CHARACTERIZATION STUDIES OF THERMOPLASTIC STARCH ENHANCED WITH [EMIM][OAC]

By

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15059

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CERTIFICATION OF APPROVAL

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Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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NOR HAZWANI BINTI MA’AMOR

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ABSTRACT

This study investigates the effect of using ionic liquid 1-ethyl-3-methylimidazolium acetate [Emim][OAc] as plasticizer for the improvement of thermoplastic starch (TPS) material. The physical and chemical properties of the TPS were studied and investigated in this project. The results of morphology analysis with scanning electron microscope (SEM), crystallography analysis by x-ray diffraction (XRD) and thermal degradation by thermogravimetric analysis (TGA) show that 70% of total plasticizer content mixed well during thermo plasticization process. [Emim][OAc] caused starch granule to disrupt as shown by SEM due to its ability to access the passages within the starch structure. By XRD analysis, it was shown that plasticized starch at 70% total plasticizer content and 1:4 [Emim][OAc]/water ratio, made disruption to the A-type crystalline structure, generated V_H-type crystalline structure and thus increased the mobility of the amorphous starch. The presence of [Emim][OAc] promote the thermal degradation of starch molecules as described by TGA as it slows the thermal decomposition rate of the starch. Therefore, plasticizer content and [Emim][OAc]/water ratio were parameters that also influencing the properties of starch-based polymer. The use of ionic liquid as an enhancement for starch as fertilizer coating material fertilizer is anticipated to reduce volatilization of ammonia into environment and increase its utilization by crops.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Most of the nitrogen (N), phosphorus (P) and potassium (K) in livestock intakes is excreted in dung and urine, which can be fertilizers contain valuable amounts of these plant available nutrients, as well as other major nutrients sulphur (S), magnesium (Mg) and trace elements. Agriculture industry needs fertilizers as its most important material. They are added to the soil so that the soil releases its nutrients which are required for good plant growth. In order to maximize efficiency, it is compulsory to get the most value from all nutrient inputs. Choosing the right source of nutrient in a particular cropping nature involves a consideration of economic, environmental, and social objectives [1].

Nevertheless, there are potential hazards and loss of using the fertilizers to the surroundings which lead to inflexibility in the limitation of its application. While livestock operations are the largest contributor to NH_3 emissions in North America, losses from N fertilizer also contribute significantly to total emissions [1]. Where significant NH_3 loss occurs following fertilization, it is possible that the crops may be under-fertilized due to this unintentional N loss.

Besides, the usage of conventional fertilizers may lead to exceeded concentration for the desired effective action [2]. A high level of concentration can lead to disagreeable side effects either in the target area, which would cause crop damage, or in the surrounding environment. Regulatory agencies are becoming more alertness on the role of N gases in the atmosphere and their possibly undesirable consequences.

Starch has a unique characteristic naturally that can be developed into biopolymer. This is a huge advantage to find the alternative of petroleum-based polymer which is depleting already and not renewable source. The idea of applying biopolymer in agricultural is important as it is biodegradable and at the same time enable the nutrients to be consumed by crops efficiently.

Starch needs plasticizer to be effective in its function as coating material for fertilizer, The favourable attributes of a plasticiser for starch are [9][15] :

a) being stable (non-volatile) both during thermal processing and in the post-processing stages
b) having little effect on starch macromolecular degradation
c) being safe to humans and environmentally friendly, and
d) being advantageous for reducing the inherent hydrophilicity of starch and for long-term stability.

Most ionic liquids (ILs), especially imidazolium-based ILs have the ability to dissolve polysaccharides such as starch [16]. Moreover, ionic liquid seem to be the most excellent plasticizer to be combined with starch to become tapioca thermoplastic starch (TTPS) because they can be customized depending on the specialized task demanded. As for the year of this project, studies by Bernot (2005) and Xie (2014) agree that the least toxic anion for imidazolium-based ionic liquid is acetate, [OAc].

1.2 Problem Statement

Starch without plasticizer is an inefficient coating material due to its high degradability. The plasticizer used for starch enhancement such as glycerol is widely used but it damages the mechanical properties of the TPS as it contributes to formation of too soft material. This is because of the hydroxyl groups contained in glycerol which it becomes water and absorbs water more easily. Thus, imidazolium-based ionic liquid, 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]) may be the solution to replace current plasticizers in TPS usage.

1.3 Objective

The objectives of this project are:

- To investigate the physical effect of TPS with different total plasticizer and [Emim][OAc] ratio.
- To study the mechanical and chemical characteristics of TPS prepared with [Emim][OAc] as plasticizer.
- To determine the optimum total plasticizer content and [Emim][OAc] ratio for fertilizer coating.

1.4 Scope of Study

The scope of study of this project includes:

1) Appreciative to the importance of managing the release of ammonia and nitrogen to the surrounding.
2) Understanding the reaction of different amount plasticizer ratio with starch during mixing.
3) Understanding the mechanical and chemical properties of the TPS produced.

CHAPTER 2

LITERATURE REVIEW

2.1 Nitrogen-based Fertilizers in Agriculture

The use of fertilizer has been the forefront in the struggle to increase world food production. Over the past two-and-a-half decades, the cumulative consumption of fertilizers has increased substantially. Malaysian fertilizer consumption has steadily increased with time [3] . All fertilizers that have ammonium (NH_4^+) are theoretically subjected to volatile loss. Even the properties of the fertilizer and its reactions once contacting the soil vary the result in N loss, the possibility for NH_3 volatilization is mainly governed by the alkalinity (pH) level of the zone surrounding the fertilizer particles and droplets[1]. Urea fertilizer reacts chemically with water in the soil, it undergoes hydrolysis and the urease enzyme when applied to the soil to produce ammonium carbonate; an unstable compound that can quickly decompose to release NH_3 gas.

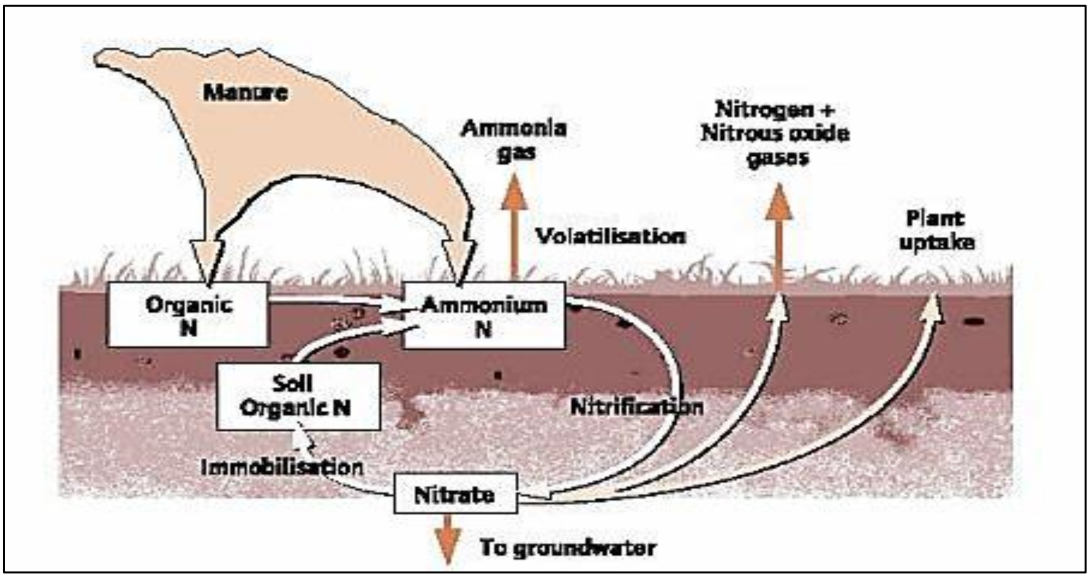

Figure 1: Nitrogen Cycle - main transformation and losses

Photo sourced from *http://adlib.everysite.co.uk/adlib/defra/content.aspx?id=000IL3890W.17USXXJ0YN2C5*

Urea undergoes these reactions whenever applied to soil.

Hydrolysis Reaction of Urea:

$$(NH_2)_2CO + 2H_2O \rightarrow (NH_4)_2CO_3$$

$$(NH_4)_2CO_3 + 2H^+ \rightarrow 2NH_4^+ + CO_2 + H_2O$$

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

Fertilizers are most frequently broadcast on the soil surface, applied as a surface band, or applied as a subsurface band, forming urea-containing fertilizer on the soil surface itself and thus increases the threat of NH_3 volatilization in the days following application [2].

A number of compounds have been experimented to investigate an effective way to block or slowing the urea hydrolysis. The product most commonly used is N-(n-Butyl)-thiophosphoric triamide (NBPT) retailed under the commercial name of Agrotain. This product is combined with urea to delay the urease enzyme for a period of several days to two weeks depending on the application rate.

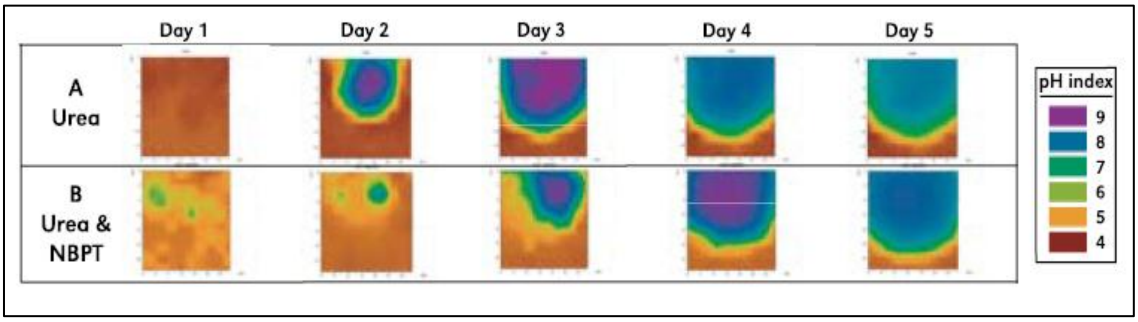

Figure 2: The Effect of (A) Urea alone or (B) Urea with NBPT urease inhibitor

Data obtained from *Agrotain International*.

The figure shows the effect of untreated urea and urea with NBPT urease inhibitor on soil pH over four (4) days of application. The soil pH increased from 4.6 to over 9 surrounding the granule within one (1) day following fertilization with untreated urea. Each image is approximately 1 in. (27 mm) square of soil [4]. Urea can be reacted with a variety of strong acids to sustain a low pH in the vicinity of the fertilizer granule or solution. Lower pH will delay the release of ammonia to the air.

2.2 Ammonia Release

The Occupational Safety and Health Administration (OSHA) have set maximum ammonia atmospheric concentration exposure limits at 50 ppm for humans [5] . High percentages of the environmental issues that have risen from intensive crops production are the effect of the excretion and volatilization of nitrogen. Urea has been widely used in Malaysian agriculture. However, ammonia (NH_3) volatilization and is a major problem encountered when urea fertilizers were used. High pH, AI and Fe oxides content and low cation exchange capacity (CEC) have been identified as causing these problems in soil [3]. The ammonia release to the air which contains oxygen gas, O_2 leads to formation of nitrous oxide, N_2O.

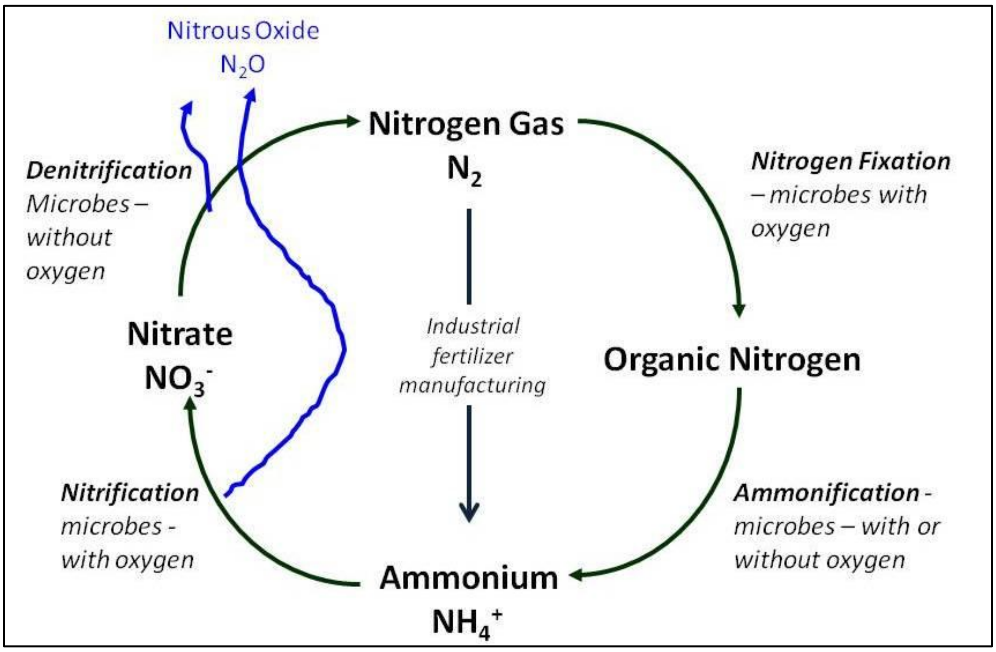

Figure 3: Simplified Cycle - Where Nitrous Oxide Emission Occurs

All of the nitrogen fixed from the atmosphere either through fertilizer manufacture, N fixation by legumes, or nitrate production by lighting enters the nitrogen cycle is returned to the atmosphere via a process called denitrification [6] . There is significant nitrogen cycling within this simplified cycle, especially between organic nitrogen, ammonium and nitrate. As we can see from Figure 3, nitrous oxide emission occurs during internal cycling as well, during the transformation from ammonium to nitrate. This process is called nitrification.

