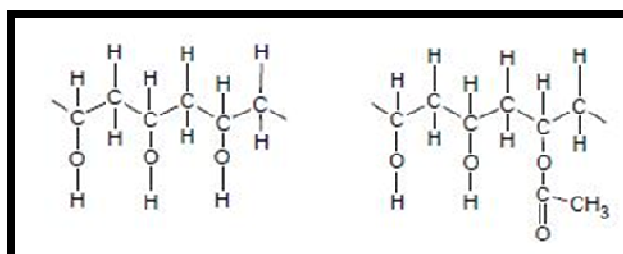


Figure 2.4: Molecular Structure of fully hydrolyzed and partially hydrolyzed PVOH (Ganbold, 2010).

Mechanical property is one of the important properties of PVOH. Among all the mechanical properties, tensile properties which include tensile strength, yield strength, modulus of elasticity (Young's modulus) and elongation at break are most well thought-out. This is because these properties offer an indication of expected film integrity under conditions of stress that would take place during processing, handling and storage.

The maximum yield strength is a vital property of the packaging films whereby it defines the maximum tensile stress and it also gives information on the maximum allowable load before plastic deformation occurs. Tensile strength is the ultimate strength which is the maximum stress applied at the point at which the packaging film breaks, while strain expresses the maximum change in the length of the film before breaking. Elastic modulus is defined by the ratio of applied stress to the corresponding strain in the region of linear elastic deformation and can be regarded as an index of stiffness and rigidity of a packaging film.

Polyvinyl alcohol (PVOH) has good film forming property which offers high tensile strength (Schellekens & Bastiansen, 1991). Fully hydrolyzed PVOH has a higher tensile strength and greater Young's modulus than partially hydrolyzed PVOH. However, it is less resistant to elongation and tearing. It was also emphasized that many factors affect mechanical properties. Those factors are additives, plasticizers and environment which include temperature and relative humidity. For instance, as the content of plasticizer increases, tensile strength decreases and elongation increases. In addition, humidity acts as a plasticizer, increasing elongation and decreasing strength (Tang & Alavi, 2011). As the temperature increases, Young's modulus, the ultimate tensile strength and elongation at break decreases. Besides that, molecular weight also influences the mechanical properties. The tensile strength of the film tends to increase as molecular weight increases (Ebewele, 1996).

Another important property of PVOH is the barrier property. All plastics are to some degree permeable to gases such as O₂, CO₂, N₂ and ethylene. It is also permeable to water vapour, aromas and light compounds in comparison with glass and metal packaging materials. Owing to this, the interaction between foods or pharmaceutical and packaging, moisture and aroma loss or uptake, reaction with

oxygen as well as the growth of aerobic microorganisms is capable of occurring and it would seriously reduce their quality and shelf life. Therefore, a good barrier plastic must be taken into account in the packaging to protect them from transmission of the above mentioned compounds and to sustain their freshness and overall quality during storage.

This PVOH film is permeable to moisture. Contradictly, it's a high barrier to all types of gases (Ganbold, 2010). This is due to the high intermolecular cohesion or high tendency to crystallize. However, its gas barrier rapidly diminishes as the hydrolysis is decreased. Furthermore, the gas barrier property of PVOH is considerably dependent on the humidity. The excellent gas barrier properties of dry PVOH significantly decreases in the presence of moisture. Among all the barrier properties, water and oxygen permeability have fundamental repercussion in the consideration of polymer films for the packaging of food and pharmaceutical products. Therefore, this characteristic has to be enhanced for the future use of PVOH.

Now, the other characteristics of PVOH will be considered. Besides the mechanical and barrier properties, viscosity, adhesive strength, water and solvent resistance as well as dispersing power increases when the molecular weight increases. However, ease of solubility is increased with decreasing molecular weight (Ganbold, 2010). On the other hand, water resistance, tensile strength and solvent resistance are increased with the increasing degree of hydrolysis, whilst flexibility, dispersing power and water sensitivity are increased with the decreasing degree of hydrolysis (Tang & Alavi, 2011). The melting point (T_m) and glass transition temperature (T_g) depend on the content and distribution of the acetyl groups and tacticity of PVOH. Furthermore, PVOH has the ability to reduce the surface tension of water.

Despite the fact that PVOH has plentiful advantages to be used as the packaging material, the cost is relatively high and has low biodegradation rate. In order to cut its cost and improve its eco-friendliness, this polymer is frequently tailored by adding other substance such as starch. From the cost and practicality points, it is preferable that the blend contains as much starch as possible (Lee, Rahman, Rahmat, & Khan, 2010).

Starch is scientifically known as polysaccharide, which consists of amylose and amylopectin portions (Lee et al., 2010). Although blending of starch and PVOH was able to increase the degradability, different polarities of starch could deteriorate the existing mechanical properties of PVOH. Based on the literature reviews, it was clearly shown that the tensile strength continuously decreases as the amount of starch increases (Tudorachi, Cascaval, Rusu, & Pruteanu, 2000). This is due to the amorphous nature of starch. However, the mechanical properties of PVOH- starch blend can be improved by the addition of cross- linker and plasticizer such as borax (Guo, Ping, & Liang, 2008).

Moreover, the water resistance of the PVOH- starch film decreases as the composition of starch in the blend increases. According to the previous studies, the water absorption of starch is stronger compared to the PVOH. This then causes the film to be too weak to be used for commercial purpose (Guo et al., 2008). This might be a result from a poor compatibility between starch and PVOH and phase separation during film preparation. The techniques for increasing the compatibility between starch and PVOH include adding stabilizer and compatibilizer to the blends. It has been proven that citric acid acts not only as a plasticizer, but also as a cross- linker (Guo et al., 2008). Therefore, the water absorption reduces as the amount of plasticizer increases.

Besides that, the crystallinity of PVOH in the PVOH- starch blend decreases significantly compared to pure PVOH. It was very clear indeed that the endothermic peak became less prominent and the melting point also decreases as the composition of starch increases in the PVOH- starch blend. As the starch is increased, the melting range is also broadened (Rahman, Lee, Rahmat, & Samad, 2010). This indicates that molecules of PVOH are restrained by the molecules of starch. It was also seen that the melting peak of PVOH is indistinct when its composition is less than 30%. This indicates that the crystalline dominancy has almost disappeared when the composition of PVOH is less than 30%. All the explanation above simply means that the thermal stability of PVOH- starch blend is not as high compared to the pure PVOH. Thus, addition of starch into PVOH actually decreases the thermal stability.

2.3 Studies on Vitamin E

In the human food diet, vitamins help to avoid biological damage which are related to the consequence of aging, chronic illness and contact to atmospheric contaminants. The most frequently quoted vitamins for best health benefits are the antioxidant vitamins such as vitamin C, E and β -carotene or familiarly known as Vitamin A. Likewise, in order to avert damage related to the consequence of processing, heat, long-term storage and also contact to atmospheric contaminants or impurities for plastics and plastic packaging which are rigid, firm and flexible, antioxidants can be added (Laermer et al., 1994).

Over the years, the most vital molecules which are able to provide this protection are products recognized as primary antioxidants. The extensively used primary antioxidant substances include BHT, Irganox1010 and 1076 (Ciba) and lately, alpha-tocopherol which is the vitamin E (Laermer et al., 1994). Chemists found alpha-tocopherol as one of the most excellent antioxidants discovered. This is because it can terminate the sequence of chemical steps which can possibly direct to the molecular damage begun by the development of free radicals (Oral, Wannomae, Rowell & Muratoglu, 2007). This ideology is applicable for not only organic substance and living organisms but it also applies for polymer structure.

Earlier literature has quoted vitamin E for its capability as an antioxidant in food and pharmaceutical packaging plastics. Those plastics include polypropylene (PP) and polyethylene (PE) (Bracco, Brunella, Zanetti, Luda, & Costa, 2007). Tocopherols, which are non-volatile, have not replaced volatile butylated hydroxyanisole or butylated hydroxytoluene (BHA/BHT) which migrates into foods. However, they appear to be new antioxidants of choice for mitigating the effects of oxygen (Aaron, Eugene, & Lauri, 2001). Nevertheless, in the middle of 1980s, the Japanese food and pharmaceutical packaging industry took up vitamin E in order to substitute the usage of BHT. The previous studies carried out by Hoffmann-La Roche, demonstrated wide range of discrete industrial advantages in various range of polymer structures and applications (Laermer et al., 1994).

One of those virtues is that polymers stabilized by vitamin E impart a reduced amount of taste and odour compared to the polymers stabilized by normal antioxidants. Vitamin E also decreases the development of gels or structural limitations in food and pharmaceutical packaging. This is due to the reason that the addition of effective free radical scavenger like vitamin E is recognized to decrease cross-linking of the branches of polymer (Oral et al., 2007). Thus, it reduces wastage and allows polymers to be processed at elevated temperatures (Laermer et al., 1994). Besides that, vitamin E will transfer in a smaller amount from the polymer compared to other antioxidants used. Therefore, it eliminates the hazard of contaminating food or medicine due to the packaging materials. Furthermore, vitamin E is also known as better-quality processing stabilizer. It has been appropriately used in the polymer packaging whereby it offers improved colour constancy (Martins, Cerqueira, & Vicente, 2012). In addition, vitamin E is further stable thermally compared to various other antioxidants. This antioxidant also puts forward a decrease in the cost of additive used. Even though it cost about three times more than the cost/lb of other antioxidants, vitamin E is only added about 1/4 to 1/5 of the required amount (Laermer et al).

