

**SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING**

**UNIVERSITI SAINS MALAYSIA**

**THE EFFECTS OF DIFFERENT PLASTICIZERS (TRIACETIN AND  
TRIETHYL CITRATE) ON POLYVINYL ALCOHOL**

By

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of the requirement for the degree of Bachelor of Engineering with Honours  
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## DECLARATION

I hereby declare that I have conducted and completed the research work and written the thesis entitled '**Studies on Different Type of Plasticizer (Triacetin and Triethyl Citrate) on Polyvinyl Alcohol**'. I also declare that it has not been previously submitted for award of any degree or diploma or other similar title of this for any other examining body or university.

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## LIST OF SYMBOLS

%	Percentage
°C	Degree Celcius (unit for temperature)
K	Kelvin (unit for temperature)
g/mol	Gram per mole (unit for molecular weight)
MPa	Mega Pascal (unit for stress)
°C/min	Degree per minute (unit for heating rate)
Min	Minutes (unit for time)
Hr	Hours (unit for time)
Wt%	Weight percent
$\delta$	Solubility parameter
ml	Mililitres (unit for liquids)
$(\text{J}/\text{cm}^3)^{1/2}$	Joule per centimetres cube (unit for solubility parameter)
Cm	Centimetres (unit for length)
mm	Milimetres (unit for length)
Mm/min	Millimetre per minute (unit for speed)
mg	Miligrams (unit for weight)
$\text{cm}^{-1}$	(unit for frequency)
°	Degree

## LIST OF ABBREVIATIONS

ASTM	American Standard Testing Mechanical
BASF	Baden Aniline and Soda Factory
DEHP	Di-(2-ethylhexyl)-phthalate
DSC	Differential Scanning Electron
FTIR	Fourier Transform Infrared
T <sub>g</sub>	Glass Transition Temperature
T <sub>m</sub>	Melting Temperature
PEG	Polyethylene glycol
PLA	Polylactic acid
PS	Polystyrene
PVA	Polyvinyl alcohol
PVC	Polyvinyl Chloride
SEM	Scanning Electron Microscope
TEC	Triethyl citrate
TRI	Triacetin
XRD	X-ray Diffractometer

# **KAJIAN MENGENAI KESAN PEMPLASTIK BERLAINAN (TRIACETIN AND TRIETIL SITRAT) PADA POLYVINIL ALKOHOL**

## **ABSTRAK**

Kerja ini bertujuan untuk mengkaji kebolegunaan untuk dua pemplastik berasaskan semulajadi yang berbeza sebagai pemplastik alternatif dalam pelbagai jenis Polyvinil Alkohol (PVA). Dua pemplastik yang berasaskan semulajadi telah dipilih iaitu Triacetin dan trietil sitrat sebagai pemplastik alternatif baru dalam PVA yang mempunyai darjah hidrolisis yang berlainan (88 dan 99%) dan mempunyai berat molekul yang sama dan keberkesanan dari segi sifat keterlarutan campuran, termal, tegangan dan morfologi juga dipelajari. PVA dan pemplastik telah dicampur dengan kaedah pengadunan larutan dan PVA telah dikeringkan untuk menghasilkan filem PVA. Pada jumlah pemplastik yang tetap, analisis DSC menunjukkan bahawa Triacetin menyebabkan pengurangan suhu peralihan kaca ( $T_g$ ) dan suhu lebur ( $T_m$ ) terhadap kedua-dua jenis PVA dengan perubahan yang lebih tinggi dalam darjah 88% hidrolisis, tetapi Trietil sitrat menunjukkan perubahan  $T_g$  dan  $T_m$  yang sedikit pada kedua-dua jenis PVA yang menunjukkan keberkesanan sistem dalam perubahan yang lebih tinggi. Morfologi campuran menunjukkan pemisahan fasa sistem PVA dengan Trietil sitrat yang menunjukkan kurang kebersanan Trietil sitrat sebagai pemplastik PVA. Sementara itu, sifat-sifat termal PVA daripada 88% hidrolisis dengan jumlah Triacetin yang berbeza menunjukkan bahawa  $T_g$  menurun secara berterusan dengan peningkatan pemplastik sehingga 15% tetapi tidak jauh berbeza dengan 20% Triacetin. Kekuatan tegangan dan modulus menunjukkan sedikit pengurangan nilai dengan meningkatnya Triacetin sehingga 10% sebelum meningkat secara tiba-tiba sekitar 32 MPa dan 80MPa, tetapi peningkatan secara berterusan dalam pemanjangan pemecahan dengan penambahan Triacetin. Kajian morfologi menunjukkan perubahan morfologi yang ketara dengan permukaan kasar pada kehadiran triacetin sebanyak 15% dan menunjukkan ia adalah penambahan pemplastik yang optimum dalam PVA.