Nitrous oxide emission occurs during nitrification, which is the conversion of ammonium to nitrate, a microbially mediated process in the presence of oxygen in soil amended with manure or fertilizer, in soil following deposition of ammonia, or in surface waters contaminated with ammonium. Nitrous oxide emission also occurs during denitrification – the conversion of nitrate back to atmospheric N_2, a microbially mediated process in the absence of oxygen in soil or manure, following manure or fertilizer application to the field, or in surface or groundwater contaminated with nitrate.[7]

It is identified nitrous oxide as the most significant greenhouse gas emitted from agriculture (40-50% of greenhouse gas emission), and recommended implementing mandatory nutrient management planning as being the strategy that has the greatest potential for mitigation [8].

“Over the past 100,000 years, concentrations of nitrous oxide in the atmosphere have rarely exceeded 280 ppb. Levels have risen since the 1920s, however, reaching a new high of 324 ppb in 2011. This increase is primarily due to agriculture.” (US EPA 2012)

Nitrous oxide has the radiative forcing 296 times that of carbon dioxide, which means that it doesn't take much of this gas to have a big effect on greenhouse gas contributions. Crutzen (1970) was one of the first scientists to link nitrous oxide with ozone depletion. He also connected it with fertilizer use.

2.3 Starch as Natural Polymer

In the urge to apply fertilizers more efficiently, bioplastic has been studied to be coating material for the starch in order to control the rate of release of ammonia to the atmosphere. Starch, a polysaccharide of granular structure, is one of the most attractive feedstock for the development of biodegradable polymers because it is relatively inexpensive, abundant and renewable. Starch plays an important role both in the development of the commercialized bio-based plastics and in the bioethanol industry. The role of starch in the development of bio based plastics could be in the development of:

a) thermoplastic starch (TPS) plastics where TPS is obtained through direct modification of starch,
b) poly(lactic acid) where its feedstock (lactic acid) is originated from starch derived sugars fermentation [9].

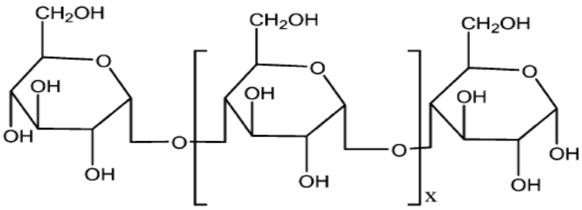

Figure 4 (a) : Amylose

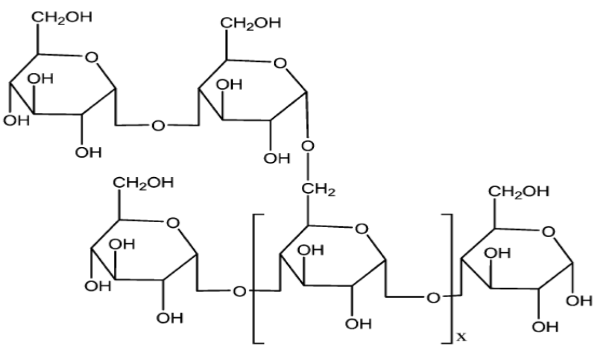

Figure 4 (b) : Amylopectin

Figure 4: Structures of Starch

Starch is composed of two homopolymers of -glucose: the linear (1,4)-linked α-D-glucan amylose, typically constituting about 30% of starch depending on the source of starch, and a highly branched (1,6)-linked α-D-glucan amylopectin (Figure 4)[10]. Commonly, amylopectin takes part in the formation of a crystalline structure and amylose does not. Pure starch is brittle and difficult to process into articles due to its relatively high glass transition and melting temperatures. The glass transition temperature, T_g of virgin dried starch is estimated to be approximately 240°C, which is above the starting point of its thermal degradation (about 220°C) [9] . High T_g and brittleness of starch are mainly caused by the presence of strong inter- and intra-molecular hydrogen bonds between the starch macromolecules. Furthermore, TPS polymers based solely on starch are extremely water sensitive and can suffer from significant molecular weight change during processing [11]. These drawbacks limit the possible shapes that can be imparted to the materials into films with adequate mechanical properties and thus of limited practical value. Therefore, starch must be modified to breakdown the crystalline granules, decrease the T_g and melting temperature (T_m).

2.4 Advantage of Plasticized Thermoplastic-Starch (TPS)

Concerning the environmental issues and shortage of oil, the use of starch has been through considerable development in non-food applications since the past few decades as the substitution of petroleum-based plastic. Polymers from renewable resources have been brought into a great attention due to their convenience, renewability, biocompatibility, and biodegradability.[12] Among this group of polymers, starch can be treated with conventional processing techniques. Conservative polymer processing techniques that often used such as extrusion, can convert raw starch into a homogeneous molten state thermoplastic starch (TPS) with the presence of low content of plasticisers such as water and glycerol.[10] The TPS batch master can be formed into various products such as sheets or films, foams and other specific shapes by ways of extrusion, injection or compression moulding, and so on.

Starch is a versatile biopolymer obtained from renewable plant resources such as maize, wheat, potato and tapioca harvests. The utilization of natural renewable polymers, such as starch and proteins, in the production of biodegradable plastics is a promising topic for research and industrial development. Starch is one of the most studied natural polymers for plastic application, owing to its availability, biodegradability, and low cost. The method of minimizing nutrient losses involves the use of slow-release fertilizers (SRF). These fertilizers can be physically prepared from the granules of the soluble fertilizers by coating them with starch, which reduce their dissolution rate.

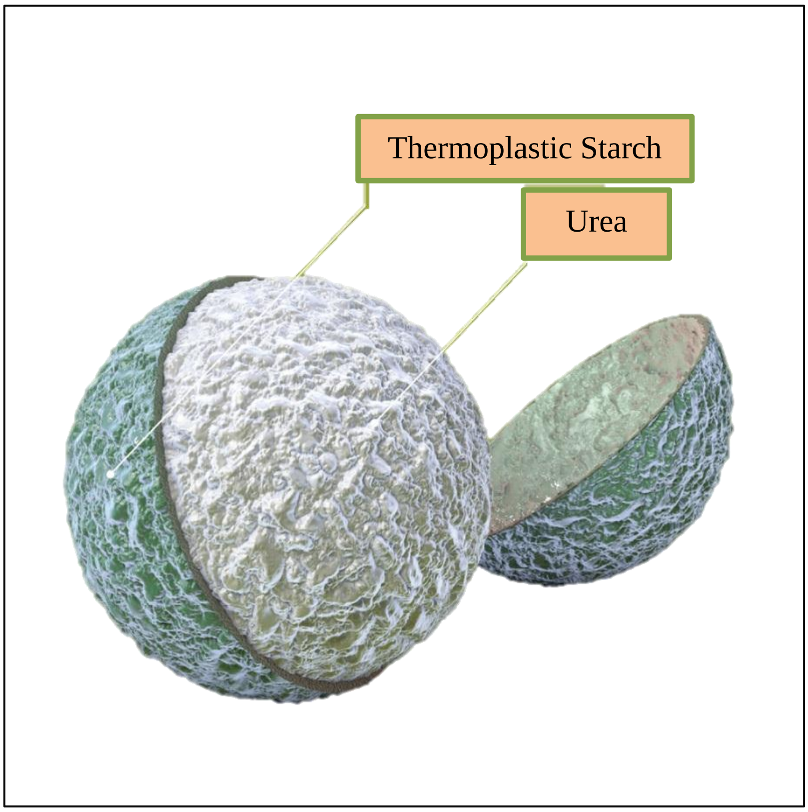

Figure 5: Thermoplastic Starch as the ammonia release stabilizer

Starch exists in a granular form in its natural state, but when subjected to shear forces at a temperature in the range 90-180 °C, in the presence of a plasticizer such as glycerol, starch loses much of its original granular structure and is transformed into a molten plastic state named thermoplastic starch, the TPS [13]. Moreover, starch naturally has unique characteristics. When on the plants, it exists in the form of granules (<1–100μm); the granule is composed of alternating amorphous and semi-crystalline shells or growth rings (100–400 nm); and the semi-crystalline shell is stacked by crystalline and amorphous lamellae (periodicity, 9–10 nm); while starch consists of two major bio-macromolecules called amylose and amylopectin.[12]

Unfortunately, starch itself has two main disadvantages in comparison with most plastics currently in use, namely that it absorbs moisture and exhibits poor mechanical properties [14]. Several approaches have been tailed to overcome these drawbacks, such as reinforcement with fibres and inorganic materials and with both degradable and non-degradable polymers.

2.5 Plasticizers for Thermoplastic Starch

During the thermoplastic processing of starch, typically between 70 and 90°C in the presence of a plasticizer, a semicrystalline granule of starch is transformed into a homogeneous material with hydrogen bond cleavage between starch molecules [15]. This process, called gelatinization, leads to loss of crystallinity and is associated with the loss of double helices as well as with the loss of lamellar and long range crystalline structure.

Plasticizers penetrate starch granules and destroy the inner hydrogen bonds of starch, and eliminate starch–starch interactions because they are replaced by starch–plasticizer interactions. The plasticized mouldable thermoplastic material, called TPS, is fit for injection moulding, extrusion or blow moulding similar to other synthetic thermoplastic polymers.

There are several substances used as plasticizers for the preparation of thermoplastic starch. Some of the most studied and reported TPS plasticizers in the literature include polyols such as glycerol, glycol, sorbitol, xylitol, maltitol, ethylene glycol, propylene glycol, butanediol, sucrose, fructose, mannose, fatty acids (such as myristate or palmitate), etc. [2]. However, the use of water alone as a plasticizer is not preferable because the resulting product will be brittle when equilibrated with ambient humidity and due to volatilization of water [9]. Mechanical properties can be affected by various factors such as the plasticiser type and content, granule remains in the matrix, the crystalline structure and crystallinity, and the extent of plasticisation of the amorphous parts.

Glycerol, a classical plasticizer of starch, is perhaps the most widely studied and used polyol plasticizer of TPS. This is because of its low cost, nontoxicity (for food and biomedical application) and high boiling point (292°C). Moreover, the hydrolysis and/or transesterification of lipids (triglycerides) into fatty acids for the biodiesel industry produce glycerol as a byproduct. Utilizing such by-products provides glycerol with an additional market driver in addition to the opportunity of improving the economics of both the biodiesel and the bioplastic industries. Nonetheless, glycerol is known to leach out during aging and humidity exposure, a major limitation for large scale applications.

However, the use of glycerol as plasticizer makes the material become too soft there was no work hardening to stabilise drawing; this could also be ascribed to possible phase separation when the plasticiser content was too high. A comparison study between glycerol and an ionic liquid by Xie (2014) proves that the use of glycerol as the plasticiser gave a weaker glass transition peak and the peak temperature was higher [12] . This phenomenon shows that the use of glycerol resulted in more crystallinity as well as less amorphous structure which was less mobile.

2.6 Ionic Liquids for ‘Green Earth’

Presently used in industry are room-temperature ionic liquid (ILs) which is considered to be green chemicals that may substitute volatile organic solvents [16]. A salt in liquid state with melting point lower than some subjective temperature such as 100℃ is called an ionic liquid (IL). While common liquids such as water and gasoline are chiefly made of electrically neutral molecules, ions and short-lived ion pairs are largely contained in ionic liquids. The ionic bond is generally stronger than the Van der Waals forces between the molecules of standard liquids. For that reason, common salts tend to melt at higher temperatures than other solid molecules. Some salts are liquid at or below room temperature [17]. Ionic liquids have many applications, such as great solvents and electrically conducting fluids which are known as electrolytes. With the low vapour pressure, ionic liquids have almost no harm towards the environment.

Imidazolium-based ionic liquids contain imidazolium cation and a diversity of anion species, depending on the purpose of process or the type of solute. In a research studying acute toxicity of ionic liquids by Bernot and his team in University of Notre Dame, they concluded that imidazolium-based ionic liquids are less toxic than other mutual chemicals such as ammonia and chlorine.