Next, the processing stability of Vitamin E was studied. Vitamin E is a tremendously successful processing stabilizer whereby it is effectual when added at low concentration. Besides that, its greater performance was confirmed to protect plastics which are exposed to stress (Laermer et al., 1994).

Based on all the reviews above, it can be clearly concluded that Vitamin E has impart its use in the packaging field. It also shows that this antioxidant has many advantages whereby it enhances the processing properties of the polymer. Thus, this paper was aimed to research on whether Vitamin E could provide the same advantages or improve the characteristics of PVOH- starch blend films.

2.4 Effect of Addition of Fillers Such as Plasticizers, Stabilizers and Cross-Linkers into PVOH and PVOH-Starch Blend

Based on the previous researches done, it can be concluded that addition of starch into PVOH decreases some of the properties of PVOH.

However, by adding fillers into this compound, some properties can be enhanced. Some examples of plasticizers used are water, selected amino acids and also glycerol (Mao, Imam, Gordon, Cinelli, & Chiellini, 2000). The most common plasticizer added into PVOH and starch blends are water and glycerol (Lawton & Fanta, 1994). Nevertheless, numerous other chemicals such as sorbitol (Park, Chough, Yun, & Yoon, 2005), citric acid (Zou, Jin, & Xin, 2008), urea (Tudorachi, Cascaval, Rusu, & Pruteanu, 2000), and complex plasticizers (Zhou, Cu, Jia, & Xie, 2009) have been effectively used.

It's known that PVOH- Starch compound has weaker properties as compared to pure PVOH film. It's well known that the mechanical properties of this blend are lower compared to pure PVOH due to the amorphous nature of starch. Thus, researches have been done using plasticizers such as glycerol and water. It was discovered that glycerol is extra successful than water to be used as plasticizer (Tang & Alavi, 2011). Addition of glycerol into PVOH- Starch blend enhanced the flexibility and elongation at break but decreased the tensile strength (Mao et al., 2000; Guo et al., 2008). Thus, in order to increase the tensile strength, a combination of 50-50 wt% of glycerol and water has been recommended. Since water has the power of plasticizing, the substances behaviour varies according to the relative humidity of the air through a sorption-desorption mechanism (Vilpoux & Avérous, 2004). This increased the tensile strength to reach its maximum value (Tang & Alavi, 2011).

Besides that, as stated above, the incorporation of starch into PVOH increases the water absorption of the compound which is then too weak to be used commercially. This is because the water absorption of starch is greater than that of water, which means that the water absorption of the PVOH- Starch composite increases as the amount of starch increases. As the concentration of glycerol increases, the water sorption of the blend decreases.

Rahman et al. (2010) stated that as the amount of glycerol decreased in the PVOH- Starch blend, the onset and end- point temperature decreased. Onset is the temperature when samples begin to melt. On the other hand, end-point is the temperature when the melting stage ends. This is due to the reason that glycerol has disrupted the rigidity arrangements of PVOH and starch. Generally, glycerol is needed to promote internal lubrication and flexible chain sliding.

As compared to polyethylene and polypropylene, PVOH undergoes thermal degradation when melt processed by having a noticeable yellow outputs (Wang, Schertiz, & Pomplun, 2001). Without the addition of stabilizers, PVOH possesses a melting point very close to its degradation temperature. Thus, stabilizers are essential to lessen the processing temperatures and the composite's viscosity.

According to Rahman et al. (2010), it was established that the onset and end-point temperatures of PVOH- Starch- Glycerol 55 (5 g, 5 g, 2.143 g) were higher than PV-S-G37 (3 g, 7 g, 1.286g) and PV-S-G46 (4 g, 6 g, 1.714 g). This might be because the rigid structure of PVOH has acted as a reinforcing agent to enhance the weak structure of starch. Therefore, higher amount of glycerol is vital to lessen the melting point of PV-S-G55 compound.

In addition, glycerol and water composed mixed plasticizer in the PVOH- Starch compound. Neither the water nor glycerin in the mixed plasticizer is free due to the interaction of hydrogen bonds among their molecules. Thus, the large molecular weight bounded molecules functioned like a plasticizer. Therefore, it's much easier for the plasticizer to form hydrogen bond with the starch in the PVOH- Starch compound which then results in higher plasticizing efficiency and the equilibrium moisture sorption was achieved (Guo et al., 2008).

On the other hand, addition of cross- linkers such as borax developed the tensile strength and lowered the elongation at break (Guo et al., 2008). In addition, borax can form a diol complexation with starch or PVOH, whereby four -OH groups of starch or PVOH form bonds with borax. Guo et al. conjectured that borax can cross-link starch and PVOH. It was also known that the enthalpy and crystallinity decrease as the concentration of borax increases. However, the melting point, T_m of

the PVOH doesn't shift to either lower or higher temperatures with increasing concentration of borax. This indicates that few changes occurred in the crystal type or the size of crystal.

Besides that, the broadening of the melting range could be explained as due to the regularity of the -OH groups already existing in PVOH, which are lost because of the cross-linking. Several factors, such as the main-chain rigidity, moisture content, cross-linking density, and chemical structure of the cross-linkers could influence the T_m of the cross-linked PVOH- Starch compound. The reason is that the cross-linking site could reduce the mobility of PVOH molecules, which hinder its ability to be crystalline.

Srinivasa, Ramesh, Kumar and Tharanathan (2003) found that pure chitosan films showed higher tensile strength of 55.46 MPa compared to pure PVOH films of only 25.24 MPa. It was also shown that the highest tensile strength was produced by the 60-40 blend of Chitosan- PVOH compared to 80- 20 and 40- 60 blend films.

FTIR spectra of chitosan, PVOH and their blends were also studied. The absorption peaks of around 1640 and 1560 cm was attributed to the asymmetric stretching and bending of acetamido groups respectively. The change in the characteristic shape of the chitosan spectra as well as shifting of peak to a lower frequency range due to hydrogen bonding between -OH of PVOH and -OH or NH_2 of chitosan were observed in the blend films.

Furthermore, Hexamethoxymethylmelamine (HMMM) can be used as a cross- linking means to improve the mechanical properties. The cross- linked PVOH- Starch with HMMM had 10% increase in overall tensile strength compared to non-cross linked PVOH- Starch compound. This increase in tensile strength was without effecting the percentage elongation of the compound (Rahmat, Rahman, Lee, & Yussuf, 2009).

The amazing part about plasticizers is that different plasticizers affect the PVOH- Starch compound in a different way. Addition of citric acid as plasticizer had the highest percentage of elongation, and then followed by sorbitol and glycerol.

This is because citric acid contains carboxyl group in it which were able to form strong hydrogen bonds with PVOH (Rahman et al., 2009).

The carboxyl groups on citric were able to form stronger hydrogen bonds between citric acid and other materials compared to the hydroxyl groups on glycerol. Tang and Alavi (2011) discovered that this cross-linking and strong hydrogen bonding improved the thermal stability of the PVOH-starch blends.

Besides, Fourier-transform infrared (FTIR) spectroscopy by Tang and Alavi (2011) explained that during the processing at 140 °C, an esterification occurred between starch and citric acid or PVOH. These esterification enhanced the water resistance or to be said that it decreased the water absorption (Guo et al., 2008). So, it can be said that citric acid acts not only as a plasticizer, but also as a cross- linker.

Furthermore, addition of epichlorohydrin as a cross- linker hydrolyzed starch-g-acrylonitrile (HSPAN) was able to lessen the phase separation when blending with polyvinyl alcohol. Prominently, it was able to surmount excessive hydrophilicity of PVOH- Starch films, principally in the appliance of products which are very sensitive to moisture exposure. When PVOH- HSPAN was cross- linked by epichlorohydrin, the tensile strength and strain at break or elongation at break increased proportionally as the amount of epichlorohydrin increases. The cross-linking aided to lessen the phase separation and ultimately endorsed compatibility (Kim, Na, Park, & Yoon, 2002).

Moreover, phosphorylation of starch also has effects on paste separation. This paste was to be used for warp sizing. It was clearly proven that, phosphorylation extends the initial demixing time and the subsidence ratio decreases. This puts forward that the initial rates of the paste separation was reduced and the separation extent of the blended pastes was decreased. Consequently, the phosphate modification enhances the paste stability (Zhu, 2003).

Next, the effects of using starch phosphate as a stabilizer was studied. Zhu (2003) also found that the incorporation of starch phosphate increases significantly the values of the initial demixing time. This was noticed especially when the

percentage of starch to PVA is high, which shows that the initial rates of phase separation are reduced. Furthermore, the separation rates are also evidently abridged on increasing the degree of substitution even though the subsidence ratios of the blended pastes containing the lowest proportions of starch showed no DS sensitivity. Such a tendency can be attributed to the amount of the stabilizer involved in the blended pastes.

Addition of plasticizers into PVOH is known to be able to reduce its melting point and thus increase its flexibility. The most commonly used plasticizers are triethylene glycol and glycerine. Besides, it has been proved that glycerine is the optimum plasticizer to increase the boiling point and decrease the dissolving temperature of PVOH.