# STUDIES ON EFFECT OF DIFFERENT PLASTICIZERS (TRACETIN AND TRIETHYL CITRATE) ON POLYVINYL ALCOHOL

## ABSTRACT

This work aims to investigate the applicability to two different natural based plasticizers as alternative plasticizers in different types of Polyvinyl Alcohol (PVA). Two natural based plasticizers were chosen which are triacetin and Triethyl citrate as new alternative plasticizers in PVA of different hydrolysis degree (88 and 99%) but similar molecular weight and the effectiveness in term of miscibility, thermal, tensile and morphological properties were studied. The PVA and plasticizer were mixed by solvent blending method and the solution of PVA compound was casted to produce plasticized PVA film. At a fix amount of plasticizer, Differential scanning calorimetry (DSC) analysis showed that the presence of Triacetin caused reduction of glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) of both types of PVA with higher changes in 88% hydrolysis degree but with Triethyl citrate, the film showed insignificant changes of  $T_g$  and slight reduction of  $T_m$  in both types of PVA suggesting higher effectiveness of the former system. Morphology of the blends indicated phase separation of the system of PVA with Triethyl citrate thus responsible for the less effectiveness of Triethyl citrate as plasticizer of PVA. Meanwhile, thermal properties of PVA of 88% hydrolysis with different amount of Triacetin indicated that  $T_g$  continuously decreased with increasing plasticizer up to 15 wt% but then did not significantly different with 20wt% Triacetin. Tensile strength and modulus indicated slight reduction of value with increasing triacetin up to 10 wt% before sudden jump to up to around 32 MPa and 80MPa, respectively but continuous increased of elongation at break with triacetin loading. Morphological study showed significant change of morphology with rough surface in the presence of 15wt% Triacetin suggesting that the optimum loading of the plasticizer in PVA.

# CHAPTER 1

## INTRODUCTION

### 1.1 Overview

During the last few years, sustainable development through the use of environmental friendly material has become the main interest all around the globe. The usage of materials that can be obtained from natural resources are becoming a potentially viable alternative to a synthetic polymer that are mainly synthesized from petroleum-based resources (Thakur & Singha, 2015). Application of bio-degradation material, stresses on physical, chemical, thermal and mechanical, and degradation properties that can be used to replace synthetic polymeric materials. In addition, bio-polymeric material are renewable sources and the easy availability of these materials are most significant advantages that related to the final cost of the material in the market. One of the example of bio-degradable material is Polyvinyl Alcohol.

PVA is a non-toxic macromolecule polymer with abundant of hydroxyl functional groups which can be synthesized from the hydrolysis of polyvinyl acetate (Li J and Li Y, 2017). There are limitations of PVA during processing in which are they are thermally unstable and cannot be process alone. PVA required high temperature to be processed, and PVA do not able to withstand high temperature due to degradation might take place. Many research works have been done on addition of plasticizer in PVA which are normally able to reduce the melting point and glass transition temperature of the PVA for example Pu-You, Cai-ying, Li-hong, and Yong-hong (2014), he reported that the addition of glycerol to PVA film shifted the  $T_g$  and  $T_m$  to a lower temperature, thus making the processing of PVA more effective. It is reported that the addition of plasticizer in the PVA change the micro-molecular and macromolecular structure of PVA to improve its thermal

stability (Nass, 1992). Several plasticizers are widely used to incorporate with PVA such as Glycerol, Glyceryl, Dibutyl Phthalate and Ethylene Glycol (Bengisu, 2001).

Plasticizer is a substance typically a solvent or liquid, that are added to a polymer to promote plasticity and flexibility and to reduce brittleness. The main role of plasticizer is to improve various properties of the polymers by increasing flexibility, decreasing tensile strength and lowering the second order transition temperature (Dodiuk & Goodman, 2013). Plasticizer is one of the additives that usually used to space out the polymer molecules, facilitating their movements and leading to enhance flexibility. Plasticizer able to penetrate into polymer and reduced the force of attraction between chains (Teegarden, 2004).

The influence are related to the changes in polymer structure and frequently measured in the decrease in glass transition temperature (A. Wypych, 2013). Plasticizer also able to modify rheological. Among the polymers that normally processed in the presence of plasticizers are PVC due to earliest uses for PVC were in flexible application due to PVC are difficult to process without incorporation with plasticizer (Nass, 1992). The most common plasticizer used in PVC is Diethylhexyl Phthalate (DEHP) (Tylkowski et al., 2017). Another polymer that usually need incorporation of plasticizer in their application is polystyrene, and the most plasticizer used in PS is Dioctylphthalate (H. F. Mark, 2013).

There are various types of plasticizers present such as glycerol, glycerine, ethylene glycol, PEG and DEHP. Many researchers start to focus on the class of products that are using biodegradable or natural based additives and plasticizers. The use of natural and/or biodegradable plasticizers, with low toxicity, non-carcinogenic, and good compatibility with several plastics, resins, rubber and elastomers in substitution of conventional plasticizers, such as phthalates and other synthetic conventional



plasticizers attracted the market along with the increasing worldwide trend towards use of biopolymers (Vieira, da Silva, dos Santos, & Beppu, 2011)

Plasticizer can be divided into two categories based which are synthetic-based and the other one is natural-based. Glycerol and Glycerine are examples of synthetic-based plasticizer while triacetin and triethyl citrate are the examples of natural-based plasticizer. Most of the plasticizer used during processing are typically toxic petroleum-based phthalates (Zheng et al., 2018). Hence, replacement of petrol-based plasticizers can be made by using natural-based plasticizers which are more eco-friendly and non-toxic. The renewable source and easy to obtain are the advantages of using this type of natural-based plasticizers. This research is mainly focused on the use of natural based plasticizer such as Triacetin and Triethyl Citrate as an alternative plasticizer to replace petrol-based plasticizer such as glycerol into PVA plastic.

Triacetin and Triethyl citrate have been assessed for several years as non-toxic and non-carcinogenic to the environment and mammals. Therefore, these two plasticizers are considered to be non-toxic and no of significant threat to wildlife (Williams, Reddy, Quinn, & Johnson, 2015). Due to non-toxicity of Triethyl citrate, they are not irritant to the skin of humans and laboratory animals (Ministers, 2002). They also known as great plasticizers which are used to produce film intended for packaging (Garcia, Gómez-Guillén, López-Caballero, & Barbosa-Cánovas, 2016). Both of plasticizers are eco-friendly, not harmful, can be possess a high water, oil and low temperature resistance as well as insignificant volatility. The contribution of Triacetin as plasticizer in Poly(lactic) Acid (PLA) has been reported Oksman, Skrifvars, and Selin (2003), they observed that the addition of Triacetin showed a positive effect in elongation at break for pure PLA which is due to softening effect. The addition of Triacetin in PLA also reduced the tensile strength indicates Triacetin is an effective plasticizer in PVA.