Table 1 : Acute Toxicity (48-h LC50) to Daphnia magna for ionic liquids and common chemicals used in manufacturing and disinfection [16]

Chemical Name	Acute Toxicity (mg/L)
Chlorine	0.12 – 0.15
Ammonia	2.90 – 6.93
Imidazolium ionic liquids	8.03 – 19.91
Phenol	10.00 – 17.00

Moreover, the anion species mixed with the imidazolium-based ionic liquid does not manipulate the toxicity of it [16].

2.7 Ionic Liquid as TPS Plasticizer

From simple grains to wood, many vegetal structures implicate the combinations of diverse biopolymers. Inside which starch granules are embedded in a continuous protein rich minor phase, the interfacial adhesion between starch (hydrophilic) and proteins (mostly hydrophobic) phases are strong enough to ensure cohesive breaking of the material: when a grain is cracked, most cracks spread through the starch granules, not at the interface between starch and proteins[15]. There is lack of understanding on the nature of the interfacial interactions between the hydrophobic and hydrophilic polymer phases.

Ionic liquids (ILs) are known as “green solvents”. They have been broadly studied for their ability to dissolve cellulose. Starch treated with a small amount of ILs can achieve a big deformation under low pressure. Plasticized starch also exhibit increased hydrophilicity due to the high polarity of the ILs [18]. The 3D structure of inherent starch may be disrupted with a plasticiser and raised temperature, a process known as “gelatinisation” or “melting”. If suitable conditions are reached, these results in a homogeneousamorphous material known as “thermoplastic starch” or “plasticised starch”, which is the essential principle in starch processing. Based on study conducted by Xie, et.al (2014), ionic liquid seems to give the best impact to the disruption of starch crystallization compared to glycerol [12] .

Many ILs have the ability to dissolve polysaccharides such as starch, especially the imidazolium-based ILs. However, mostly used ILs that contains Cl^- ions can be corrosive due to the high possibility for formation of HCl and lead to macromolecular degradation of starch [16]. Therefore, 1-ethyl-3-methylimidazolium [Emim][OAc] which has very low vapour pressure, high thermal stability and relatively low viscosity at room temperature which allow it to be used with starch in a wide range of processing conditions [12].

CHAPTER 3

METHODOLOGY

This project will study on the potential of ionic liquid as plasticizer of starch to form thermoplastic starch (TPS) to delay the release of ammonia to surrounding which causes unhealthy environment and not economic to agriculture. Firstly, the starch needs to be prepared by extracting tapioca. Ionic liquid used as plasticizer is 1-ethyl-3-methylimidazolium acetate [Emim][OAc]. For this project, [Emim][OAc] will be obtained from Centre of Ionic Liquids Centre of Universiti Teknologi PETRONAS (UTP).

3.1 Methods of Experiment

The experimental program consisted of three (3) parts:

1) Extraction of tapioca starch.
2) Preparation of tapioca thermoplastic starch (TTPS).
3) Characterization of chemical and physical properties of the thermoplastic starch by using Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) and Thermo gravimetric Analysis (TGA).

3.1.1 Extraction of Tapioca Starch

The fresh root is grown under an equal environmental condition and is harvested. Fresh root will be cleaned to remove sand, impurities, and peel. Then, fresh root will be cut and crushed into small pieces. The crushed tapiocas are then blended with water. Next, by using a filter cloth, the blended tapioca is squeezed for its juice into a big basin. The juice was left for 40 hours for the tapioca to be fully settles to the bottom of the liquid juice. After the sedimentation is completed, the extract of tapioca starch can be obtained. Next, the extract is dried in an oven for 24 hours at 55°C to reduce the moisture content to approximately 10% (dry basis).

Figure 6 : Pure tapioca starch extracted from 5 kilograms of tapioca

Figure 7: Tapioca starch after 24 hours of drying at 55°C

In the tapioca starch extraction, starch slurry from coarse unit consisting starch granule, tapioca pulp and water. Tapioca pulp or fibre acts as a fibrous network holding the starch granules together. The main compositions of tapioca pulp are cellulose, hemi-cellulose, and lignin. The starch granule is divided into free starch and bound starch. The bound starch granule remains in the fibre or pulp complex and is difficult to extract, while the free starch granule is not bound inside the pulp complex structure [19].

3.1.2 Preparation of Tapioca Thermoplastic Starch (TTPS)

Starch was well blended with specific amounts of water & [Emim][OAc] (sourced from UTP Ionic Liquid Centre) to achieve different total [Emim][Oac] plasticizer loading with varying plasticizer/water ratio [10]. Different weightage of dry starch will be tested with vary ratio of plasticizer and water ratio.

a) 50%, 70% and 90% based on dry starch
b) Ion/water ratio of 1:8, 1:6, 1:4, 2:3, 3:2 and 2:1.

Firstly,[Emim][OAc] and water were mixed for 5 minutes and mixed with starch powder according to the ratio planned for this study to find the optimum use of plasticizer. The detail on the calculated ratio is shown in ***Appendix A***.

The mixture is heated at specific temperature (50°C) under continuous stirring for about forty (40) minutes until the mixture gelatinized.

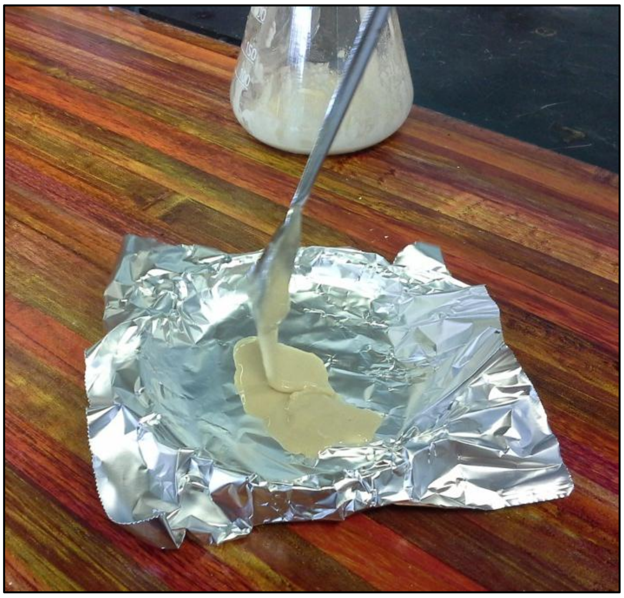

Figure 8: Homogenized Mixture of Thermoplastic Starch

3.1.3 Characterization Studies on Chemical and Physical Properties of TPS

a) The starch samples were put on circular metal stubs previously covered with double-sided adhesive under vacuum. The morphology of starch samples with coating will be examined using a scanning electron microscope (SEM) [12].

b) X-ray diffractometer (XRD) equipped with a graphite monochromator, a copper target, and a scintillation counter detector. The XRD patterns will be recorded and the crystallinity will be calculated [12].

$$X_c = \frac{\Sigma^{n}{}_{i=1} A_{ci}}{A_t}$$

where A_{ci} is the area under each crystalline peak with index i, and A_t is the total area (both amorphous background and crystalline peak) under diffractogram.

c) The TPS prepared will undergo thermo-gravimetric analysis (TGA) for the purpose of investigating its durability. Thermo gravimetric analyser will be used with 40 μL aluminium crucibles. A sample mass of about 5 mg will be used for each run. The samples need to be heated from 25°C to550°C at 10°C/min under nitrogen environment. The mass loss and decomposition based on temperatures will be recorded.

3.4 Project Timeline

Table 2 : Timeline of Research Studies for FYP II

Project Activities	**Week No**														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Extraction of Tapioca Starch	🟧	🟧													
Preparation of Thermoplastic Starch (TPS) samples with [Emim][OAc]			🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧					
Test analysis on the chemical & mechanical properties of the TPS samples • Scanning Electron Microscope (SEM) • X-ray Diffraction (XRD) • Thermogravimetric Analysis (TGA)					🟧	🟧	🟧	🟧	🟧	🟧					
Submission of Progress Report								🟪							
Pre-EDX											🟪				
Submission of Report Draft												🟪			
Submission of Soft-bound Report													🟪		
Submission of Technical Paper													🟪		
Oral Presentation (Viva)														🟪	
Submission of Hard-bound Report															🟪

CHAPTER 4

RESULTS & DISCUSSION

While preparing the samples for this study, four (4) ratios were initially planned for each total plasticizer content in order to identify the most effective and safe total plasticizer for the thermoplastic starch as shown in ***Appendix A***.

However, while preparing for the third ionic liquid and water ratio which is 3:2, the plasticizer could not mix well with the starch and formed into a very heterogeneous. This is due the high viscosity of ionic liquid [Emim][OAc]. Hence, the student decided that the ratio with higher ionic liquid content (third and fourth ratio label) should not be continued.

Figure 9: Sample 503, a sample with higher ionic liquid content which became hard and stick to the glass container

Nevertheless, with Supervisor’s advice, the student has added two (2) new ratio labels for the experiment that is 1:6 and 1:8 (***Appendix A***), which are with much smaller content of ionic liquid than water. Furthermore, the smaller content of ionic liquid can contribute to less toxicity while might improve the thermoplastic starch’s function in coating.

Meanwhile for the total plasticizer content of 90% based on dry starch, the plasticization process which involves mixing with stirring for 45 minutes at 50°C did not homogenized well. Non-homogenous mixture of starch and plasticizer leads to incomplete plasticization on the starch structure. This was shown when the dried TPS formed yellowish brown and think sticky lining as shown in figure below.

Figure 10: Non-homogenized Mixture of Starch & Plasticizer After 24hours of Drying at 55°C

These observations were not stated in any literature reviews done by the student. Thus the sample preparation for samples with 90% total plasticizer content was not proceeded to minimize the amount of [Emim][OAc] used as plasticizer for more environmental friendly coating material.

4.1 Morphology Behaviour

In order to understand the morphology of the samples after processing, the samples were analyzed with scanning electron microscope (SEM). An accelerating voltage of 10 kV and spot size 30μm were used. Different kinds of morphology are shown by different samples. Based on the previous study, from the normal surface images, a higher amount of plasticizer could result in a more apparent granular morphology [20]. As have been mentioned in the methodology earlier, the plasticizer content is manipulated based on the percentage content and [Emim][OAc]/water ratio.

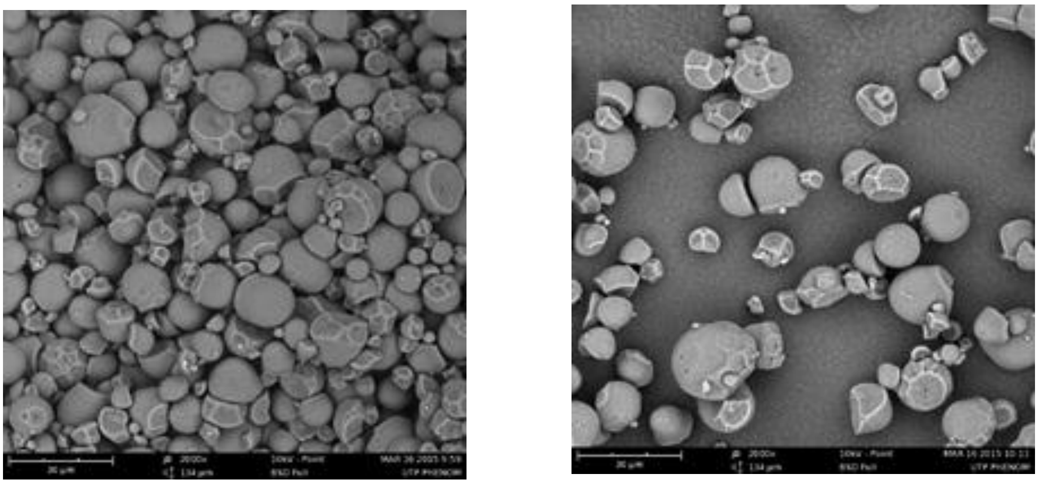

Figure 10(a): Sample 500 – 50% Water (Control)

Figure 10(b): Sample 700 - 70% Water (Control)

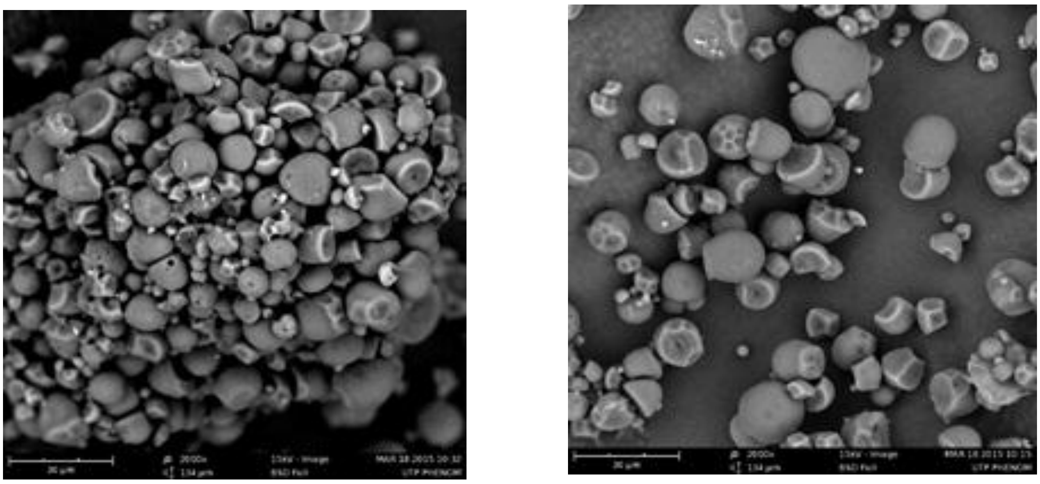

Figure 10(c): Sample 506 - 50% (1:8)