As known commonly, the higher the degree of hydrolysis of PVOH, the T_m and glass transition temperature, T_g are higher too (Jyongsik & Dong, 2003). The Kelly- Bueche equation can be used to estimate the relationship of T_g for PVOH and plasticizer. Similar to T_g ; there is a relationship between T_m and the amount of plasticizer. Jyongsik and Dong (2003) found that as the amount of glycerin increases, the T_m of the PVOH diminishes. This was interpreted that glycerin increased the segmental mobility of PVOH and decreased the crystallite region of PVOH.

Jyongsik and Dong (2003) also discussed on the heat of fusion of PVOH with respect to the amount of glycerin. The heat of fusion of PVOH considerably decreased as the amount of glycerin increased. This phenomenon indicates that the crystallinity of PVOH is reduced according to the amount of glycerin. As the amount of glycerin increases, the activity of a PVOH gradually diminishes and the hydrogen-bonding interaction between the glycerins also increases. Therefore, the effect of a plasticizer is reduced gradually and the phase separation of glycerin in PVOH occurs at last stage.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Materials and Apparatus

The materials and apparatus used in this research were as listed below:

1. Fully hydrolysed Polyvinyl Alcohol (PVOH) grade K-17C (Viscosity 24-30 mPa.s, saponification 98.7-99.7 mol%, ash < 0.7%)
2. Native Cassava Starch (CSS)
3. Vitamin E
4. Distilled water
5. Water bath
6. Petri dishes
7. INSTRON 5848 MicroTester,
8. Perkin Elmer DSC
9. S-3400N Scanning Electron Microscope
10. Perkin Elmer PC spectrometer

3.2 Formulations

The formulations for the various blends of PVOH- CSS- Vitamin E are shown below in Table 3.1.

Table 3.1: Composition of PVOH- CSS- Vitamin E in preparation of cast films using 0, 0.1 and 0.3 g of Vitamin E

| Sample | PVOH: CSS (wt %) | PVOH (g) | CSS (g) | Vitamin E (g) |
|----------|------------------|----------|---------|---------------|
| PVT-82 | 80: 20 | 8 | 2 | 0 |
| PVT-73 | 70:30 | 7 | 3 | 0 |
| PVT-64 | 60:60 | 6 | 4 | 0 |
| PVT-55 | 50:50 | 5 | 5 | 0 |
| PV | 100:0 | 10 | 0 | 0 |
| PVT-82-1 | 80: 20 | 8 | 2 | 0.1 |
| PVT-73-1 | 70:30 | 7 | 3 | 0.1 |
| PVT-64-1 | 60:60 | 6 | 4 | 0.1 |
| PVT-55-1 | 50:50 | 5 | 5 | 0.1 |
| PV-1 | 100:0 | 10 | 0 | 0.1 |
| PVT-82-3 | 80: 20 | 8 | 2 | 0.3 |
| PVT-73-3 | 70:30 | 7 | 3 | 0.3 |
| PVT-64-3 | 60:60 | 6 | 4 | 0.3 |
| PVT-55-3 | 50:50 | 5 | 5 | 0.3 |
| PV-3 | 100:0 | 10 | 0 | 0.3 |

3.3 Sample Compounding/ Preparation

The solution cast samples of PVOH-CSS-Vitamin E was prepared as shown in Table 3.1. Samples were prepared by dissolving PVOH powder and CSS in 300 ml of distilled water and then it was heated in a water bath at 97 ± 2 °C for 30 min until the

particles of PVOH disappeared. Fully hydrolyzed PVOH requires at least 90 °C to dissolve in water. A motor driven stirrer was also set at 800 rpm in order to help the mixture to fully dissolve and gelatinize. Then, 100 ml of distilled water was added to refill the vaporized water during the first heating and this mixture was heated at 97 ± 2 °C for 30 min again. Finally, once the solution was removed from the water bath, Vitamin E was added using suction tube and it was manually stirred using spatula.

The mixtures were casted with similar weights of 30 g on Petri dishes. The samples were then further dried in an oven at 65 °C to achieve constant weight. All the samples were immediately sealed in polyethylene bags and were then stored under room temperature of 25 °C for conditioning purpose (average moisture content 10%).

3.4 Analysis/ Test of Properties

3.4.1 Mechanical Properties

Tensile test was performed to evaluate the tensile strength and elongation at break with accordance to the ASTM D882-10 standard. This test was conducted in the form of standard rectangle-shaped test specimens. It was tested using the INSTRON 5848 MicroTester. A number of ten specimens for each formulation were prepared for this test. The width and thickness of the specimen were measured at the center of each specimen and within 5 mm of each end of the gage length. The thickness measured specimen was then placed in the grips of the testing machine and the grips was tightened evenly and firmly to prevent slippage. The extension rate was 12.5 mm/min. The tensile strength, percentage of elongation at break and also modulus of elasticity were recorded.

3.4.2 Physical Properties

Scanning Electron Microscopy (SEM) test was conducted to evaluate the morphology and compatibility of the PVOH- Starch- Vitamin E blend compound. This test was conducted by using S-3400N Scanning Electron Microscope. The samples were first cut in a square shape of 10mm by 10mm. Then, the samples were coated with gold and palladium using EMITECH SC7620 Sputter Coater before placed into the S-3400N Scanning Electron Microscope.

3.4.3 Thermal Analysis

Differential Scanning Calorimetry (DSC) was performed to investigate the enthalpy of formation. This test method was done to determine the temperature at which the materials start to decompose or react and the extent of the mass change by Perkin Elmer. Specimen of 5 ± 0.1 mg was placed on the aluminium pan. A sealed empty pan was used as reference material. The scanning was carried out from 50 °C to 250 °C at a scanning rate of 10 °C min⁻¹ under dry nitrogen of 99.9+ % purity at a purge rate of 20 ± 5 mL min⁻¹.

3.4.4 Chemical Interactions and Bonding

Fourier transform infrared spectroscopy (FTIR) was used to identify chemical features and shifts due to interactions between functional groups via a Bruker FTIR with a resolution of 2 cm⁻¹. The FTIR was used in reflectance mode using a Golden Gate attenuated total reflectance attachment with a diamond objective.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Mechanical Properties

4.1.1 Tensile Strength

Tensile strength is the ultimate strength which is the maximum stress applied at the point at which the polymer breaks. Figure 4.1 indicates that the tensile strength of the PVOH- Starch blend generally decreases as the amount of starch increases. Pure PVOH demonstrated the highest tensile strength of 17.5 MPa compared to the PVOH- Starch blend. Pure PVOH film as shown in the section of Morphology Observations shows smooth surface in its polymer matrix. However, it could be observed from the section of Morphology Observations also that the addition of starch into PVOH caused formation of agglomeration of starch particles and then it led to formation of voids on the matrix of the polymer. Comparing those figures in the Morphology Observations section, it could be seen that the size of the agglomerated starch particles increased as the amount of starch increased. These agglomeration and voids led to poor interfacial adhesion between the two components (Toh, Lai, & Rahman, 2011). Thus, the tensile strength decreases.

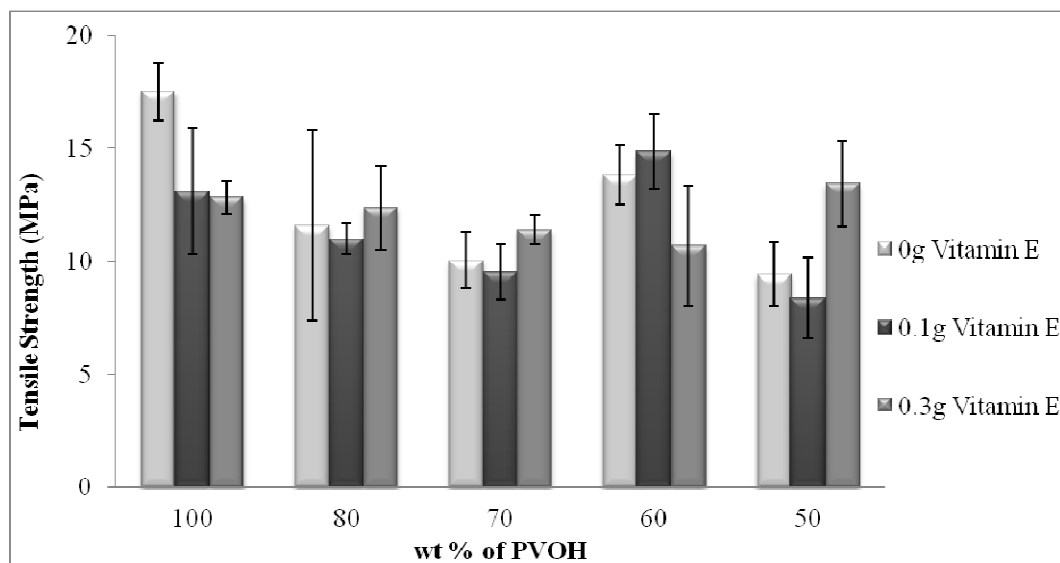


Figure 4.1: Tensile Strength (MPa) of PVOH- Starch blends with 0, 0.1 and 0.3 g of Vitamin E

In general, compound with crystalline structures exhibits higher tensile strength than amorphous materials. However, it could be noticed that there was a sudden increase in tensile strength (13.8 MPa) for the 60/40 wt% PVOH- Starch blend. It was also observed in the Scanning Electron Microscopy (SEM) figure 60/40 wt% PVOH- Starch blend in the Morphology Observations section is well dispersed. There was very little presence of void or agglomeration in this blend's structure. Little presence of voids and agglomeration caused the surface adhesion between the two components to be strong. Thus, it directly increased the tensile strength of the 60/40 wt % PVOH-starch blend film.