However, not much work done on the use of Triacetin and Triethyl citrate in PVA. As mentioned above, Glycerol and Glycerine are the plasticizer that usually used to incorporates with plasticizer. However, by having various types of plasticizer to incorporates with PVA might give several advantages. Triacetin and Triethyl citrate are plasticizer that shared the same function as conventional plasticizer which is they increase the flexibility and reduce the process temperature of polymer. In addition, the unique characteristic of these plasticizers, both are natural-based plasticizer which not contribute to health problem and environmental friendly. Hence, PVA compound that had been plasticized by using natural-based plasticizer able to enhance its properties while not giving any harmful substance to the human health and environment.

## **1.2 Problem Statement**

This research is mainly focused on the used on Triacetin and Triethyl citrate as an alternative plasticizer for different types of PVA. As mentioned above, PVA usually incorporates with conventional plasticizer such as Glycerol, PEG and Glycerine. The replacement of synthetic-based plasticizer with natural-based plasticizer become the main interest to study. Since there is not much work done on the use of Triacetin and Triethyl citrate in PVA since PVA usually blends with Glycerol and Glycerine hence, there are several criteria that need to be in concern.

To have successfully plasticizer in polymer, the plasticizer must be miscible or at least compatible to avoid phase separation between polymer and plasticizer. In other words, efficient plasticizer in a polymer can be achieve if the plasticizer is miscible throughout the matrix of PVA. Generally, the miscibility between plasticizer and polymer can be observed from solubility parameter of two components. This act as first indication to choose suitable plasticizer to incorporate with polymers. The efficiency of plasticizer in polymer can be shown by the physical properties and thermal properties of the

plasticized polymer such increasing in flexibility and low processing temperature and glass transition temperature.

PVA is widely used by blending with polymer compound for various industrial applications to enhance the mechanical properties due to its compatible structure and hydrophilic properties. The solubility behaviour of PVA much depends on degree of hydrolysis and degree of polymerization (Ambrosio & Tanner, 2012). Fully hydrolysed PVA (99%-100% hydrolyse) with low acetate content has different behaviour in solubility compare to partially hydrolysed PVA (88-87% hydrolysed) usually has around 12% acetate content. Different in acetate content could affect the interaction between plasticizer and PVA are the main concern due to different types of PVA used in this research since acetate group is hydrophobic.

The properties, miscibility and applicability of plasticizer in certain polymer is affected by the amount of plasticizer used. Efficiency of plasticizer in a polymer can be observed at certain percent of plasticizer content which known as the optimum value of plasticizer that works effectively in the polymer (Rajabi-Siahboomi, 2017). The optimum value can be obtained from various composition of plasticizer as desired properties of plasticized polymer is achieved. The effect of Triacetin or Triethyl Citrates on PVA were studied to observe the performance of PVA after plasticized with two types of plasticizers. Tensile test are performed to determine tensile strength, elongation at break and modulus.

### **1.3 Research Objective**

This study was conducted to investigate the applicability of different plasticizers, triacetin and triethyl citrate in Polyvinyl alcohol.

The objectives of this research are as listed:

- a) To determine the miscibility and efficiency of plasticizers by calculating solubility parameter and measuring  $T_g$  of the PVA compound.
- b) To examine the effect of different acetate contents in PVA on the properties of plasticised PVA.
- c) To study the effect of different compositions of plasticizer on tensile and thermal properties of PVA compound.

In order to achieve the objectives, in this research, the miscibility of the triacetin and triethyl citrate as a plasticizer in PVA with different types of PVA based on their values of acetate content was studied. There are two types of PVA with similar molecular weight but different acetate content which are PVA with 88% hydrolysed (partially hydrolysed) and the other one in PVA with 99% hydrolysed (fully hydrolysed) were investigated. One plasticizer was selected from the miscibility test to incorporate with these two types of PVA. Overall, for this section the ability of plasticizer to incorporate with different type of PVA in terms of their percentage of hydrolysed also is studied.

#### **1.4 Thesis outline**

This thesis contains five chapters, Chapter 1 includes the introduction of the research background which also provides the objective of this research. In chapter 1 also include the problem statements related to the research. Chapter 2 concludes the literature reviews and studies on natural-based plasticizer which nowadays popular in replacing the petrol-based plasticizer. Chapter 3 explains the materials and experimental works of this research. These include material used in this project, sample preparation and testing method involved in this study. Chapter 4 discussed the data interpretation.

The results were obtained from sample testing using DSC, SEM, XRD, and tensile test. In this project, the solubility parameter and Fox Equation also studies. Finally, in Chapter 5, it concludes the project and provides recommendations for improvement in future works.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Biodegradable Polymer

Polymeric materials had been used widely in worldwide. There are many applications nowadays are using polymeric material in order to replace heavy materials such as metal. In recent years there has been an increase in interest in biodegradable polymers. Researcher start to concern about biodegradable polymer which nowadays had been widely used over the world. Biodegradable polymeric materials are now one of the main plastic that grows drastically and some products that made from them are becoming available in the marketplace (Yu, 2009).

Biodegradation such as biotic degradation, is a chemical degradation of polymers, which involve the action of microorganisms to accelerate the degradation process such as bacteria, fungi and algae. Generally, biodegradable polymer is a polymer where the degradation mechanism happen through the action of microorganisms (Leja & Lewandowicz, 2010). In addition, biodegradation is considered a type of degradation involving biological activity. Biodegradation also is a fragmentation of the polymers into lower molecular mass species by abiotic reactions, i.e. oxidation, photodegradation or hydrolysis, or biotic reactions, i.e. degradations by microorganisms (Vroman & Tighzert, 2009).