Figure 10(d): Sample 706 - 70% (1:8)

Figure 11: SEM Images of TPS Samples

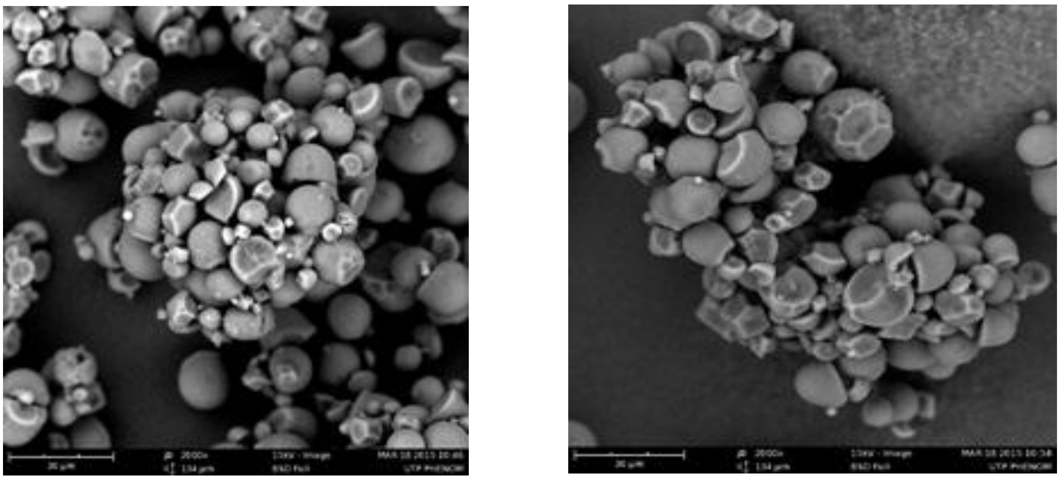

Figure 10(e): Sample 501 - 50% (1:4)

Figure 10(f): Sample 701 - 70% (1:4)

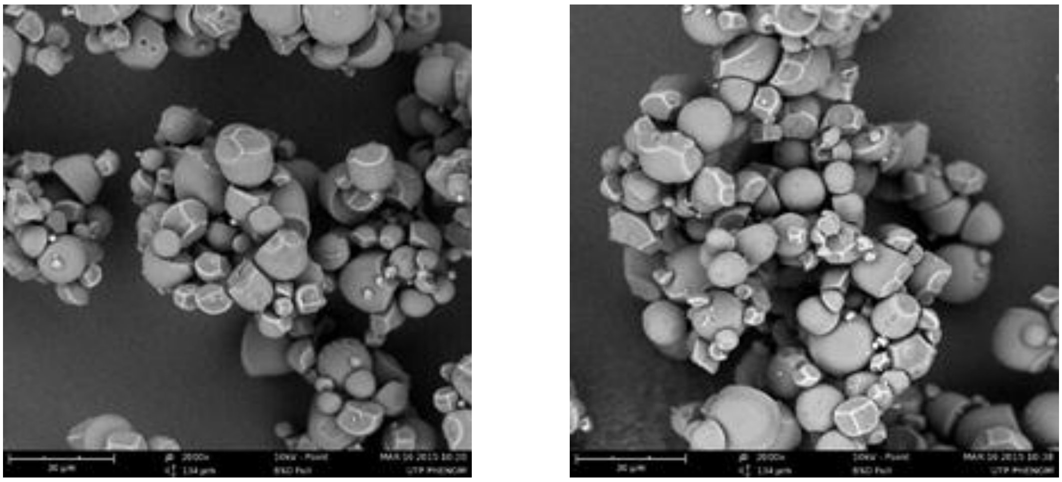

Figure 10(g): Sample 502 - 50% (2:3)

Figure 10(h): Sample 702 - 70% (2:3)

Figure 10: SEM Images of TPS Samples

Figure 10(a) and 10(b) are sample of natural starch with 50% and 70% water content respectively with no [Emim][OAc]. The images show that the starch granules are scattered freely without bound. By using water as primary plasticizer, the granules will absorb water, swell and lose crystallinity [21].

Based on the images, a higher amount of [Emim][OAc] could result in a more apparent granular morphology. In particular, most remaining starch granules could be observed as contained in Figure 10(d), while 502 and 702 showed a lumpy and coagulated granules as shown in Figure 10(g) and 10(h) respectively. These indicate that [Emim][OAc] could directly access a loosely organized region in the center of starch by channels and cavities, which lead to alteration in the granule morphology [22]. This was as expected as the gelatinization temperature increases with the use of ionic liquid and water as plasticizer instead of water only by itself, by other mean, slowing the gelatinization process.

Among the [Emim][OAc] plasticized samples, the ones with high ratio seemed to have the most granular surface as demonstrate by Figure 10(e), 10(f), 10(g) and 10(h). These results demonstrate a stronger effect of [Emim][OAc] on the disruption of granules during processing as discussed by Xie (2014) [12].

The rupture images in the Figure 10(c) and 10(d) above show that samples the lower plasticizer content makes the TPS to be more brittle, which was as predicted as plasticizers commonly make polymers more malleable. Sample 706 in Figure 10(d) seemed to be more brittle than 701 in Figure 10(f). This shows better plasticization effect of [Emim][OAc].

4.2 Crystallography Characteristic

To study the mechanical properties of the samples, x-ray diffraction (XRD) analysis was conducted to investigate the crystallization effect on the TPS with different plasticizer ratios.

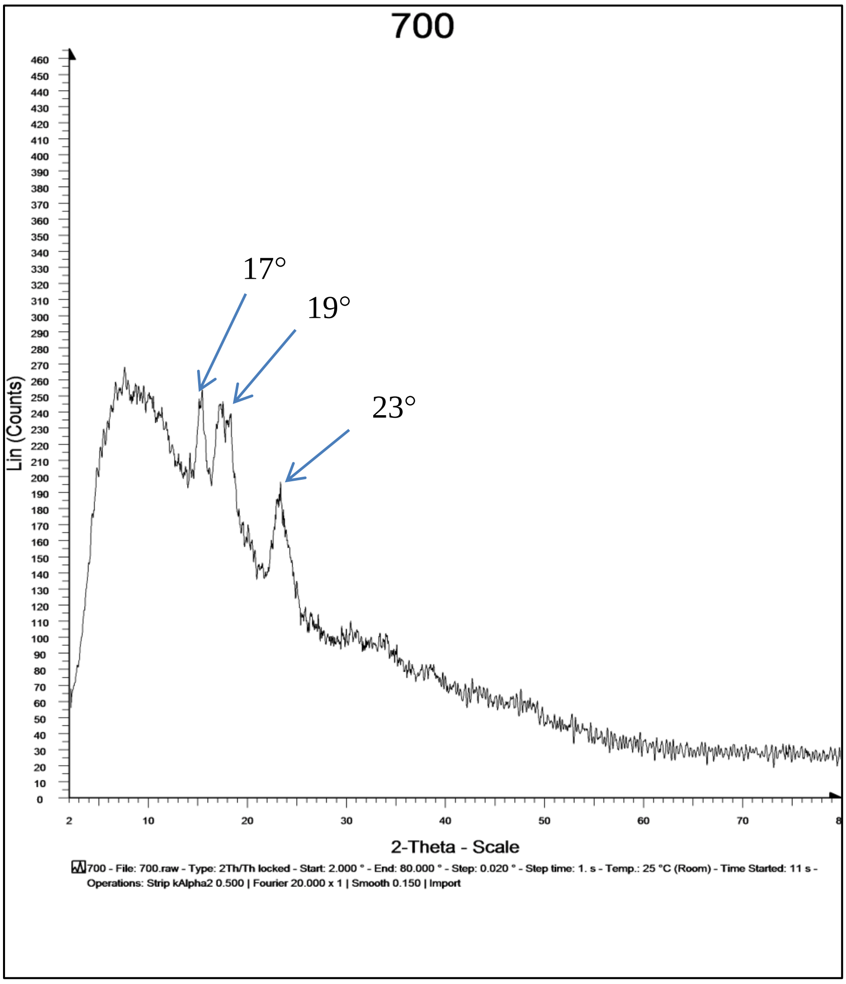

Figure 12: XRD Analysis on Starch with 70% Water Content Only

Figure 11 shows the pattern of the native starch with water but without [Emim][OAc] as plasticizer. It is appeared to have strong diffraction which are shown as sharp peaks at 17°, 19° and 23° which reveals the B-type crystalline structure. Starch with water produces a lot of B-type crystallization structure and this prevent the mobility of the amorphous structure.

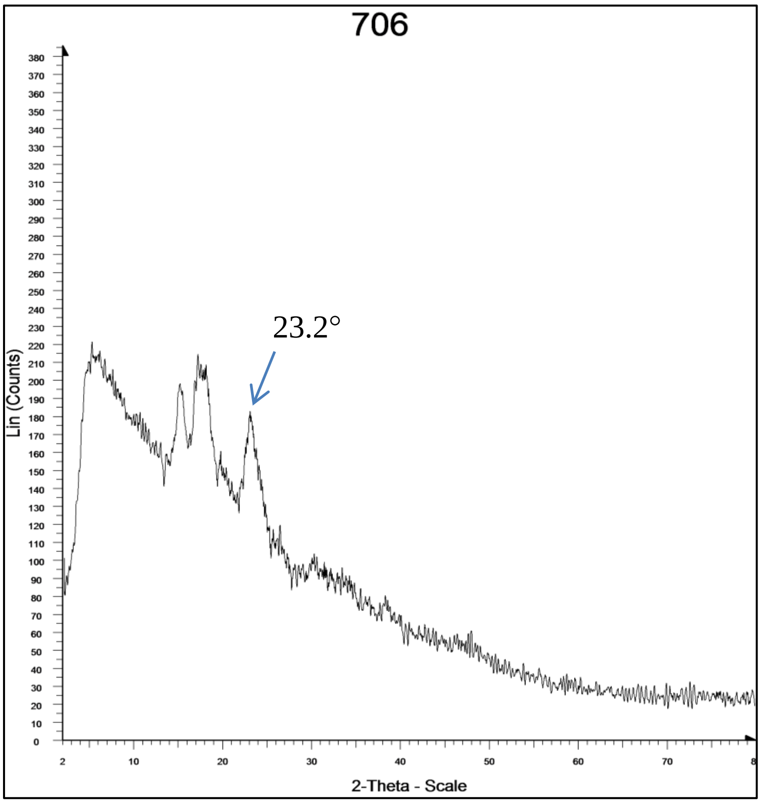

Figure 12(a): 706 - 70% (1:8)

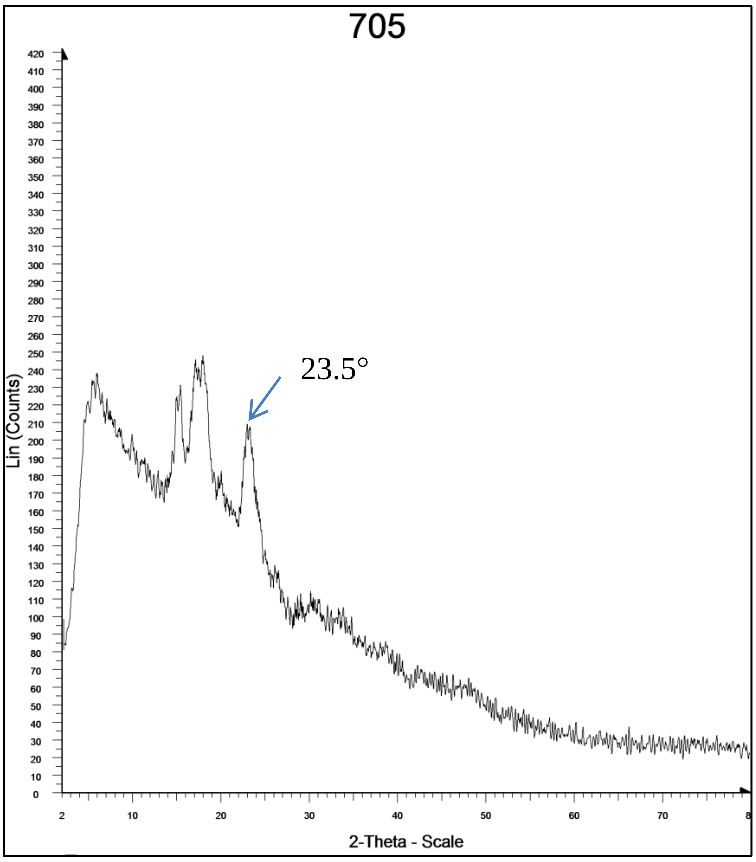

Figure 12(b): 706 - 70% (1:6)

Figure 13: XRD Graph Analysis on TPS with 70% Plasticizer Content

Figure 12(a) and 12(b) shows the crystallization effects on TPS with increasing [Emim][OAc] and water ratio in plasticizer content of 70% based on the dry starch.