Figure 4.1 also shows that the tensile strength decreases significantly after the addition of 0.1 g of Vitamin E. This is because addition of 0.1 g of Vitamin E caused formation of agglomeration in the polymer matrix of the PVOH-starch-vitamin E blend. Besides, the hydrophobic Vitamin E in the form of oil was not dispersed well in the polymer matrix. These uneven dispersion and formation of agglomeration caused poor surface adhesion between the three components as supported in the SEM figure of 70/30 wt % PVOH/starch with 0.1 g of Vitamin E as shown in the Morphology Observations section. Hence, the tensile strength decreased significantly. This is also consistent with the result of Bracco et al. (2007) also studied that in low

concentrations; Vitamin E showed poor absorption and caused poor dispersion in the polymer matrix. It is obvious that this is due to the reason that the amount of Vitamin E was insufficient to promote the stability. Thus, it inhibited the strength of the polymer matrix.

Furthermore, Kangarlou, Haririan, and Gholipour (2008) also stated that addition of low concentration of plasticizers such as Vitamin E reduced the tensile strength. This is due to the reason that the intra- and inter- chain nature or disposition of the Vitamin E molecule reduced the large compactness of the entanglement in the polymer matrix (Kangarlou et al., 2008).

However, Figure 4.1 also shows that addition of 0.3 g of Vitamin E enhanced the tensile strength. The SEM figure of 70/30 wt % PVOH/starch with 0.3 g of Vitamin E in the Morphology Observations section shows that 0.3 g of Vitamin E managed to reduce the agglomeration and also shows the Vitamin E is well dispersed in the polymer matrix. Reduction in agglomeration and well dispersed matrix led to betterment in its surface adhesion between the three components. This justifies the increase in tensile strength after addition of 0.3 g of Vitamin E.

Furthermore, the molecular structure of Vitamin E is made up of an aromatic chromophore with two functional groups and a long aliphatic side chain which exposes the semi-planar molecule to easily interpose into the spaces of the polymer matrix (Kangarlou et al., 2008). This explains the reason of increment in tensile strength after addition of 0.3 g of Vitamin E into the PVOH-starch polymer matrix.

Besides that, the presence of oxygen in the molecular structure of Vitamin E which can be seen from Figure 4.2 increased the permanent dipole bonding between the polymer chains. In addition, phenyl rings in the Vitamin E caused steric hindrance to rotation within the blend and also electronic attraction of resonating electrons between adjacent molecules (Ebewele, 1996). These factors also assisted to raise the tensile strength.

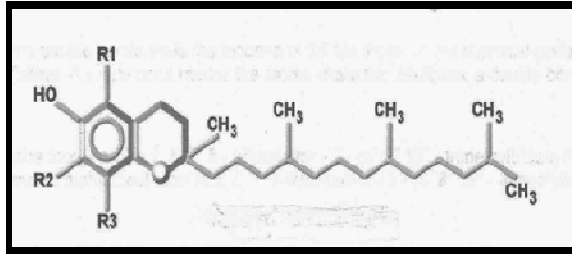


Figure 4.2: Molecular Structure of Vitamin E (Moussa, Peter, Silvia, & Leontino, 2007).

4.1.2 Elongation at Break

Elongation at break is the strain on a polymer film when it breaks. The percentage of elongation at break also represents the ability of the polymer film to stretch. Figure 4.3 shows that the percentage of elongation at break decreased significantly as the amount of starch increased. The highest percentage of elongation was observed at 95 % for pure PVOH. However, the elongation at break decreased to 10 % for the 60/40 wt% PVOH/starch film. The deterioration of this elongation at break property may be due to the relatively poor compatibility between PVOH and Starch. This may be also due to the poor interface adhesion between fibrous PVOH structure and the starch matrix which caused the compound to be brittle (Tang & Alavi, 2011).

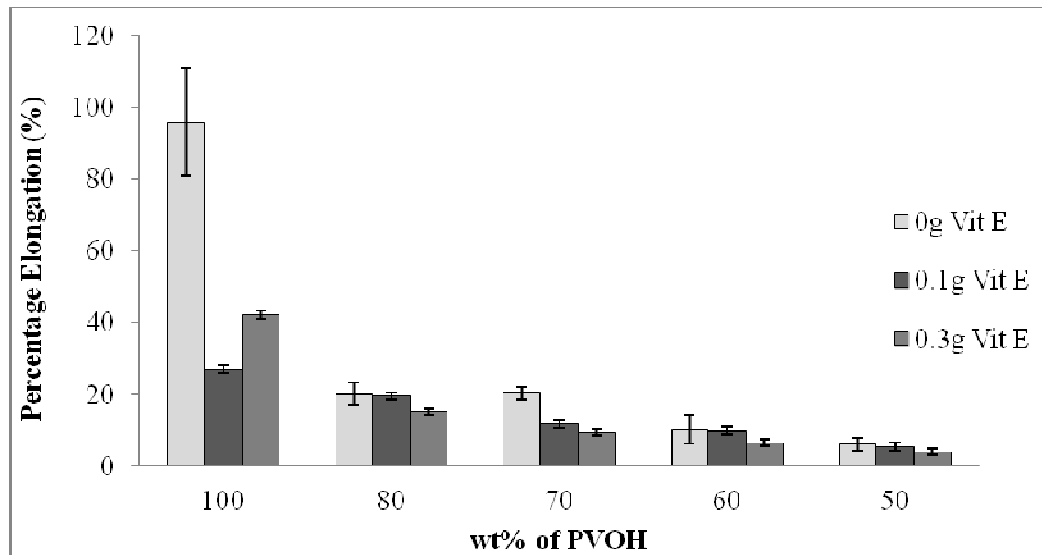


Figure 4.3: Percentage of Elongation at break for various PVOH- Starch compound with 0, 0.1 and 0.3 g of Vitamin E

As it could be seen, pure PVOH showed the highest percentage of elongation at break. This is also because pure PVOH is susceptible to undergo large plastic deformation. Nevertheless, addition of starch into the PVOH's matrix causes the rigidity of the film to be disrupted. This causes the PVOH- starch film to undergo smaller plastic deformation compared to pure PVOH. This is because the stress exerted cannot be transferred equally to the plastic PVOH matrix. The stress which was exerted will focus on the voids which are occupied by the starch particles and also the agglomerated starch particles. Similar findings were also obtained by Zhao et al. (2006) whereby it was found that the percentage of elongation at break decreased as the amount of starch increased.

Besides that, Figure 4.3 also shows that the incorporation of Vitamin E significantly decreased the percentage of elongation at break of the PVOH- starch films. The elongation at break for 70/30 wt % PVOH/ starch decreased from 20 % to 11 % and 9 % with the addition of 0.1 and 0.3 g of Vitamin E respectively. Similar trend was obtained by Martins et al. (2012) whereby the percentage of elongation at break decreased with the addition of Vitamin E into chitosan films. It was also reported by Jongjareonrak, Benjakul, Visessanguan, and Tanaka (2008) that the

percentage of elongation at break decreased when Vitamin E was added on fish skin gelatine films.

This is due to the reason that inclusion of hydrophobic Vitamin E into PVOH-starch film could cause the development of structural discontinuities. This then led the structure of the film to have less chain mobility. Less chain mobility also caused it to have less flexibility. Thus, it resulted in lesser resistance to break when the polymer film is stretched (Martins, Cerqueira, & Vicente, 2012). Generally, addition of oil into polysaccharide films decreases the elongation at break. This is due to the reason that lipids in the Vitamin E are not capable of forming continuous and cohesive matrices.

4.1.3 Modulus of Elasticity

Young modulus which is also known as the modulus of elasticity, is defined as the ratio of the uniaxial stress over the uniaxial strain in the range of stress in which Hooke Law holds, which means stress divide by strain. This modulus is also defined as the stiffness or the resistance of the material to undergo plastic deformation. Figure 4.4 indicates the modulus of various PVOH- Starch compounds with 0, 0.1 and 0.3 g of Vitamin E.