Biodegradable polymers are classified into two groups: natural polymers which obtained from natural resources such as from biomass product (starch, animal and proteins) also synthetic polymers which produced from oil (poly caprolactones or aromatic co-polyester). The polymers which produced from feedstocks derived such as

petroleum resources (non-renewable resources) or from biological resources (renewable resources) (Vroman & Tighzert, 2009). Generally, biodegradable polymers are classified according to their chemical composition, origin and synthesis method, processing method, economic importance, and application (Shivam, 2016).

According to Phale, Agnihotri, and Khale (2014), there are several advantages of biodegradation polymers. In drug delivery application, biodegradable polymer found to be non-toxic substance and they are highly desirable in these situations because they degrade in the body to biologically inert and compatible molecules. They can be broken down into biologically acceptable molecules that are metabolized and removed from body via normal metabolic pathway.

Another advantage of biodegradable polymer is, biodegradable polymer more beneficial in environmental terms than their petrochemical counterparts. The compatibility with the environmental shows biodegradable polymers are consider to be environmentally attractive compare to non-biodegradable polymers (Bastioli & Limited, 2005). Due to its environmental friendly, biodegradable polymers are more desirable and a series of natural or synthetic materials has been used such as thermoplastic starch, gelatin, PLA, etc (Thakur & Thakur, 2015a).

Biodegradable polymers also provide some disadvantages that are in concern. Although biodegradable polymers seem widely used in medical application due to its compatibility and non-toxicity, these kinds of polymers do not enjoy large clinical uses. This concern is the toxicity of biodegradation by-products, since the toxicity of biomaterials are come from low molecular weight compounds that have leached from the biomaterials into the body of patients (Ikada & Tsuji, 2000). The by-products include monomers that remaining unpolymerized, additives and ethylene dioxide remaining unremoved.

There are many applications of biodegradable nowadays in industries. One of the application is, biodegradable polymers are used in food packaging and materials packaging. This can be seen in Germany, they start to endorse and encourage the widespread application of biodegradable packaging material. This can help in reducing the volume of inert materials disposed, scarcity of space (Shivam, 2016). BASF also started in working on further development of biodegradable plastics based upon polyester and starch. Example for this case is Eco-flex which it is a fully biodegradable plastic material that was introduced to consumers by BASF in 2001. This material is has better properties that suitable as a packaging such as resistant to water, grease, hygienic for disposable wrapping, decompose in normal composting systems.

Another application of biodegradable polymers is in medical devices. The biodegradable materials able to dissolve and be absorbed into human body. This is due to the non-toxicity of the materials that able to convert into non-harmful substance which are compatible with human body (Platt & Limited, 2006). Applications in medical devices are includes biodegradable plastic screws, devices for internal drug deposition, orthopaedic mouldings, drug carrier, cardiovascular and intestinal supports and in polymer tissues.

### **2.1.1 Polyvinyl Alcohol**

Polyvinyl alcohol (PVA) is considered as one of the most widely used biodegradable polymer in industries, which is essentially made from polyvinyl acetate through hydrolysis, is easily degradable by biological organisms (Razzak & Darwis, 2001). PVA is an artificial polymer that has been used during the first half of the 20<sup>th</sup> century worldwide (Gaaz et al., 2015). PVA is a common and well-known polymer that possesses salient features such as water solubility, ease-of-use, able to form film-



forming property, and most important features is its biodegradability (Tan, Ching, Poh, Abdullah, & Gan, 2015). PVA also found to be non-toxicity and harmless, hence they are widely used thermoplastic polymer that is benign to living tissues. In addition, since PVA is a biodegradable polymer, and its degradability is enhanced through hydrolysis because of the presence of hydroxyl groups on the carbon atoms (Gaaz et al., 2015).

PVA is an odourless and tasteless, translucent, white or cream coloured granular powder. The physical and chemical characteristics and its specific functional uses depend on the degree of polymerization and the degree of hydrolysis. The physical properties of commercial PVA are related to molecular weight of PVA itself, degree of hydrolysis, degree of chain branching, the amount of crosslinking between polymer chains and the type of concentration of additives added. Moreover, other characteristic such as stiffness, water solubility and strength can be controlled (Fornasiero & Graziani, 2006). In addition, PVA also can be classified into two classes namely: partially hydrolysed and fully hydrolysed (Saxena, 2004). As mentioned earlier about PVA that is hydrophilic behaviour, it also can be slightly soluble in ethanol, but insoluble in other organic solvents. Figure 2.1 shows the chemical structure of polyvinyl alcohol.

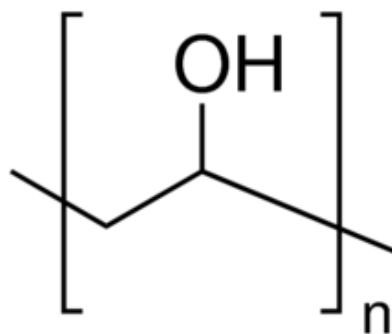


Figure 2.1: The chemical structure of Polyvinyl alcohol.

PVA has been applied in commercial, industrial, medical, also in food sectors and has been used to produce many end products. For medical devices product, PVA

hydrogels and membranes have been developed for biomedical application such as contact lenses, haemodialysis also for implantable medical materials to replace cartilage (Baker, Walsh, Schwartz, & Boyan, 2012). PVA also widely used in packaging industries since it is used as a moisture barrier film for food supplement tablets and for foods that contain inclusions or dry food with inclusions that need to be protected from moisture uptake (Saxena, 2004).