After processing the starch with ionic liquid and water plasticizer solution, in toting with the original B-type characteristic peaks (main peak at 2θ = 23.°), all of the starch samples displayed peaks at 2θ of around 6.°, 15.°, 20.°,and 21.°, which were characterize as the V_H-type crystalline structure, a single-helical amylose structure. This is related to the one formed by amylose lipid helical complexes which is well known for thermally processed starch-based materials.

Sample 706 as shown in Figure 12(a) has the least ionic liquid with ratio only 1:8 of water. The graph indicates sharp half sharp peak and smaller narrow peaks which represent the crystalline structures still forming until at the 23.2°. The same is observed for Sample 705 in Figure 12(b) with the 1:6 ratio of ionic liquid and water, crystalline structures can be found based on the sharp diffraction peaks produced.

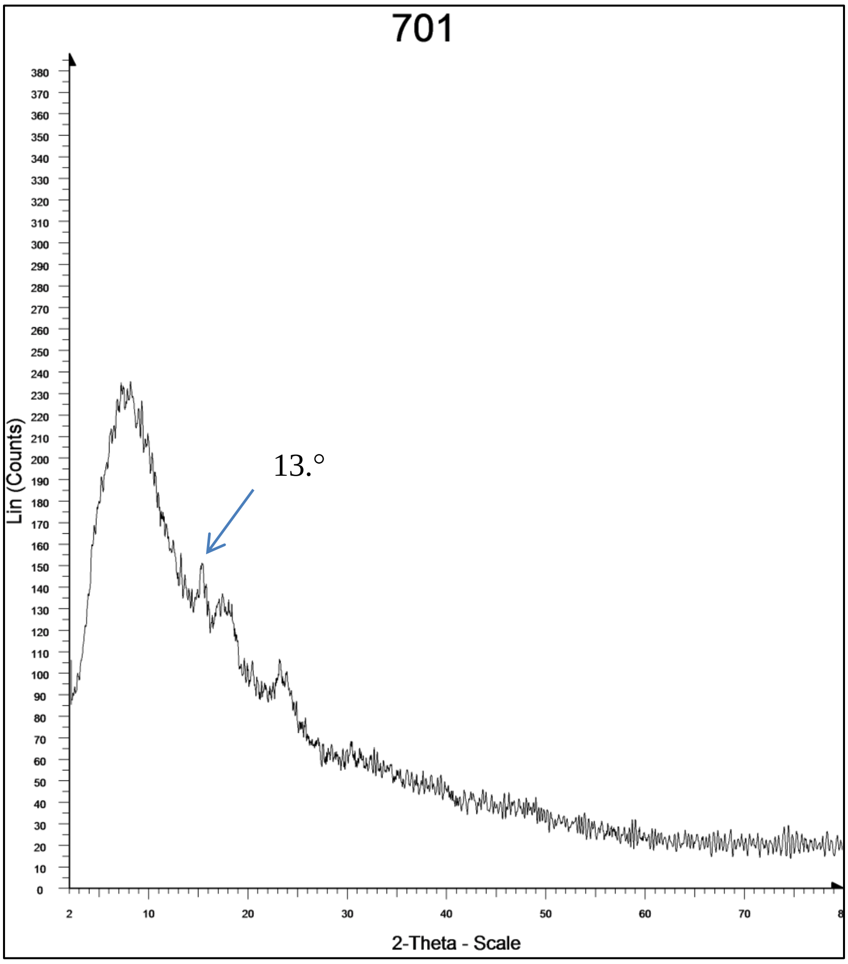

Figure 14: XRD Analysis on Sample 701with 70% Plasticizer Content, Ratio of 1:4

Figure 13 which refers to Sample 701 has medium amount of ionic liquid with ionic liquid-water ratio of 1:4, there is wide area under meshed-up smaller peaks. This shows the amorphous structure of the material. There is a small peak at 13.° however after that, the crystal formation decrease abruptly. Therefore, the plasticised starch samples some newly formed V-type crystalline structures mainly induced by the processing or some crystalline structures that were not destroyed by the compression moulding process.

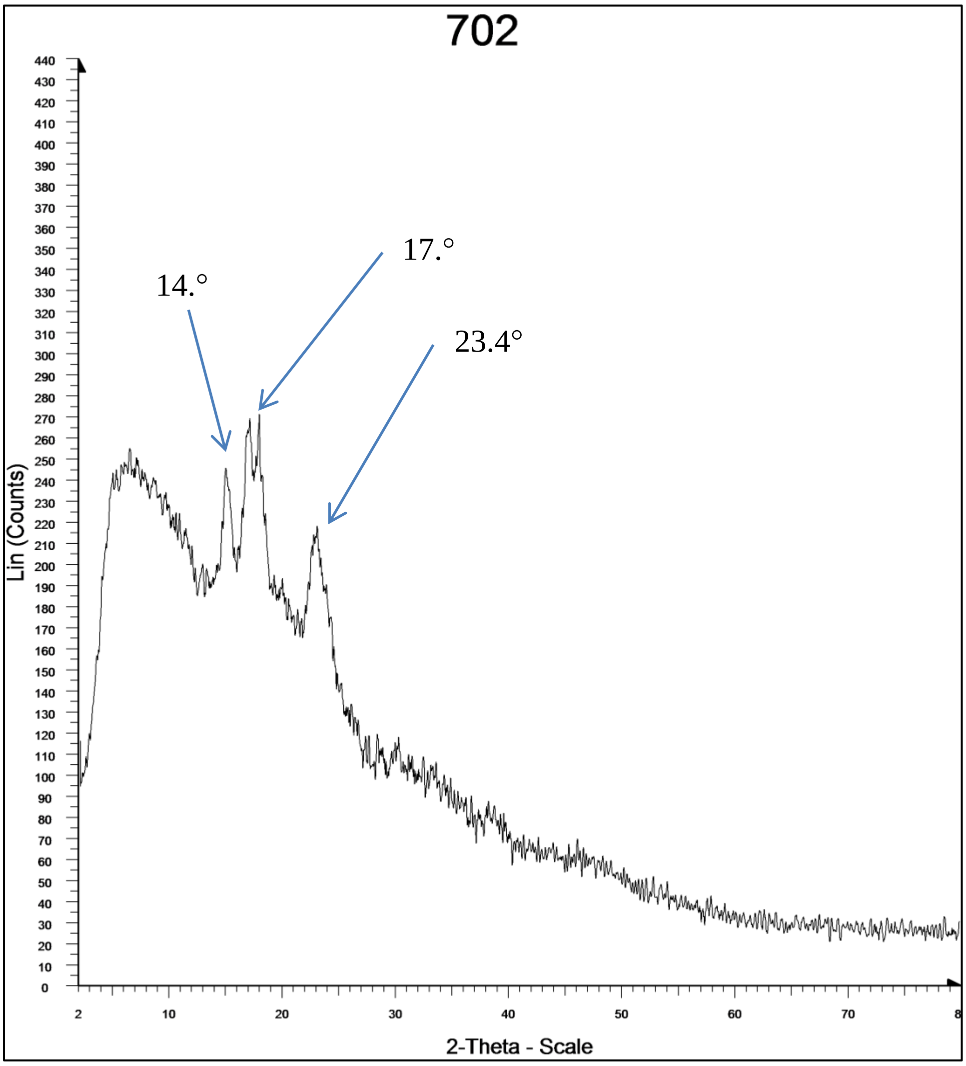

Figure 15: XRD Analysis on Sample 701with 70% Plasticizer Content, Ratio of 2:3

As shown in Figure 14, Sample 702 with 2:3 ionic liquid-water ratio, there is a lot of crystalline structures because there are strong diffraction peaks at 14.°, 17.° and 23.4° which is different from the result pattern expected. This sample was predicted to have more amorphous structures as there is more ionic liquid mixed in the plasticizer content. However, this result shows that there is a threshold of ionic liquid with water content in order to be effective plasticizer, which is 50:50 [Emim][OAc] and water.

This XRD analysis reveals that [Emim][OAc] at low concentrations disrupted the original B-type crystalline structure, generated less V-type crystalline structure, and increased the mobility of the amorphous starch, a higher water content (lower [Emim][OAc] content) resulted in less complete melting of granular crystallites [18].

In addition, the formation of the single-helical structure appeared to be obstructed with the enhancement of starch by [Emim][OAc]. This is because hydrogen bonding between the O_3^- and O_2 oxygen atoms of sequential residues forms single helices of starch. It is proposed that the effect of obstructing helix formation is due to the strong interaction between acetate anion in [Emim][OAc] and starch hydroxyl groups, hindering hydrogen bonding in the starch polymer and making it hard for the amylose molecules to form single or double helices [12] . The reality that [Emim][OAc] plasticised starch has low crystallinity can be beneficial to the production of biopolymer especially for electrically conductive materials which need to be basically amorphous.

Almost all samples containing plasticizer represent amorphous structures. However, the diffraction pattern of some samples did not show a very accurate result as expected. This might be because there was not enough stirring while preparing the sample. Hence the molecules of the starch and plasticizer did not bond well. The results were attached in ***Appendix B***.

4.3 Thermal Analysis

Previously studies have shown that ionic liquid has an effect of reducing the molecular weight of starch during solution processing with heat [12]. To study the chemical properties of the thermoplastic starch samples, thermo gravimetric analysis (TGA) was conducted on five (5) of the samples having different percentage of plasticizer content and [Emim][OAc] ratio. These samples were chosen as they represent TPS with varying ratio for medium plasticizer contents, which we found that 90% plasticizer content is not economic and environmental friendly.

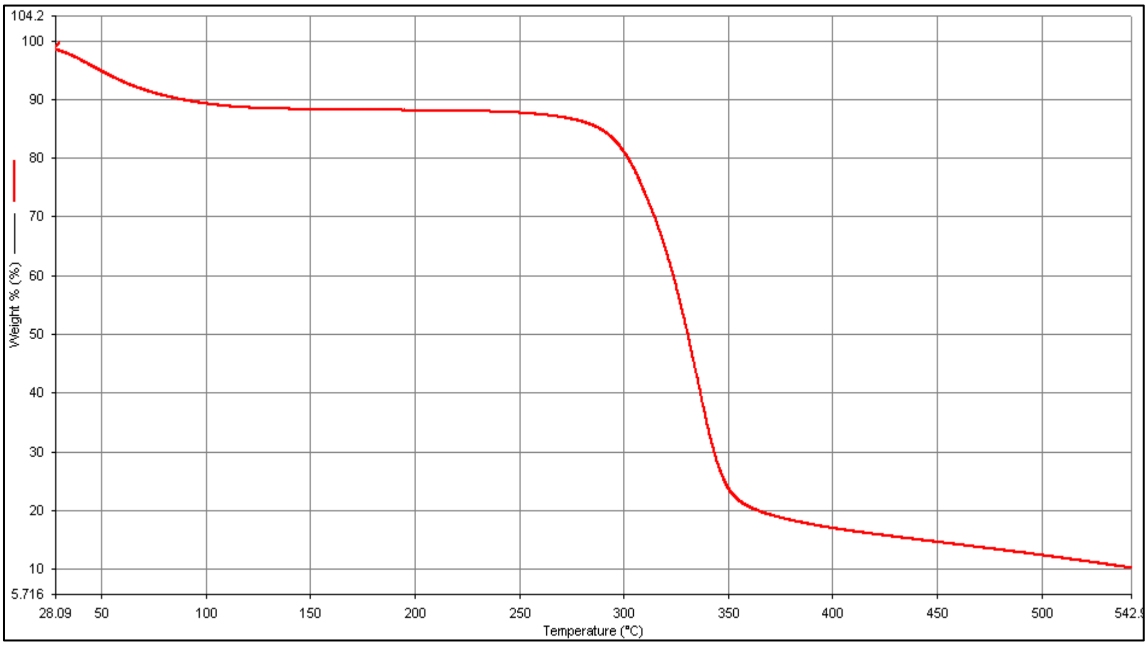

Figure 16: Degradation of Natural Starch with Water

Figure 12 demonstrates the percentage of weight of the natural starch without [Emim][OAc] as plasticizer during increasing temperature. The sample first loses its weight until 75°C and maintained about another 170°C until it degrades abruptly at 278°C to 345°C. After that, the sample continues degrading linearly. It is discussed that there are three (3) phases of degradation which are; the losses of water content in the first 100°C (boiling point of water), the losses of plasticized starch structure from 278°C to 345°C, and then the impurities in the sample from 346°C afterwards.