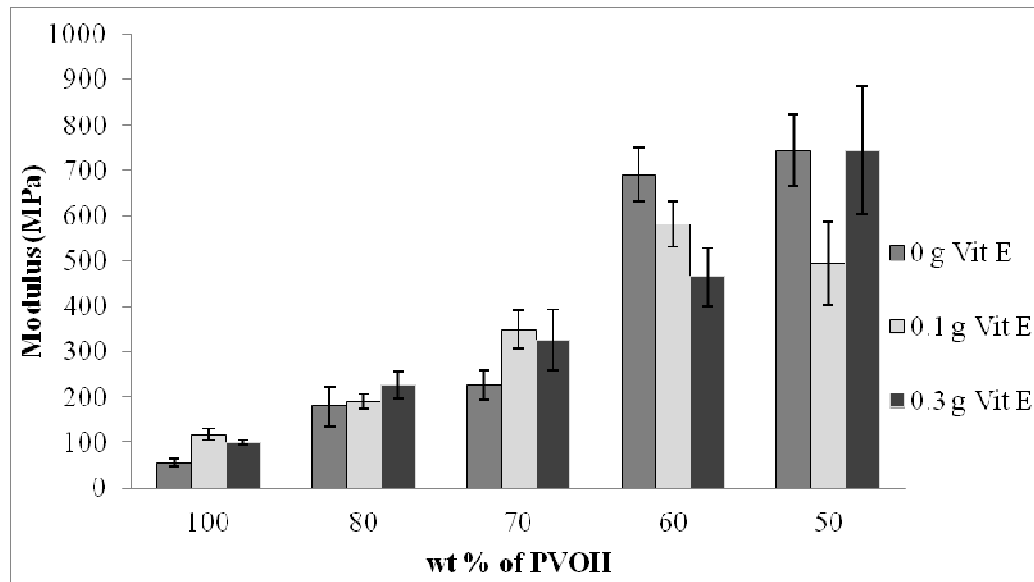


Figure 4.4: Modulus (MPa) of PVOH- Starch Compounds with 0, 0.1 and 0.3 g of Vitamin E

From Figure 4.4, it can be clearly seen that the modulus of elasticity increases as the amount of starch increased. The highest modulus of elasticity was found to be for the 50/50 wt% PVOH- Starch film with the value of 745.4 MPa. It was also observed that the modulus of elasticity increased when 0.1 and 0.3 g of Vitamin E was added into the PVOH- starch blend film. This is due to the difference in the characteristic of the polymer compound and also because of the stiffening effect of the starch and Vitamin E granules. Addition of stiff starch particles into the PVOH's matrix would lead to the enhancement of modulus of elasticity (Kocsis & Fakirov, 2009). A similar finding was reported by Toh et al. (2011) whereby the modulus of elasticity increased as the amount of starch increased.

4.2 Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry (DSC) test was conducted to determine the enthalpy of melting (ΔH_m) of the polymer film. It was stated by Hourston & Song (2006) that the change in enthalpy of melting was used to determine the reactive interactions of polymer blends. Figure 4.5 shows the DSC thermogram of 50/50 wt% PVOH/ Starch blend. The thermal scan was carried out from 50 °C to 250 °C. The thermal scanning shown in Figure 4.5 was selected to show the melting point of PVOH sample in the range of 230 – 250 °C. The scanning was stopped at a temperature below 250 °C to ensure the hydroxyl groups of PVOH do not get dehydrated (Lee et al., 2009). The melting stage can be detected through the presence of peak as shown in Figure 4.5.

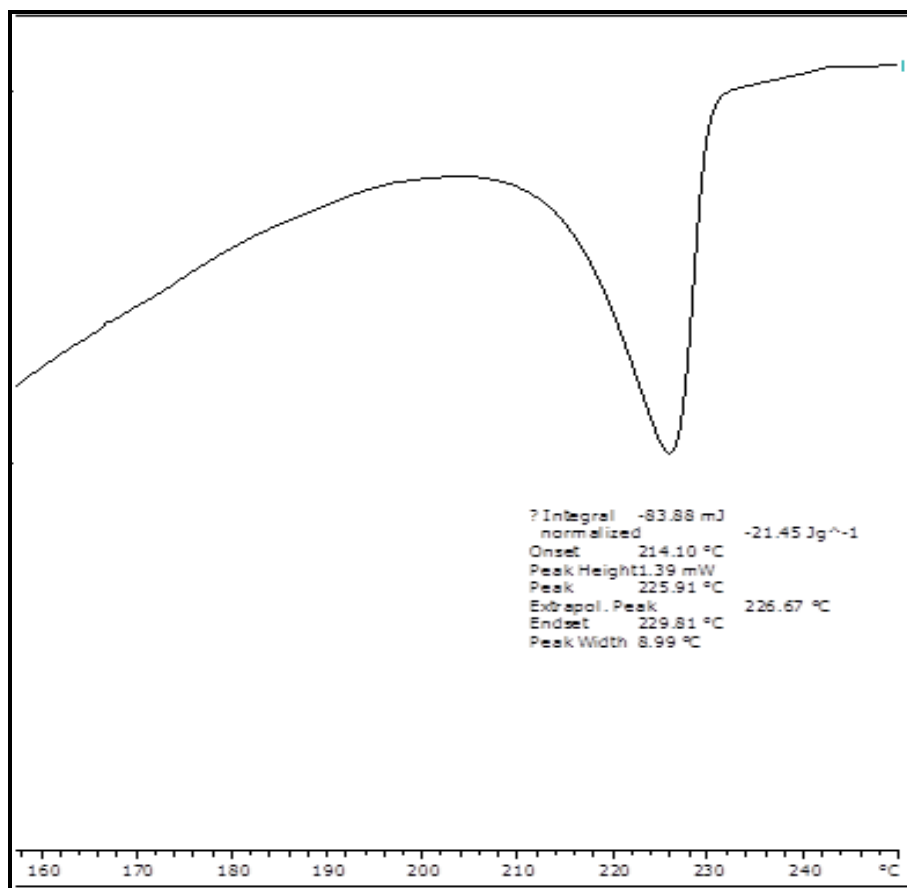


Figure 4.5: DSC thermogram of 50/50 wt% of PVOH/Starch

Figure 4.5 indicates that enthalpy of melting (ΔH_m), onset temperature and end- point temperature of 50/50 wt% PVOH/starch film are -21.45 J/g, 214.10 °C and 229.81 °C respectively. Similar findings were also reported by Lee et al. (2010) whereby for 50/50 wt % PVOH/starch film, the enthalpy of melting (ΔH_m), onset temperature and end- point temperature are 28.96 J/g, 215.70 °C and 229.50 °C respectively. Figure 4.6 indicates the enthalpy of melting (ΔH_m) for the PVOH-Starch-Vitamin E blends. It was clearly shown that the enthalpy of melting, ΔH_m decreased as the amount of starch increased. This is due to the reason that the intermolecular interaction in the compound has decreased (Hourston & Song, 2006). Higher ΔH_m values of 80/20 wt % PVOH/starch (54.4 J/g) compared to 70/30 wt % PVOH/starch (50.47 J/g) proved that the intermolecular interactions present in 80/20 wt % PVOH/starch was stronger. Thus, larger amount of energy was essential to break the bonds and free the polymer chains from the rigid and crystal structures (Lee et al., 2010). This intermolecular interaction is due to the presence of hydrogen bonds between PVOH and starch (Lee et al., 2009). Conversely, compounds with higher percentage of starch had lower ΔH_m . Compounds with less crystalline region or more amorphous nature does not require high amount of energy to break the bonds due to the relatively weak intermolecular forces (Lee et al., 2009).

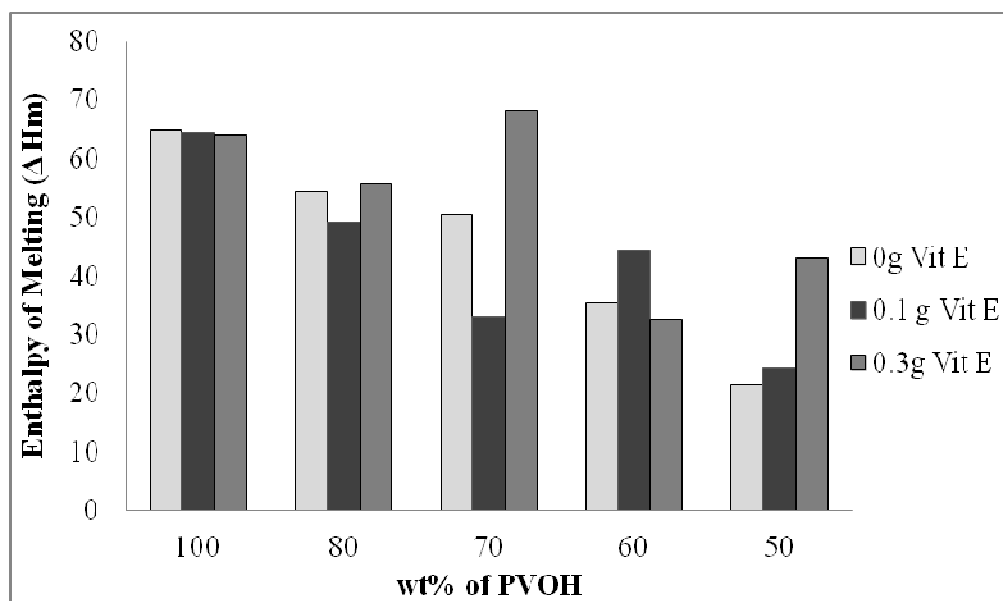


Figure 4.6: Enthalpy of Melting of PVOH- Starch Compounds with 0, 0.1 and 0.3 g of Vitamin E

Now, comparing both the Figure 4.1 and 4.6, it could be clearly seen that both the figures showed the similar trend. This proved the correlation between crystallinity, molecular interaction and properties such as tensile strength and the enthalpy of melting. The ΔH_m supported the results of the tensile strength whereby the 60/40 wt% with 0.1 g of Vitamin E required the highest amount of energy to break the bond compared to the other PVOH- Starch with 0.1 g of Vitamin E blends.