Among the most widely used biodegradation polymer in industries is PVA. PVA is a non-toxic macromolecule polymer with abundant of hydroxyl functional groups which can be obtained from the hydrolysis of polyvinyl acetate (Li J and Li Y, 2017). There are limitations of PVA during processing which are they are thermally unstable and cannot be process alone. PVA required high temperature to process, and PVA do not able to withstand high temperature due to degradation might take place. Hence, addition of plasticizer in PVA will able to reduce the melting point and glass transition temperature of the PVA. Hence, the addition of plasticizer in the PVA change the micro-molecular and macromolecular structure of PVA to improve its thermal stability.

As mentioned above, the chemical and physical properties of PVA may vary based on percentage of hydrolysis which determines the PVA grades and its molecular weights. PVA is partially crystalline upon formation and is characterized by properties such as chemical resistance, water solubility, and biodegradability. The molecular weight obtained for PVA may vary depending of the length/content of vinyl acetate polymer and the level of hydrolysis to eliminate acetate (Gaaz et al., 2015). As the PVA is characterized by its molecular weight (Mw) and hydrolysis degree (HD) with the carbon chain contains hydroxyl groups attached to the methane carbon, it will shows different properties such as in electrical conductivity and the dielectric relaxation (Hdidar,

Chouikhi, Fattoum, & Arous, 2017). For example, by studying the dielectric properties, it showed the enhancement of the PVA chain mobility following the increase of the hydrolysis degree.

Generally, PVA is a copolymer of Polyvinyl alcohol and Polyvinyl acetate (PVAc) due to PVA is produced by the polymerization of vinyl acetate to PVAc, followed by hydrolysis of PVAc to PVA. Commercial PVA grades are available with high degree of hydrolysis which usually above 98.5% (fully hydrolysed). The degree of hydrolysis or the amount of acetate content in the polymer affect its chemical properties, solubility and the crystallizability of PVA. The degrees of hydrolysis also affect the solubility of PVA in water. In general, PVA containing high degree of hydrolysis are more difficult to dissolve in water due to very extremely OH bond makes the H-bond are not stable hence leads to insolubility and incompatibility (Hassan & Peppas, 2000).

Generally, at 100% hydrolysis, all acetate groups have been converted to hydroxyl groups on the main polymer chain, resulting in high degrees of crystallinity. Advantageous of using this fully hydrolysed of PVA, it contributed to good mechanical and chemical properties but the solubility is decreases noticeably. Although the solubility of PVA is increased at partially hydrolysed (87%-88%), the mechanical and chemical properties are compromised. By having acetate group in PVA structure that are hydrophobic which they dislike water, they still tend to help PVA dissolve readily in water by detracts from structural regularity and decreases molecular. It also stabilized the hydrogen bonding formation with desired aqueous solubility due to partially acetate content in PVA inhibits the formation of hydrogen bonding and decrease inter and intra-molecular forces (LaPorte, 2017). Figure 2.2 shows the hydrophilic and hydrophobic part in PVA.

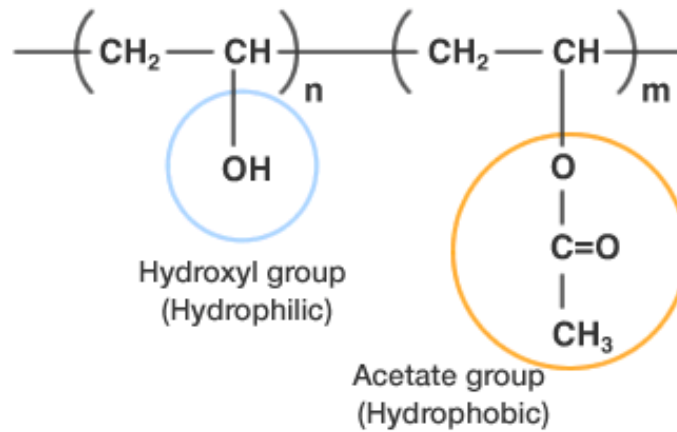


Figure 2.2: The hydrophilic and hydrophobic part in PVA

### 2.1.2 Polymerization/production of Polyvinyl Alcohol

Unlike most polymers, PVA is not prepared by polymerization of the vinyl monomer itself. The monomer of PVA does not exist in stable form hence it re-arranged to its tautomer, acetyl-dehyde. This is because, PVA cannot undergo polymerization from its own monomer, but through poly (vinyl acetate) (PVAc) due to the instability of vinyl monomer. Figure 2.4 shows hydrolysis reaction of PVAc to PVA. PVA is produced by the polymerization of vinyl acetate to PVAc, followed by hydrolysis of PVAc to PVA to produce partial or complete hydrolysis of polyvinyl acetate to remove acetate groups (Chang et al., 2003). Simple flow of production of PVA are shown if Figure 2.3.

Based on Figure 2.5, PVA can only be obtained through a saponification process from PVAc or alcoholysis by reacting PVAc with methanol (Tan et al., 2015). PVA can be hydrolysed from PVAc into two different grades, fully or partially hydrolysed based on their applications (O dian, 2004). The degree of hydrolysis indicates the number of residual acetate groups that are present in the polymer in which saponification or alcoholysis has not taken place. Apart from compatibility, crystallizability, the degree of

hydrolysis also will eventually affect the properties of PVA including its solubility (Ng, Ching, Awanis, Ishenny, & Rahman, 2014).