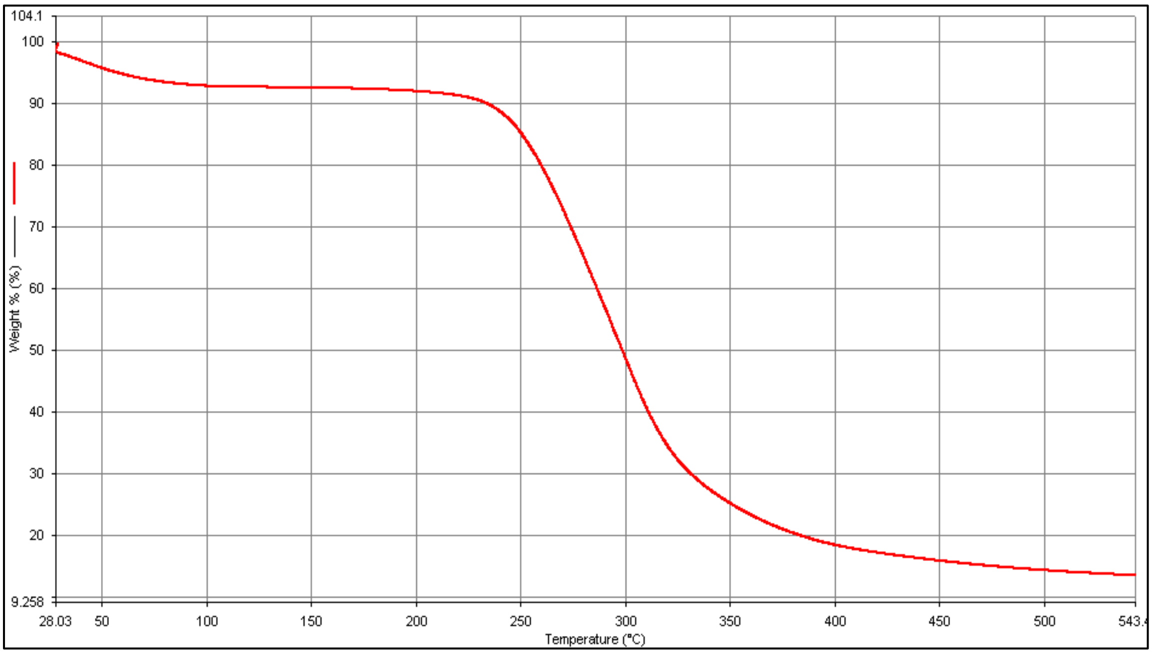

Figure 17: Degradation Graph of TPS with 50% Plasticizer Content & [Emim][OAc]/water Ratio of 1:4

As shown in Figure 16, after addition of 1.00 gram of [Emim][OAc] and 4.00 grams of water to 10.00 grams starch sample, the first phase of degradation which is loss of water content happens as usual in the first 100°C but it maintained its weight above 90% compared to sample in Figure 12. For this sample, the degradation of plasticized starch occurred slowly from 93% until 24% weight at 240°C to 355°C. This shows that the plasticization of starch with [Emim][OAc] makes a stronger material as it can sustain at high temperature for a longer time.

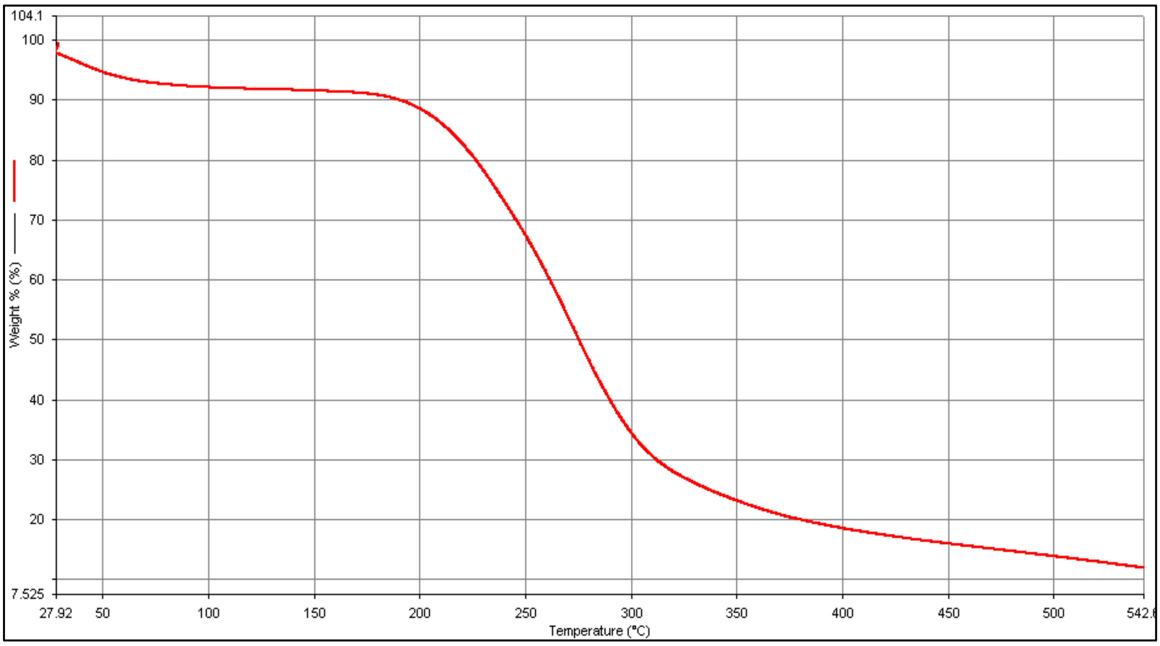

Figure 18: Degradation Graph of TPS with 50% Plasticizer Content & [Emim][OAc]/water Ratio of 2:3

In Figure 17, it shows that with 1.40 grams of [Emim][OAc] and 5.60 grams of water in the 10.00 grams thermoplastic starch sample, the first phase of degradation which is loss of water content happens as usual in the first 100°C and it maintained its weight at 91%. The second phase of degradation occurred slowly from 91% until 25% at 180°C to 325°C, which is was started at earlier and lower temperature. However, it still can hold its weight for longer temperature which is in longer time. This shows that the plasticization of starch with more [Emim][OAc] makes the thermoplastic starch even more ductile.

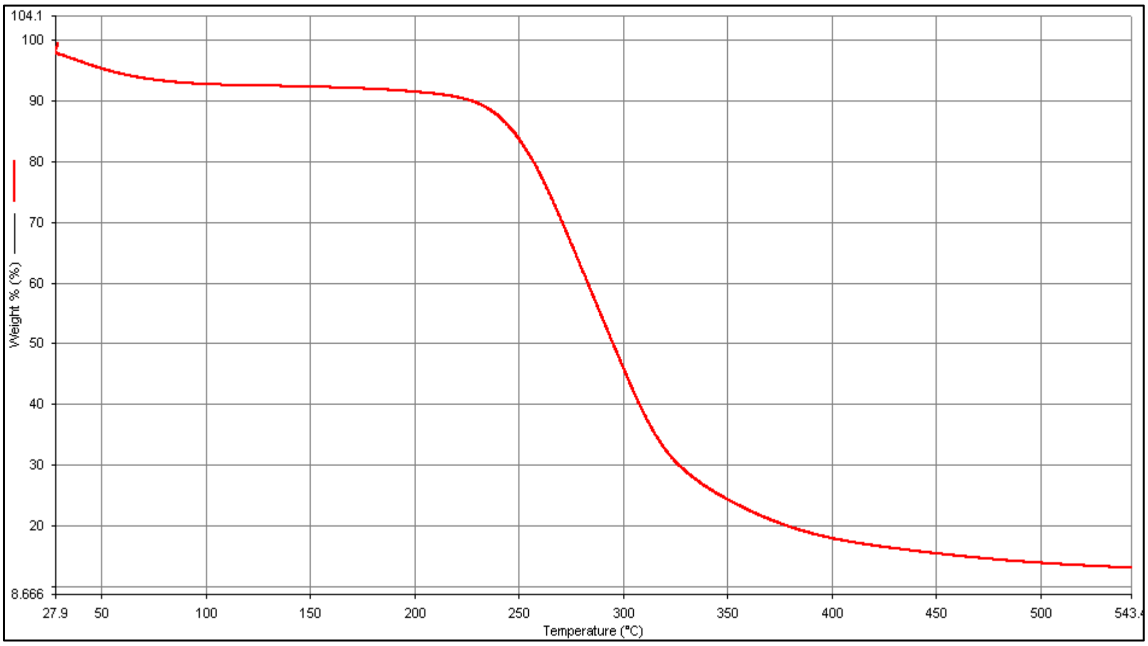

Figure 19: Degradation Graph of TPS with 70% Plasticizer Content & [Emim][OAc]/water Ratio of 1:4

Next, sample with more plasticizer content which is 2.00 grams of [Emim][OAc] and 3.00 grams of water in the 10.00 grams thermoplastic starch sample shows the first phase of degradation which is loss of water content happens as usual in the first 100°C but it maintained its weight above 90% as shown in Figure 18. The second degradation occurred in a longer period from 92% until 22% at 180°C to 355°C, which is was started at earlier and lower temperature compared to sample in Figure 17 which have the same ratio of [Emim][OAc]/water but different plasticizer percentage content. It can hold its weight for longer temperature which is in longer time. This shows that the plasticizer percentage content affect the chemical properties of different samples even with a same [Emim][OAc]/water ratio.

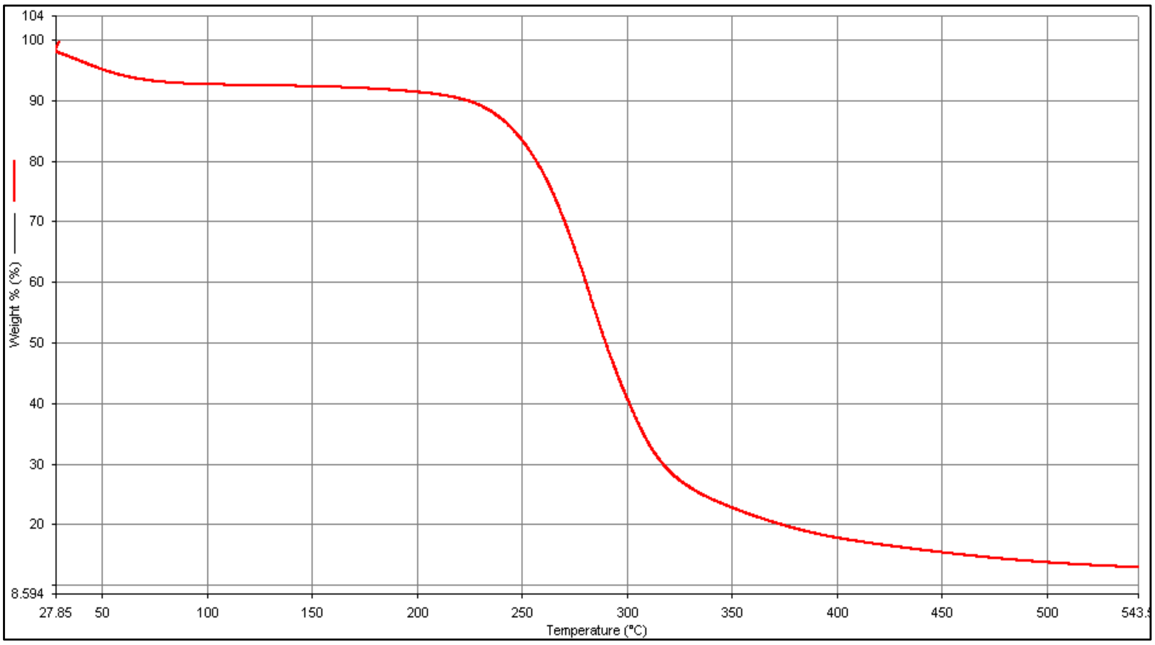

Figure 20: Degradation Graph of TPS with 70% Plasticizer Content & [Emim][OAc]/water Ratio of 2:3

Lastly, thermal analysis was conducted in a thermoplastic starch sample containing 2.80 grams of [Emim][OAc] and 4.20 grams of water in the 10.00 grams is shown in Figure 19. The first phase of degradation which is loss of water content happens as expected in the first 100°C and further maintained its weight above 90% just like in the other samples. However the second degradation started when at 225°C, which is not as expected as compared to Figure 14, the sample should start its second phase of degradation earlier at lower temperature. It degraded from 92% until 21% weight at 225°C to 355°C, which is was started at later and higher temperature compared to sample in Figure 14 which have the same ratio of [Emim][OAc]/water but lower plasticizer percentage content. It held its weight for shorter temperature which is in shorter time. This sample is an evident of defect due to incomplete stirring during the sample preparation. Incomplete stirring leads to non-homogenous mixture and makes the plasticizer did not blend well with the amylose of the starch.