The outcomes in Figure 4.6 indicated that when small amount of Vitamin E which is 0.1 g was added, the stabilizing effect was weakened because it disrupted little of the physical bonding interaction between PVOH and Starch. However, the molecular interactions became stronger again when the amount of Vitamin E was increased to 0.3 g.

4.3 Morphology Observations

The morphology plays a major role in determining and proving the properties and interaction of the polymer blends. The scanning electron micrographs in Figure 4.7-4.11 show the phase structures of the various PVOH-starch blends with different concentrations of starch. The scanning was done with a magnification of 3000 times. From Figure 4.8- 4.11, it could be seen that as the amount of starch increases, the formation of agglomeration and voids also increased. These Figure 4.8- 4.11 also show that as the amount of starch increases, the dispersion of starch in the PVOH matrix becomes worse.

Figure 4.7 of pure PVOH shows the surface is very smooth compared to the other PVOH-starch blends as shown in Figures 4.8- 4.11. However, in Figure 4.8, starch granules are coarsely dispersed in the PVOH matrix. In Figure 4.9, the 70/30 wt % PVOH/starch polymer surface appears to be rougher and more brittle compared to the 80/20 wt % PVOH/starch blend in Figure 4.8. It could be clearly seen in Figure 4.9 that the PVOH are finely dispersed in starch granules, but the granules of starch agglomerated between the PVOH matrixes.