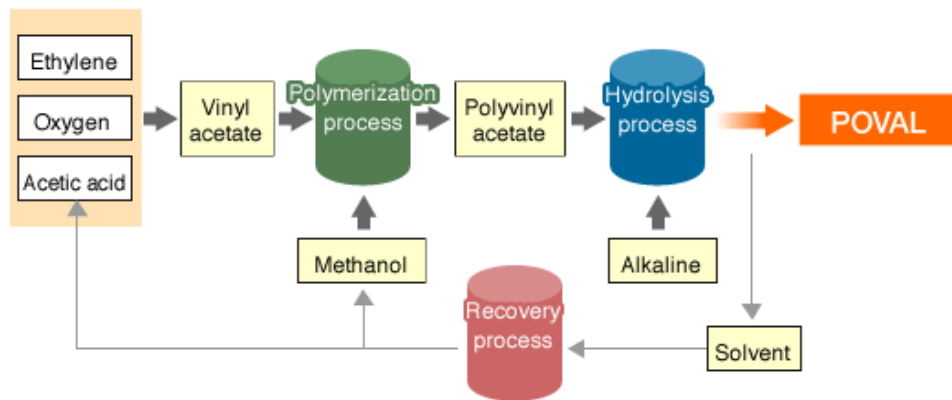


Figure 2.3: Production route of PVA

The hydrolysis of PVAc to PVA can be done by base catalysed alcoholysis or by the acid initiated hydrolysis of PVAc. This process controls the amount of hydroxyl groups (called the degree of hydrolysis). The solubility and membrane water resistance of PVA vary greatly depending on the degree of hydrolysis. In this process, the acidic traces of sodium acetate formed in the base catalysed alcoholysis affect the properties of PVA, primarily the stability. With the condition of methanol in the presence of sodium methoxide, the formation of PVA can be take place as follows:

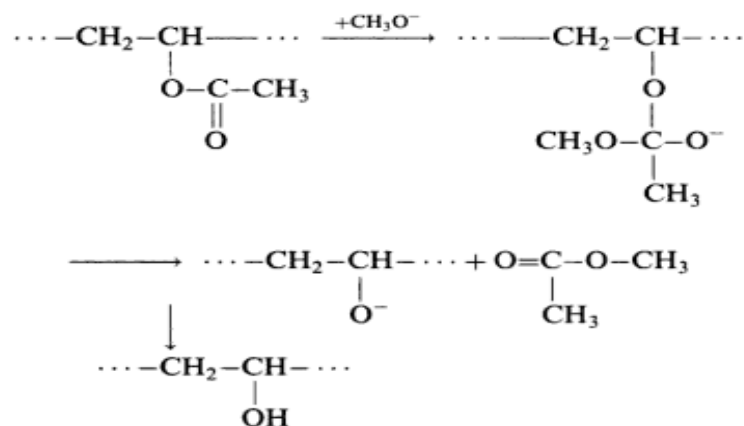


Figure 2.4: Hydrolysis reaction from PVAc to PVA

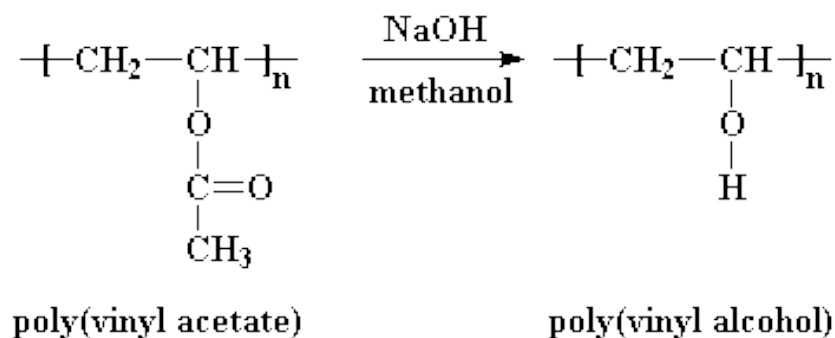


Figure 2.5: Alcoholysis process of PVAc to PVA

In terms of manufacturing facilities and production in industry, PVA is generally manufactured by hydrolysing the acetate group in PVAc with methanol in the presence of anhydrous sodium or aqueous sodium hydroxide at moderate temperatures and pressures. The end-product is PVA hydrolysed in excess. The definitions of fully, intermediate and partially hydrolysed PVA in terms of degree of hydrolysis vary within industry.

### 2.1.3 Advantages and Disadvantages of Polyvinyl Alcohol

PVA have been the target of a worldwide industries due to some advantages that PVA can contributed. Nowadays, PVA is widely used thermoplastic polymer that is benign to living tissues due to its properties which is harmless and non-toxic. The similarity in properties such as they are biodegradable polymer which can convert themselves into non-toxic substances in human body thus makes it suitable and compatible with human tissues (Gaaz et al., 2015). Biocompatible PVA has a structure that can absorb protein molecules and engage with minimal cell adhesion and has no toxic effects, therefore, PVA membranes have been widely developed for biomedical (J. M. Yang, Su, & Yang, 2004). Much research had been conducted on factors that can modify or optimize PVA properties, such as aqueous solubility, swelling, permeability, and drug release rate for these applications.

The versatility and excellent film-forming properties of PVA itself, e.g., biodegradability, good strength, and superior appearance, make it a highly suitable polymer for the application of tablet film coating (Koo et al., 2011). Because of its properties in which are they can produce high film strength, good adhesion and has thickening properties, PVA is commonly used in cosmetic preparation.