The results clearly suggest that with use of [Emim][OAc], thermal degradation happened at a lower temperature while can hold its coating properties for a longer time and higher temperature. Enhancement with ionic liquid also contributes to inhibition of bacterial or fungi growth on the starch as the thermoplastic starch will degrade earlier and destroys the hydrogen bonds between the amylose. It is thus proposed that the existence of [Emim][OAc] could promote good thermal degradation of starch molecules and is a potential plasticizer for TPS.

CHAPTER 5

CONCLUSION & RECOMMENDATION

In this study, the characteristics of starch-based films were investigated with the plasticization effect of [Emim][OAc] on the starch. [Emim][OAc] is chosen for this study because of its least toxicity among the ionic liquids and less vapor pressure causing it not to easily volatilize to the environment. Tapioca is being used as the source of starch and the main biopolymer for this project, which is identified to have exertion in granule disruption and poor reactivity. Glycerol which is commonly used as plasticizer, has been found to give poor mechanical properties to the starch [12]. Thus, the use of [Emim][OAc] has shown to be effective in plasticization of starch. The SEM images of the different TPS samples obviously tell the better structure of the starch when it is mixed with more [Emim][OAc]. The starch granules coagulate and form lumpy structure which is more ductile and difficult to gelatinize instead of being scattered freely and brittle as native starch.

The XRD results reveal that [Emim][OAc] at a low concentration disrupted the original B-type crystalline structure, produced less V-type crystalline structure, and the mobility of the amorphous starch increased. Thus, a highly amorphous structure contributed to higher flexibility as shown by mechanical tests and a lower glass transition temperature but stronger glass transition peak.

Even though the TGA results might show the thermal degradation of starch start to occur at lower temperature than native starch, it is shown that plasticization by [Emim][OAc] inhibited bacterial attack to the starch-based materials. The longer range of biodegradation in TPS samples with more [Emim][OAc] proves that the affectively of the plasticization makes the starch to degrade in a more controllable manner.

Based on the samples experimented, it is suggested that starch with around 60% to 70% of plasticizer content is the best with [Emim][OAc]/water ratio of 1:4 and 1:5. Although samples with 2:3 ratio are also investigated in this study, the enhancement of TPS with [Emim][OAc] can be very effective for coating material even in smaller amount of it. Moreover, this will reduce the cost and less hazardous impact to environment. [Emim][OAc] could be a capable plasticizer for starch to promote “green” materials with controlled biodegradation rates in order to meet application needs.

The rapid release of ammonia to the environment contributed to economic loss and environmental defect. When the use of biopolymer such as starch instead of petroleum-based polymer is introduced, it is a good alternative for a cleaner environment. The addition of ionic liquid as plasticizer in TPS improves the material by increasing its stability, flexibility, and encourages inhibition of bacterial attack to the starch. Therefore it is assumed that ionic liquid can be a good plasticizer for TPS and can be used as coating material for fertilizer in improving ammonia uptake of crops and plants.

It is recommended that the total plasticizer content between 51% to 69% based on the dry starch with [Emim][OAc]/water ratio of 1:5 might be also optimum plasticizer content for the TPS. It is suggested as the total of [Emim][OAc] used can be minimized and optimum attributes for fertilizer coating could be achieved. This study also recommended to manipulate the stirring time and temperature during the process of mixing the starch with plasticizers which also known as plasticization. It is because the conditions of plasticization process affect the structures and also the physical and chemical behaviors of TPS produced.

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APPENDICES

Appendix A

Calculated Weight Ratio of Thermoplastic Starch (TPS) Samples: 50%

Based on dry starch : 50%					
Label	**Ratio**	**Starch (g)**	**[Emim][OAc] (g)**	**Water (g)**	**Total (g)**
500	**Control**	10.000	0.000	5.000	**15**
501	1:4	10.000	1.000	4.000	**15**
502	2:3	10.000	2.000	3.000	**15**
503	3:2	10.000	3.000	2.000	**15**
504	2:1	10.000	3.333	1.667	**15**
505	1:6	10.000	0.714	4.286	**15**
506	1:8	10.000	0.556	4.444	**15**

Appendix A

Calculated Weight Ratio of Thermoplastic Starch (TPS) Samples: 70%

Based on dry starch : 70%					
Label	**Ratio**	**Starch (g)**	**[Emim][OAc] (g)**	**Water (g)**	**Total (g)**
700	**Control**	10.000	0.000	7.000	**17**
701	1:4	10.000	1.400	5.600	**17**
702	2:3	10.000	2.800	4.200	**17**
703	3:2	10.000	4.200	2.800	**17**
704	2:1	10.000	4.667	2.333	**17**
705	1:6	10.000	1.000	6.000	**17**
706	1:8	10.000	0.778	6.222	**17**

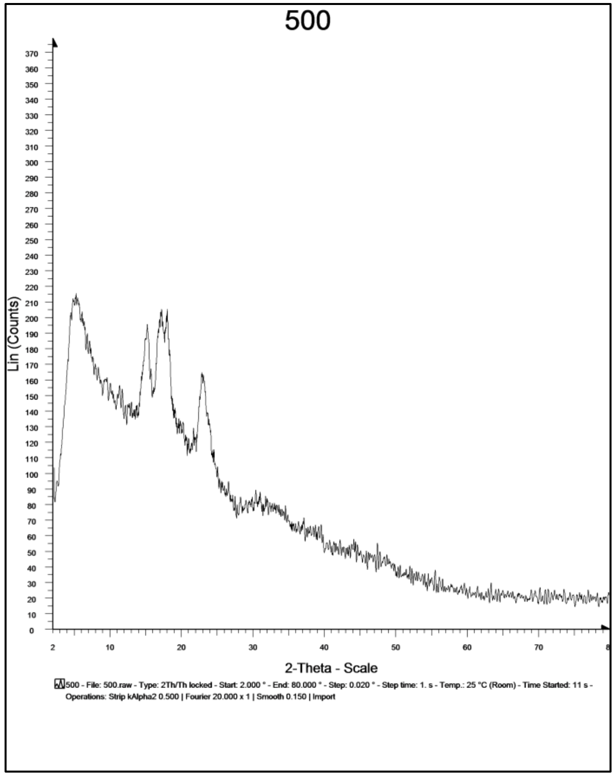
Appendix A

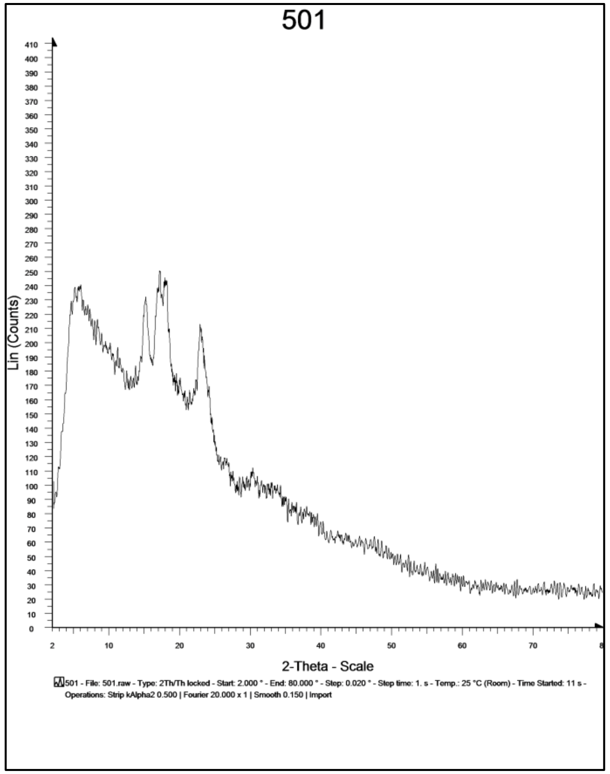
Calculated Weight Ratio of Thermoplastic Starch (TPS) Samples: 90%

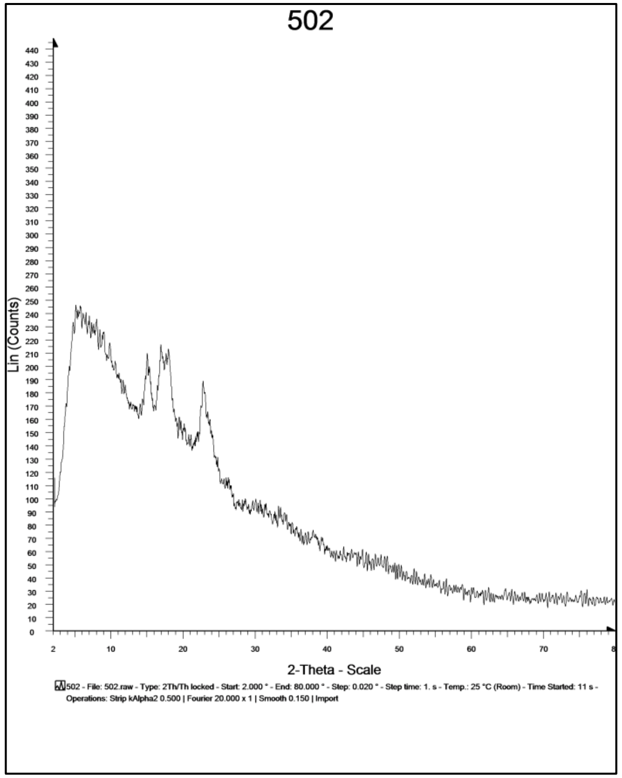
Based on dry starch : 90%					
Label	**Ratio**	**Starch (g)**	**[Emim][OAc] (g)**	**Water (g)**	**Total (g)**
900	**control**	10.000	0.000	9.000	**19**
901	1:4	10.000	1.800	7.200	**19**
902	2:3	10.000	3.600	5.400	**19**
903	3:2	10.000	5.400	3.600	**19**
904	2:1	10.000	6.000	3.000	**19**
905	1:6	10.000	1.286	7.714	**19**
906	1:8	10.000	1.000	8.000	**19**