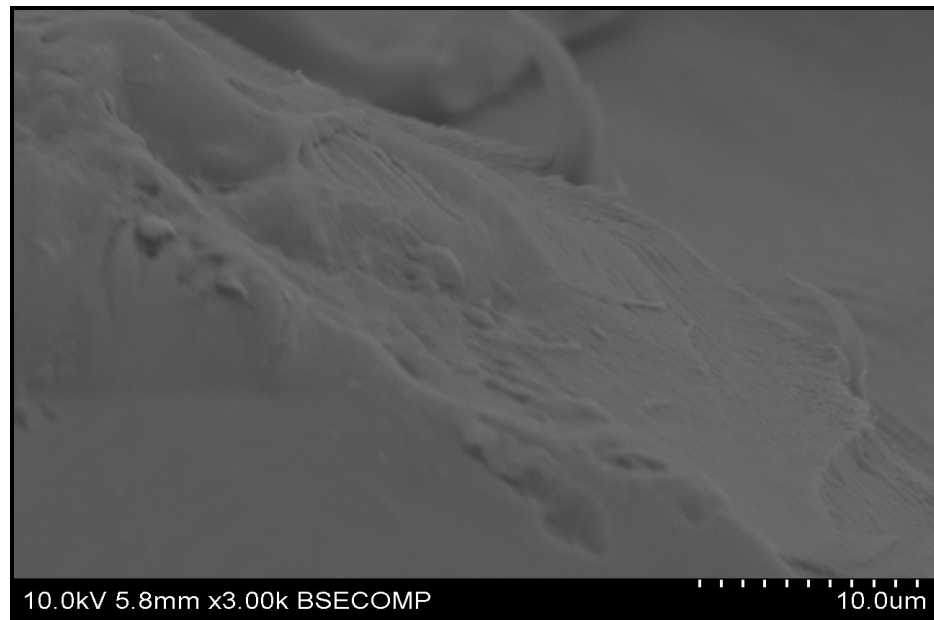


Figure 4.7: SEM micrograph of Pure PVOH

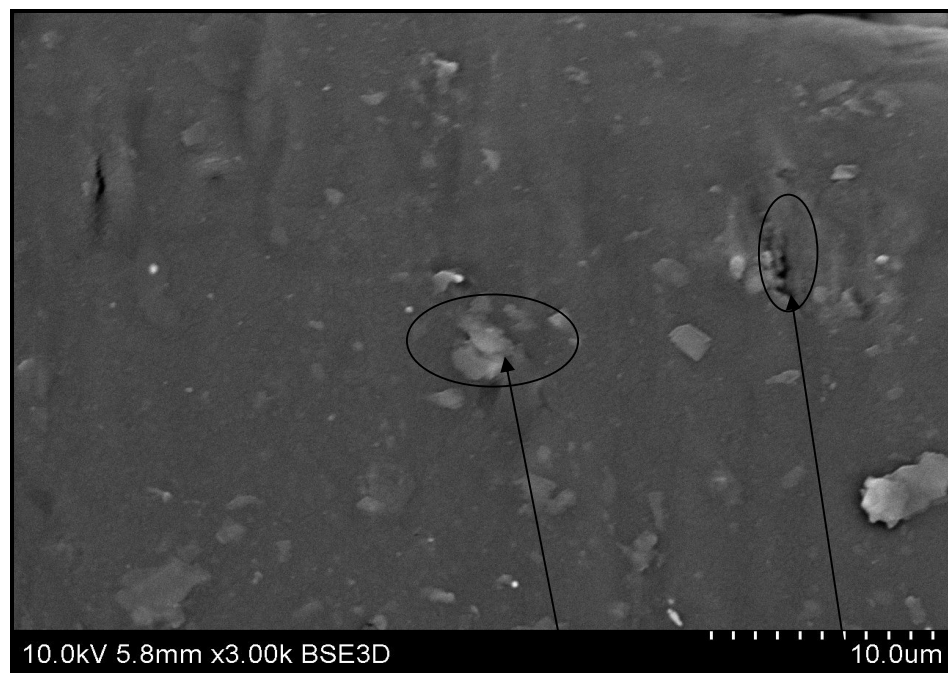


Figure 4.8: SEM micrograph of 80/20 wt % of PVOH/starch

Agglomeration

Voids

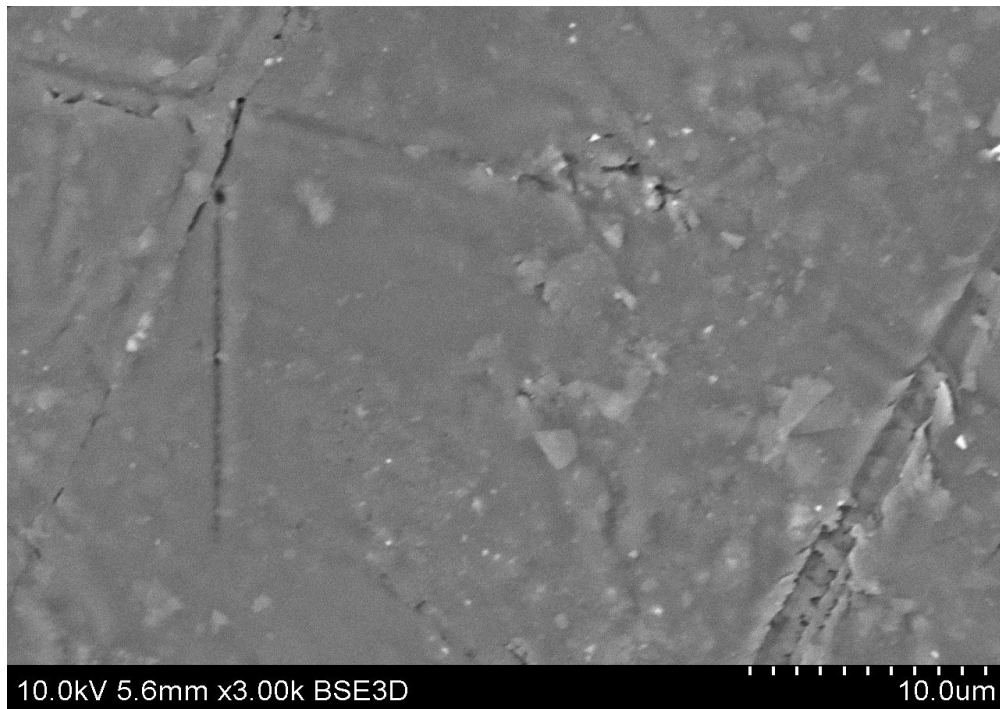


Figure 4.9: SEM micrograph of 70/30 wt % of PVOH/starch

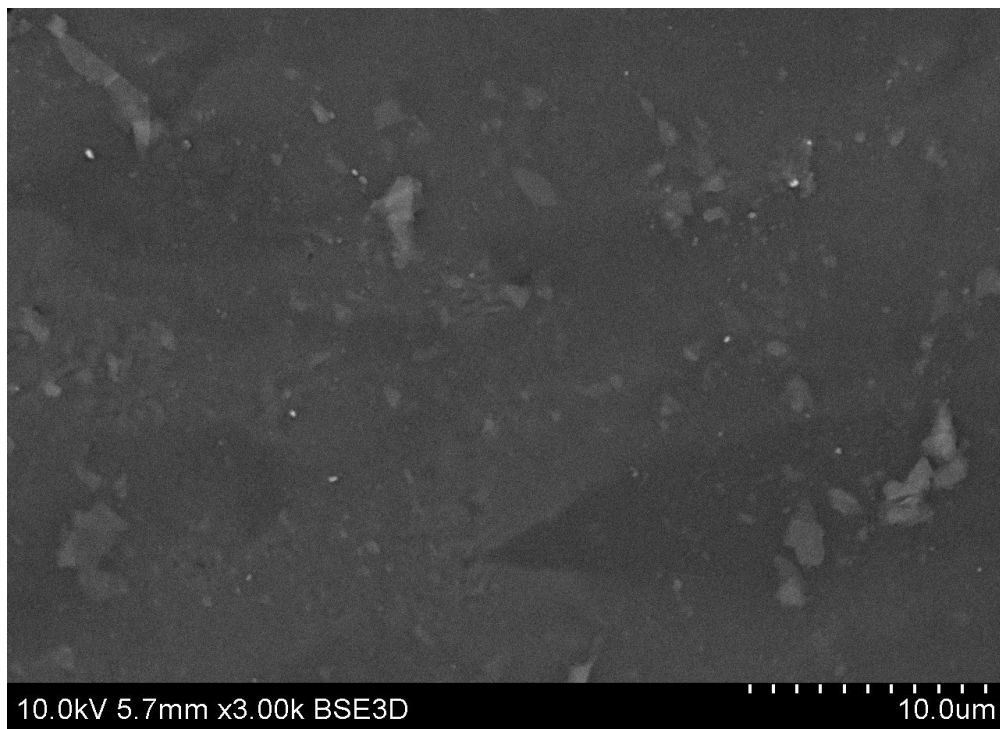


Figure 4.10: SEM micrograph of 60/40 wt % of PVOH/starch

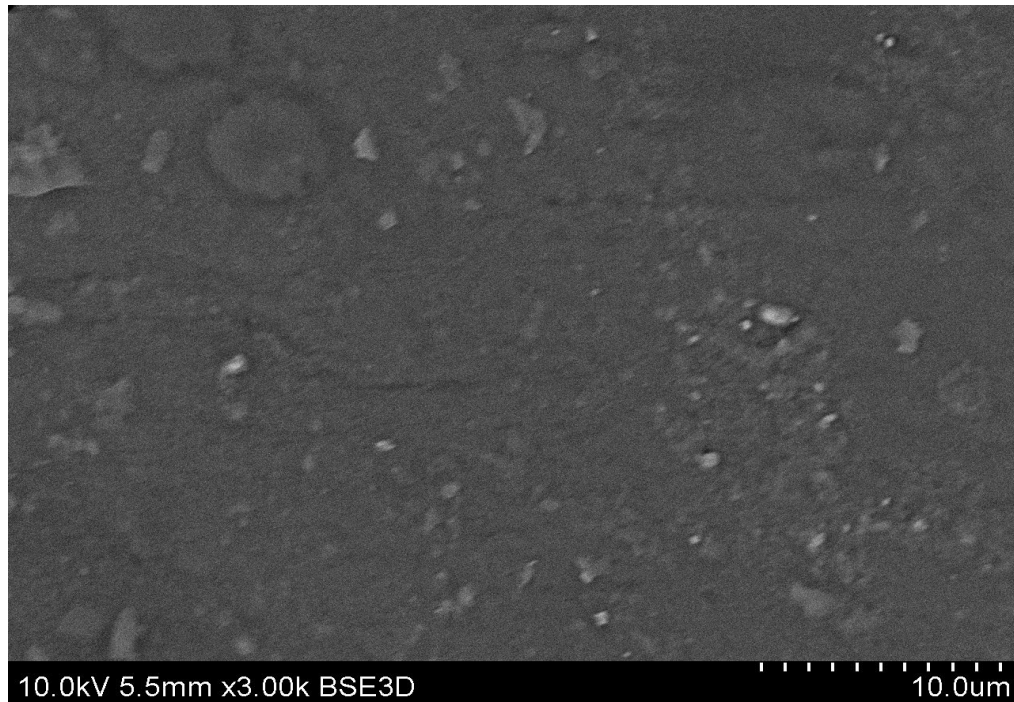


Figure 4.11: SEM micrograph of 50/50 wt % of PVOH/starch

However, it could be seen in Figure 4.10 of 60/40 wt % PVOH/starch blend that the starch particles are less agglomerated and it is dispersed well in the PVOH matrix. This also explains the increment in tensile strength for the 60/40 wt % PVOH-starch blend. Thus, it could be said that fine distribution or dispersion of starch in PVOH matrix is vital to improve the tensile strength of the PVOH-starch blend films.

Comparing the entire above Figure 4.8- 4.11, it could be seen that the size of the agglomerated starch particles in the PVOH matrix also increases as the amount of starch increases. It is observed from the above micrographs that the amount of agglomeration also increases as the amount of starch increases in the PVOH matrix. The agglomerated particles of starch in 80/20 wt % of PVOH/starch blend is much lesser compared to the agglomeration of starch in the 70/30 wt % PVOH /starch blend.

The scanning electron micrographs of Figure 4.12 and 4.13 show the phase structures of 70/30 wt % of PVOH/starch blend with 0.1 and 0.3 g of Vitamin E respectively. Comparing Figures 4.9 and 4.12, it could be seen that there are much more agglomerated starch particles and also formation of voids after the addition of 0.1 g of Vitamin E. This also explains the decrease in tensile strength after addition of 0.1 g of Vitamin E. However, it can be seen from Figure 4.13 that there are much lesser agglomeration of starch particles and also very little formation of void due to Vitamin E. Thus, it could be said that addition of 0.3 g of Vitamin E into PVOH-starch blend managed to reduce the agglomeration and thus also the voids.

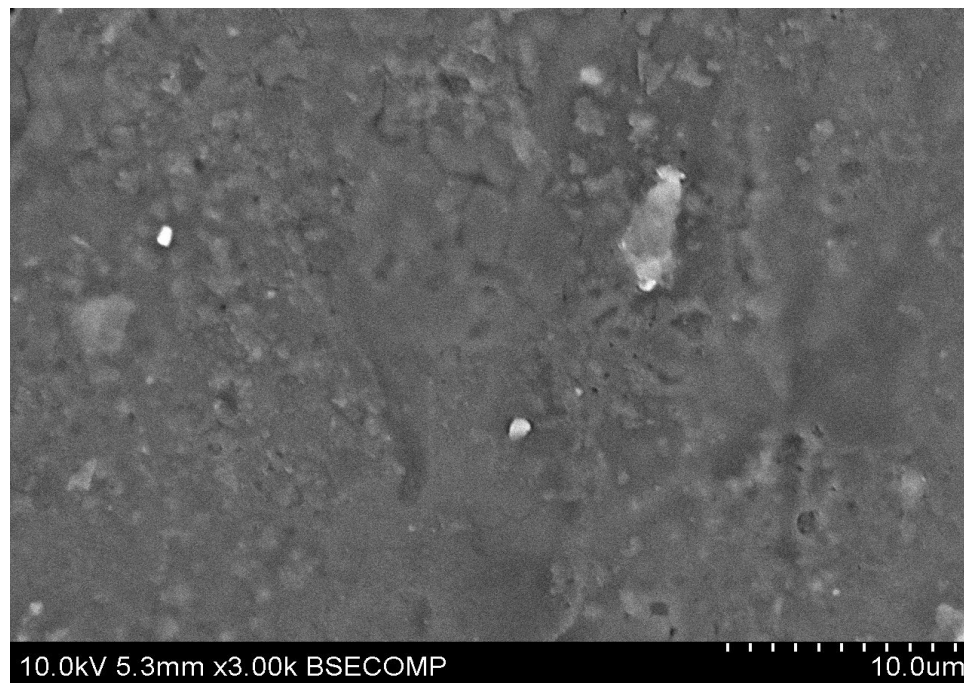


Figure 4.12: SEM micrograph of 70/30 wt % PVOH/starch with 0.1 g of Vitamin E

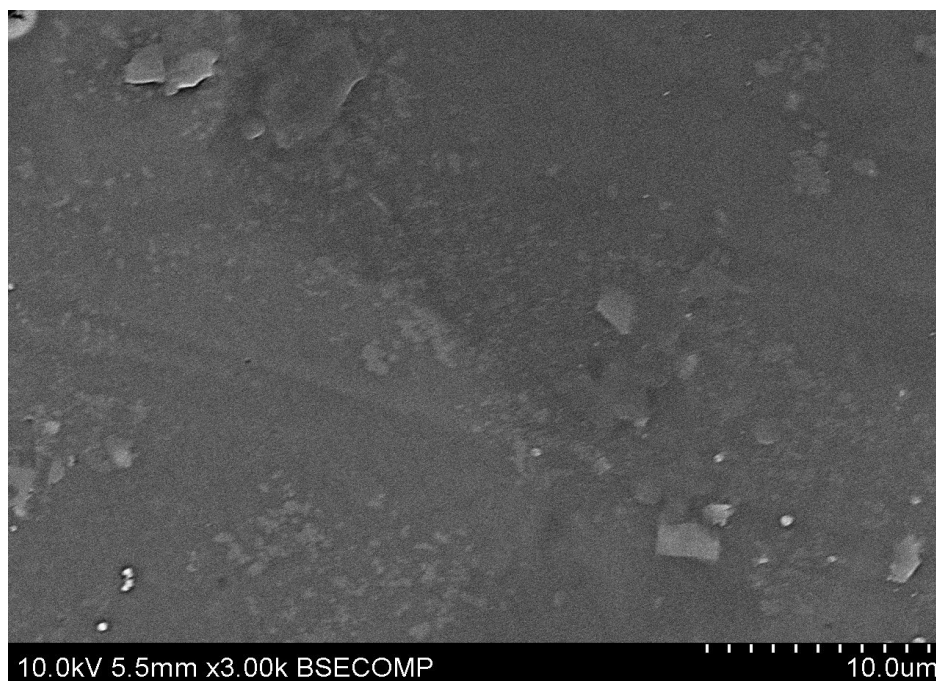


Figure 4.13: SEM micrograph of 70/30 wt % PVOH/starch with 0.3 g of Vitamin E

4.4 Fourier Transform Infrared (FTIR) Spectroscopy

The effect of Vitamin E in PVOH-starch blend films was evaluated by Fourier Transform Infrared (FTIR) Spectroscopy analysis. Addition of these three compounds caused changes in the physical bonds and also the chemical interactions and these changes are reflected by the shifts or changes in the spectral peaks. Figures 4.14 and 4.15 show the FTIR spectra of 50/50 wt % PVOH/starch blend and the 50/50 wt % PVOH/starch blend with 0.3 g of Vitamin E respectively.