Polyvinyl alcohol which excellent in film forming, but it is rarely used account of various disadvantages. Usually the use of PVA containing preparations consist of PVA, plasticizers and talc. Disadvantages of these preparations are the slow dissolution during the preparation of the aqueous coating solution, the high viscosity, the low concentration spraying solution, the use of plasticizer and the slow dissolution rate of film coating. Although PVA has good mechanical properties during dry state, its high hydrophilicity limits its applications (Zhu, Wang, Xu, Gao, & Liu, 2013)

In addition, there are limitations of PVA during processing which are they are thermally unstable and cannot be process alone. PVA required high temperature to process, and PVA do not able to withstand high temperature due to degradation might take place (Magalhães, Toledo Filho, & Fairbairn, 2013). Thermal analysis has shown that the melting point of PVA fibers begins at approximately 200°C and thermal degradation initiates at about 239°C. Hence, addition of plasticizer in PVA is required to reduce the melting point and glass transition temperature of the PVA. The addition of plasticizer in the PVA changes the micro-molecular and macromolecular structure of PVA to improve its thermal stability (Jiang, Jiang, Zhang, Dai, & Zhang, 2012).

#### **2.1.4 Modification on Polyvinyl Alcohol**

PVA has many excellent properties and able to form excellent film properties with good adhesion behaviour. However, the PVA film has the weaknesses of low elongation at break, poor decomposition temperature and high glass transition temperature (Jia Pu-you, 2014). These drawbacks affect the applications of PVA widely. Many studies have been conducted to overcome these limitations. Strategies to modify PVA properties include addition of plasticizers, heat treatment, polymer blends, copolymers, and cross-linking (Koo et al., 2011).

Heat treatment can be done to PVA to modify its crystallinity and morphology. PVA can be heated to different temperature to observe the changing of its crystallinity and morphology which can be tested by using X-Ray Diffractometers (XRD) and Scanning Electron Microscope (SEM). According to (Wijanarko, Kusumaatmaja, Chotimah, Roto, & Triyana, 2016) it indicated that heat treatment on PVA resulted in changes in crystallinity. Heat treatment also contributed to the increasing level of stiffness of PVA (Wong, Zinke-Allmang, & Wan, 2010).

PVA also has the disadvantage of instability in the water. To overcome that problem, the polymers should be crosslinked (chemically or physically) to form the three-dimensional structure, consequently improve the stability and physical properties of PVA (Wijanarko et al., 2016). As mentioned earlier PVA is a biodegradable polymer which they are non-toxic and compatible with human tissue and applicable for medical devices applications. However, by improving its stability, they need to crosslink and researcher indicates that physical crosslinking to PVA does not cause toxicity issues because it does not require crosslinking agents.



Nowadays, polymer blending has been a most useful method for improving or modifying the physicochemical properties of polymer materials. Most important property for the polymer blend is the miscibility of its ingredients, as it affects the mechanical properties, the morphology, the permeability, and the degradation (Nishio & Manley, 1988). PVA also can be modified in order to improve its properties and resolve their limitations. For example, the introduction of PAN into PVA film. In this research, the blend is expected to adjust the physicochemical properties of PVA film (Zhu et al., 2013).

Another method to modify PVA is by incorporating plasticizer. Plasticizer normally incorporated into PVA to reduce processing temperature thus the PVA could be able to process at lower temperature. Good mechanical properties of the plasticized PVA can also be obtained as the PVA can be processed easily without degrade. One of the example of plasticizer can be used is glycerol, which the residual glycerol in the blends played a role of a plasticizer, which reduces the interactions among the macromolecules, which resulted in the decrease of the hardness as well as elastic modulus in PVA (Mohsin, Hossin, & Haik, 2011).

## **2.2 Plasticizer**

In industry, the processing of the material needs to be concern in order to produce quality product from quality material. Some of processing method and parameter are able to change the properties of materials during processing. In order to avoid that, modification of materials need to be done by adding non-toxic materials such as plasticizer to make the processing more ease.

Plasticizer is an important class of low molecular weight non-volatile compounds that is widely used in polymer industries as additives (Vieira et al., 2011). The primary role of plasticizers is to enhance the flexibility and the process-ability of polymers by decreasing the glass transition temperature ( $T_g$ ), thus improving workability and distensibility. They also reduce physical properties like hardness, elastic modulus, and increase fracture and impact resistance, (Johnson et al, 1991). The properties of the plasticized polymer such as degree of crystallinity, optical clarity, electrical conductivity, fire behaviour and resistance to biological degradation are also affected by the incorporation of plasticizer.

When incorporated into the polymer system, plasticizers can increase the free volume between the polymer chains which allows the chain segments to move and rotate more freely allowing for increased movement of polymer chains with respect to each other, thus decreasing the polymer glass transition temperature ( $T_g$ ) and melt viscosity (Lim & Hoag, 2013). In other words, plasticizer must diffuse into polymer structure and disrupt the intermolecular interaction of the polymer and creates free volume (Felton, 2016)

Currently, there are numerous type of plasticizer with a range of attributes that can be selected for specific applications to meet material requirements. The great variety of plasticizer and its numerous functions in order to lead the polymer material to meet product quality with specific requirements (Vieira et al., 2011). Several plasticizers that usually used in industry are, glycerol, diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), and dioctyl adipate. A wide range of plasticizers may be employed ranging from the inexpensive plasticizer such as DIDP to more expensive materials such as butyl benzyl phthalate (Ghosh, 2017). In addition, Phthalate acid ester found to be applications as plasticizer to PVC.

In industry, polyesters and PVC are the most frequently used plasticizer followed by polyvinylidene fluoride, polyurethanes, epoxy, acrylics and polyamides (Alger, 2017). Plasticizer used in polymers can be divided into two categories which are petroleum-based plasticizers and natural-based plasticizer (Bocqué, Voirin, Lapinte, Caillol, & Robin, 2016). Examples of petroleum-based plasticizers are glycerol and DIDP. Meanwhile, natural-based plasticizers such as triacetin. Due to some problem that relate to human health and environment, the usage of petroleum-based plasticizer should be minimized.