Appendix B

X-ray Diffraction (XRD) Graph Results of Different TPS Samples

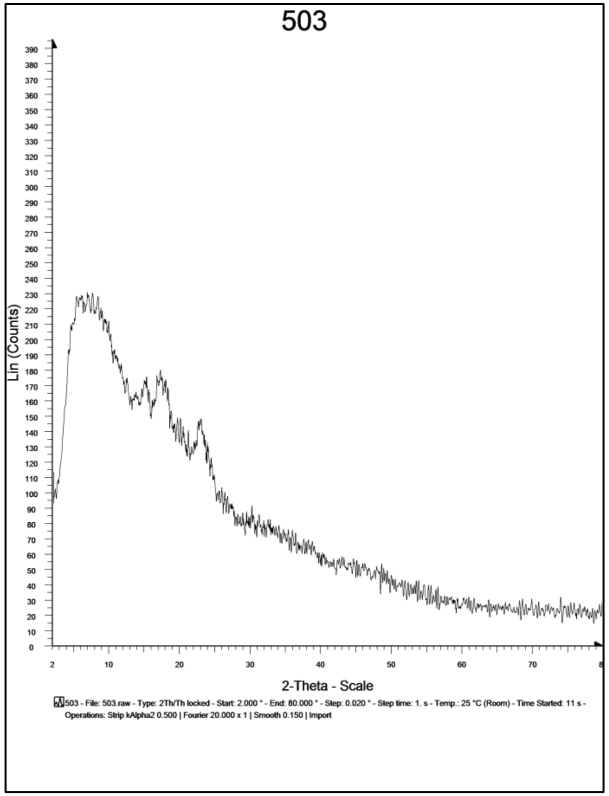


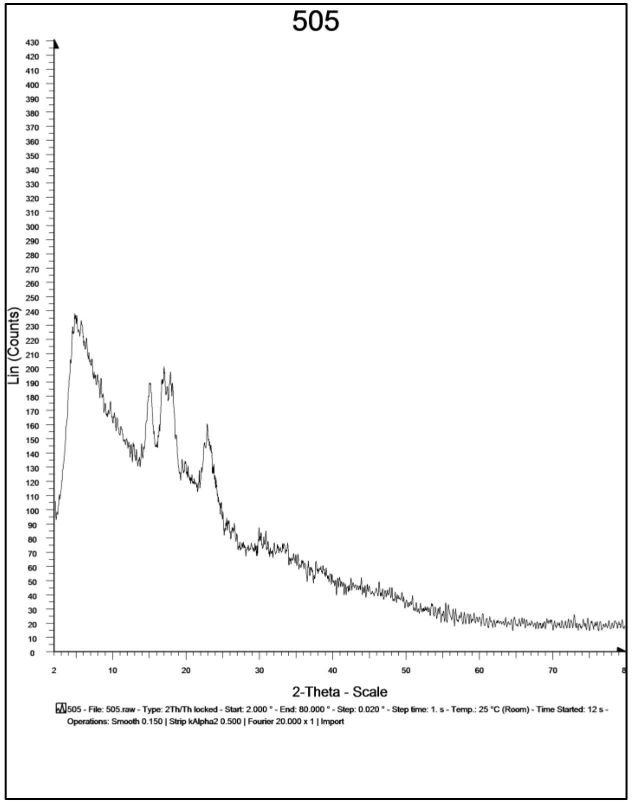


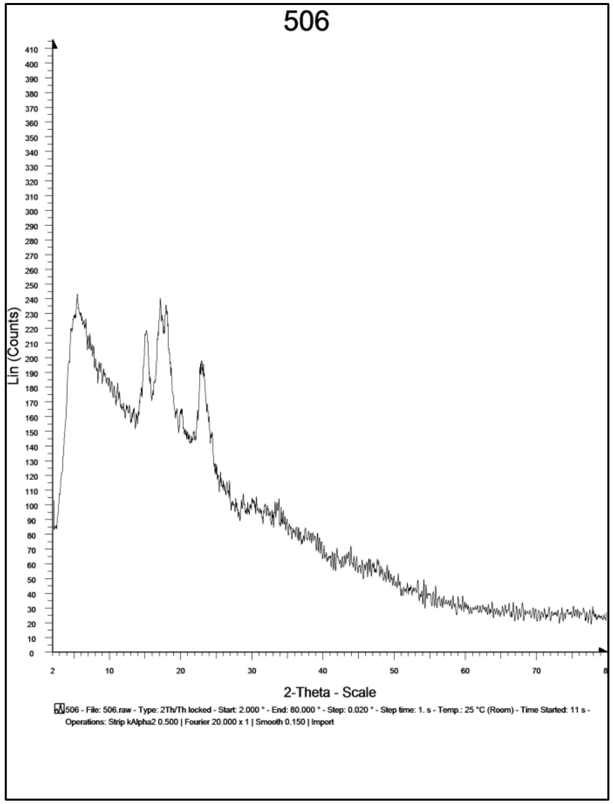


Appendix B

X-ray Diffraction (XRD) Graph Results of Different TPS Samples

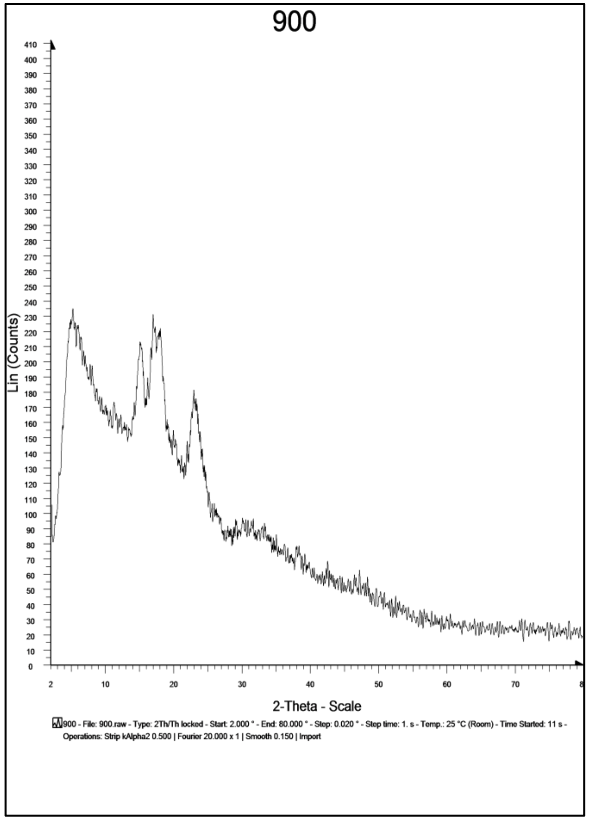


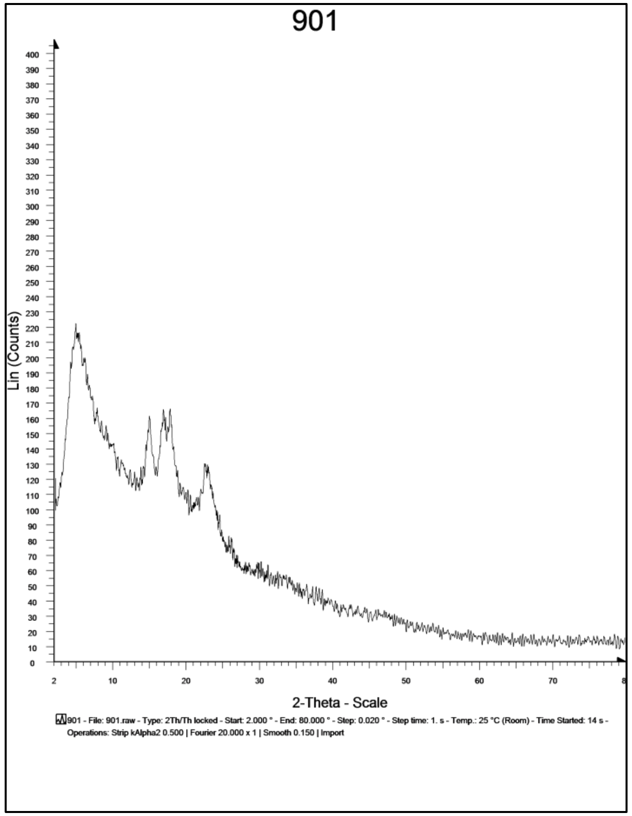


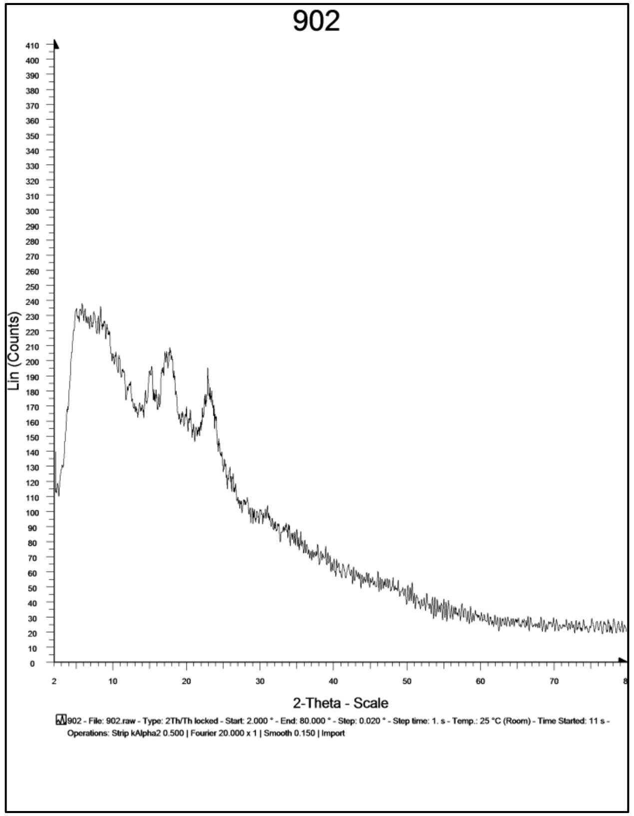


Appendix B

X-ray Diffraction (XRD) Graph Results of Different TPS Samples







Material Safety Data Sheet

1-Ethyl-3-methylimidazolium acetate

Revision Date:	12/01/2010
Date Issued:	6/28/2011

1 IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND THE COMPANY/UNDERTAKING

Product name	1-Ethyl-3-methylimidazolium acetate
Product code	IL-0189
CAS	143314-17-4
Supplier	IoLiTec Ionic Liquids Technologies GmbH Salzstrasse 184 D – 74076 Heilbronn Germany
Telephone	+49 (0)7131-89839-0
Fax	+49 (0)7131-89839-109
Emergency telephone	+49 (0)179-5322578
Email	msds@iolitec.de

2 HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

Classification (REGULTATION (EC) No 1272/2008)

Caution! Substance not yet fully tested. Risks cannot be excluded if the product is handled inappropriately. For laboratory use only!

Classification (67/548/EEC or 1999/45/EC)

Caution! Substance not yet fully tested. Risks cannot be excluded if the product is handled inappropriately. For laboratory use only!

2.2 Label elements

Labelling (REGULATION (EC) No 1272/2008)

Substance not yet fully tested.

Hazard statements

H-phrases	Substance not yet fully tested.

Precautionary statements

P phrases

P262:	Do not get in eyes, on skin, or on clothing
P280:	Wear protective gloves/ protective clothing/ eye protection/ face protection
P305 + P351 + P338:	IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do – continue rinsing.
P313:	Get medical advice/attention

Labelling (67/548/EEC or 1999/45/EC)

Substance not yet fully tested.

Risk phrases	Not fully tested substance.
Safety phrases	
S: 24/25	Avoid contact with skin and eyes.
S: 26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S: 36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
S:28,2	After contact with skin, wash immediately with plenty of water and liquid soap.

3 COMPOSITION/INFORMATION ON INGREDIENTS

Ingredient name	Contents	Health(Class)	Risk(R/No.)
1-Ethyl-3-methylimidazolium acetate	>95%	Substance not yet fully tested!	

4 FIRST AID MEASURES

General	Contaminated clothing should be removed and washed before being reused.
Inhalation	Move the exposed person to fresh air at once. If respiratory problems, provide artificial respiration/oxygen.
Ingestion	Immediately rinse mouth and provide fresh air. Do not induce vomiting. Get medical attention immediately.
Skin	Wash the skin immediately with soap and water.
Eyes	Promptly wash eyes with plenty of water while lifting the eye lids. Continue to rinse for at least 15 minutes. Get medical attention immediately. Continue to rinse.

5 FIRE FIGHTING MEASURES

Extinguishing media	Use: Water spray, fog or mist. Carbon dioxides (CO_2). Dry chemicals, sand, dolomite etc.
Special fire fighting procedures	Avoid water in straight hose stream, will scatter and spread fire. Keep run-off water out of

	sewers and water sources. Dike for water control.
Unusual fire & explosion hazards	Fire causes formation of toxic gases.
Protective measures in fire	Wear self-contained breathing apparatus as combustion may produce hazardous fumes.

6 ACCIDENTAL RELEASE MEASURES

Personal precautions during spill	Wear protective clothing and avoid inhalation of vapor, skin or eye contact.
Precautions to protect environment	Avoid washing into water courses. Avoid contaminating public drains or water supply.
Spill cleanup methods	Avoid contact with skin or inhalation of spillage, dust or vapor, Avoid dust formation. Collect and reclaim or dispose in sealed containers in license waste. Extinguish all ignition sources. Avoid sparks, flames, heat and smoking. Ventilate.

7 HANDLING AND STORAGE

Usage precautions	Keep away from heat, sparks and open flame. Do not use in confined spaces without adequate ventilation and/or respirator.
Storage precautions	Store at moderate temperatures in dry, well ventilated area.
Storage criteria	Chemical storage.

8 EXPOSURE CONTROLS AND PERSONAL PROTECTION

Protective equipment	Safety goggles. Chemical resident gloves. Protective clothing.
Process control measures	Provide eyewash station and safety shower. Use engineering controls to reduce air contamination to permissible exposure levels.
Ventilation	Provide adequate general and local exhaust ventilation.
Respirators	Use high efficiency particulate respirator with appropriate filter.
Other protection	Wear overalls and industrial shoes.

9 PHYSICAL AND CHEMICAL PROPERTIES

Appearance	liquid
Color	yellow to brown.
Odor/taste	No characteristic odor.

10 STABILITY AND REACTIVITY

Stability	No particular stability concerns.
Conditions to avoid	Avoid contact to strong oxidizers and bases.
Hazardous Decomposition Products	High temperatures generate: Corrosive gases/vapor/fumes of: Carbon dioxide (CO_2). Carbon monoxide (CO). Nitrous gases (NOx).

11 TOXICOLOGICAL INFORMATION

Ingestion	not available.
Skin	not available.
Eyes	not available

Data on the toxicity of this product are not available. Hazardous properties cannot be excluded.

12 ECOLOGICAL INFORMATION

Environmental hazards	Avoid washing into water courses. Avoid contaminating public drains or water supply.

13 DISPOSAL CONSIDERATIONS

Disposal method	Contact specialist disposal companies. Dispose of in accordance with Local Authority requirements. Recover and reclaim or recycle, if practical.

14 TRANSPORT INFORMATION

General	Not classified as dangerous for transport purposes.
UN No.	0
Road transport notes	Not classified as dangerous for road transport.
Rail transport notes	Not classified as dangerous for rail transport.
Sea transport notes	Not classified as dangerous for sea transport.
Air transport notes	Not classified as dangerous for air transport.

15 REGULATORY INFORMATION

Label for supply	Substance not yet fully tested.

P phrases

P262:	Do not get in eyes, on skin, or on clothing
P280:	Wear protective gloves/ protective clothing/ eye protection/ face protection
P305 + P351 + P338:	IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do – continue rinsing.
P313:	Get medical advice/attention

Safety phrases

S: 24/25	Avoid contact with skin and eyes.
S: 26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S: 36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
S:28,2	After contact with skin, wash immediately with plenty of water and liquid soap.

Country specific information

Germany	WGK: 3	(Self-Classification)

16 OTHER INFORMATION

DISCLAIMER

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