From the spectra in Figure 4.14 and 4.15, the strong absorption peak at 3474 cm^{-1} and 3503 cm^{-1} is attributed to the O-H stretching vibration. It could be seen that the stretching of the O-H bond increased as 0.3 g of Vitamin E is added into the PVOH-starch blend. The increase in stretching of the O-H band implies that the O-H bond had become stronger after the addition of 0.3 g of Vitamin E. This is because addition of Vitamin E in the form of oil caused it to behave as a lubricant. This then caused the PVOH-starch- vitamin E blend films to become soft. This then led the O-

H bond to be more flexible and thus it can undergo more stretching compared to the PVOH-starch blend without addition of Vitamin E.

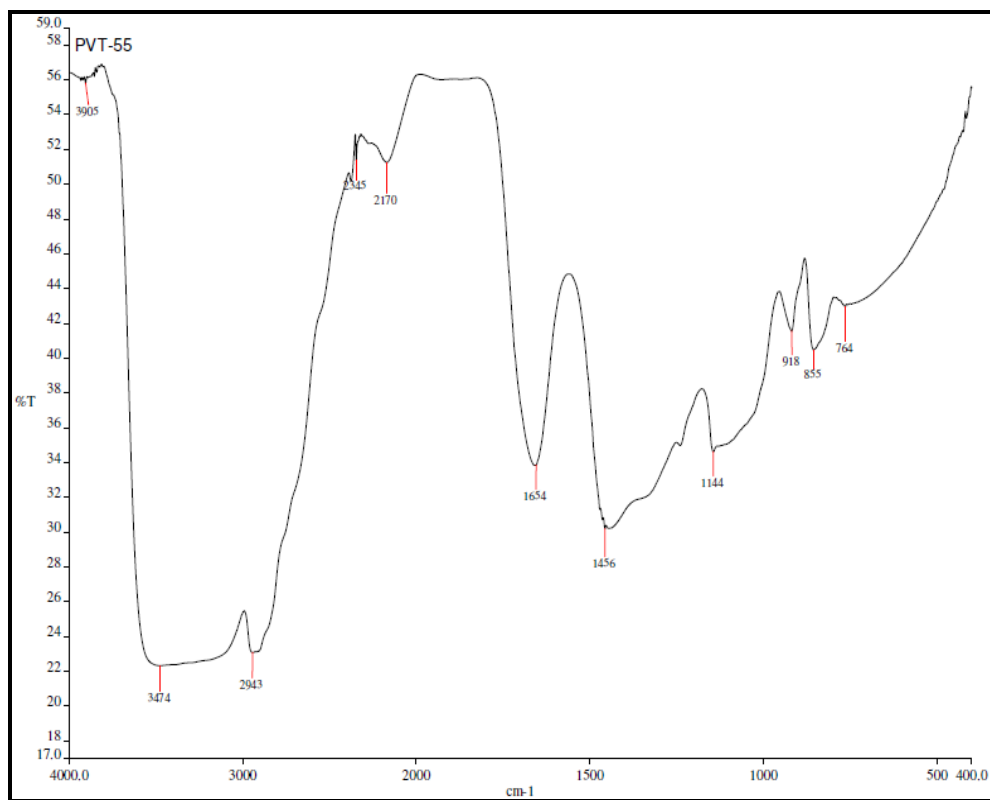


Figure 4.14: FTIR spectra of 50/50 wt % PVOH/starch blend

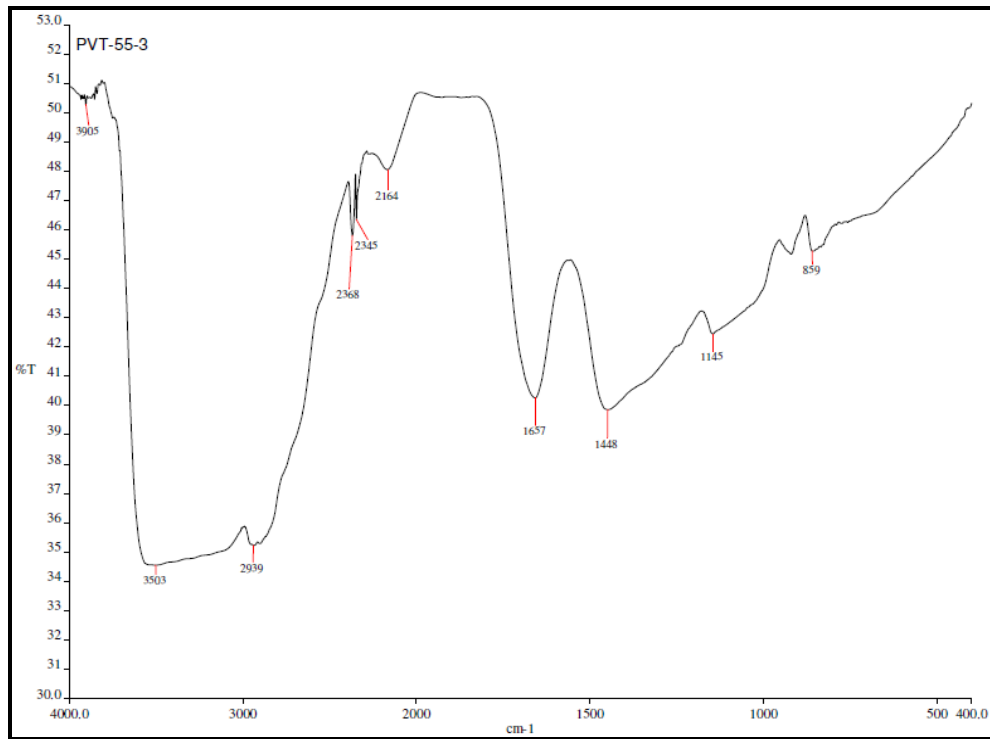


Figure 4.15: FTIR spectra of 50/50 wt % PVOH/starch blend with 0.3g Vitamin E

This FTIR results proved that there are correlation between the O-H bond strength, tensile strength and also the enthalpy of melting. It could be clearly seen from Figure 4.1 that the tensile strength increases with the addition of 0.3 g of Vitamin E. Thus, it can be said that one of the reason of increment is due to the increase in strength of the O-H bond. In addition, from Figure 4.6, the enthalpy of melting for 50/50 wt% PVOH/starch blend film also had an increase after the addition of 0.3 g of Vitamin E. This result also correlates with the FTIR result. Hence, it could be said that increase in the strength of the O-H bonds, increased the enthalpy of melting and also the tensile strength of the films.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

It can be concluded that addition of 0.1 g of Vitamin E was not able to increase the tensile strength of the PVOH-starch blend film due to the reason that it caused poor surface adhesion. Addition of 0.3 g of Vitamin E enhanced the tensile strength of the PVOH-starch blend film. Thus, higher amount of Vitamin E is needed to enhance the tensile strength of this polymer film by 42 %. Besides that, addition of Vitamin E into the PVOH-starch blend film decreases the percentage of elongation at break of the polymer film by 10 % and 20 % respectively for both 0.1 and 0.3 g of Vitamin E. Addition of Vitamin E into the PVOH-starch blend increased the modulus of elasticity of the polymer film. This indicates that the polymer film becomes stiffer as Vitamin E is added into the PVOH-starch blend film.

Furthermore, addition of 0.3 g of Vitamin E was found to increase the enthalpy of melting of the PVOH-starch blend films. This is due to the reason that the intermolecular bonding has become stronger with the addition of 0.3 g of Vitamin E.

5.2 Recommendations

For future research purpose, it is recommended that researchers should:

- Add higher percentage of Vitamin E to evaluate the above properties. Further research should be done to evaluate whether higher amount of Vitamin E will be able to further enhance the mechanical properties of the PVOH-starch blend film.
- Investigate on the barrier properties such as water resistance of the PVOH-starch blend film after the addition of Vitamin E.
- Evaluate on the biodegradability of the PVOH-starch blend film after the addition of Vitamin E.
- Evaluate on the crystallinity of the PVOH-starch blend film after the addition of Vitamin E.
- Investigate on the thermal stability of the PVOH-starch blend film after the addition of Vitamin E.

This plastic film is recommended to be used as food and pharmaceutical packaging films. This plastic film is considered safe to be used for food and pharmaceutical as it has high mechanical properties and also decreased water or moisture absorption. Besides that, Vitamin E is safe and it does not harm the health of human. Thus, this PVOH-starch- Vitamin E blend plastic film will not endanger our lives as well.

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