### **2.2.1 Common plasticizer in Polyvinyl Alcohol**

Many studies have been done to study the properties of PVA plasticized by various types of plasticizers. One of the plasticizers commonly incorporated in PVA is glycerol. According to Mohsin et al. (2011), he studied the thermo-mechanical behaviour of membranes based on blending of PVA with different weight percentages (wt %) of glycerol. In this research, he was found that the thermal properties particularly the melting point for PVA blends exhibit a reduced value proportional to the glycerol content. The hardness and elastic modulus were also found to decrease with an increase in plasticizer content.

Meanwhile, Pu-You et al. (2014) studied the properties of plasticized (PVA) films were prepared by the casting method using glycerine as the plasticizer. They reported that the plasticizer can effectively destroyed the hydrogen bonding between PVA molecules and the glass transition temperature of decreased with the addition of Glycerine. Based on their experimental work, it was found that the  $T_g$  of modified PVA is lower than pure PVA, it also has high elongation at break and high solubility compare to PVA itself.

Plasticizer has the main role in this case, which it able to destroy the hydrogen bond between PVA molecules and decrease the crystallinity and melting point of PVA (REN et al., 2012). They suggested that Glycerine could interact with PVA molecules and replace the hydrogen bonding within PVA molecules. This will cause the interruption of crystallization of PVA and hydrogen bond between molecules. Glycerine also able to modify the thermal stability of PVA and lowered the glass

### **2.3 Natural-based Plasticizer**

During the last decade, the worldwide production of plasticizers was around 5 million tons per year (Vieira et al., 2011). Early in 1912, the usage of triphenyl phosphate as a plasticizer was increased as the plastic industry grows. Phthalic acid esters were found application as plasticizers around 1920 and become the largest and popular class of plasticizer that most industries used (Bocqué et al., 2016). The great variety choice of plastic products and its wide applications have led to the development of new and improved plasticizers in order to meet product quality and specification requirements.

As the plastic industries continuously grow, the demand for plasticizer is also increased. Various types of plasticizers were introduced and can be selected for specific applications to meet product requirement. However, researchers start to concern, regarding the usage of phthalates and their effects on human health and the environment due to toxic problem (E. Grossman, 2009). Since then, manufacturer started to replace phthalate with another plasticizer to prevent problem that related to health.

Nowadays, there is increasing interest in the use of natural-based plasticizers that are low toxicity, migration, and do not lead to environmental problems (Samarth & Mahanwar, 2015). This group includes epoxidized triglyceride vegetable oils from soybean oil, linseed oil, castor-oil. For biopolymers, it is preferable to use biodegradable and natural-based plasticizers for example triacetin or triethyl citrate. Natural-based plasticizers which are made from renewable and biodegradable resources has the potential to reduce cost since these renewable materials can be obtained abundantly. Even though various applications that use synthetic plasticizer as an additive but in some applications, natural-based plasticizer can contribute to enhance the polymeric materials properties. In addition, many researchers are interested in studying biopolymers such as PVA and PLA which nowadays have been widely used over the world. The successful application of these natural based plasticizers in biopolymers would be a great benefit.

Natural-based plasticizers which can obtain abundantly could be able to replace synthetic plasticizers which required high cost to blend it with polymeric materials. Since the use of synthetic plasticizers which could give impact on human health and the environment hence this is one of the alternative way to avoid those cases (Cadogan, 1991). Furthermore, natural-based plasticizers are renewable resources that offer large platform to design bio-based plasticizer. Even though it is impossible to completely replaced synthetic plasticizer, but in some applications natural-based plasticizer would be able to contribute to enhance mechanical properties in some biodegradable polymers (Vieira et al., 2011)

### **2.3.1 Triacetin**

Triacetin (C<sub>9</sub>H<sub>14</sub>O<sub>6</sub>), is also known as glyceryl triacetate. Triacetin is a clear, colourless acetate ester which widely used in pharmaceutical excipient used in

manufacturing of capsule and tablets, it is also used as a plasticizer and solvent. The physical appearance of triacetin is a transparent liquid and the texture is a bit oily. Furthermore, triacetin also being used in the perfume and cosmetic industries (Kibbe & Association, 2000). Figure 2.6 shows the chemical structure of Triacetin.

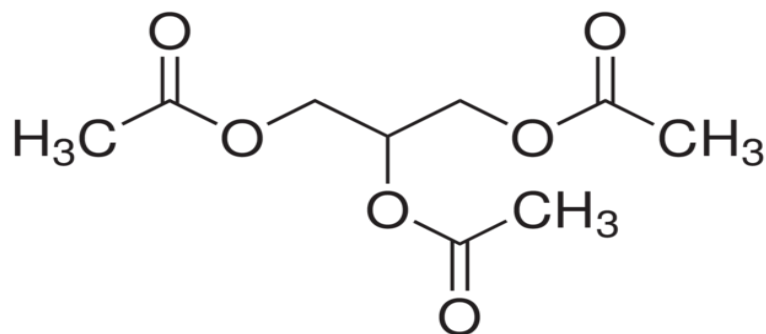


Figure 2.6: Chemical Structure of triacetin (or glyceryl triacetate)

Triacetin is one of the biocompatible plasticizer as an application to biomaterials (Niaounakis, 2014). Biocompatible plasticizers include triethyl citrate, tri-n-butyl citrate, acetyl triethyl citrate and triacetin. Triacetin also listed in the FDA Generally regarded As Safe (GRAS) list. Triacetin has been found to be non-toxic in long-term feeding tests in animals. Furthermore, according to the toxicology report from 2002, Triacetin and a group of related triglycerides does not represent a hazard to human health and environmental.

Triacetin is a complex reaction between glycerol and acetic acid as a reactant over acid catalyst following the mechanism in the Figure 2.7.