# STUDY ON THERMOPLASTIC CASSAVA STARCH MODIFICATIONS VIA CHEMICAL, PHOTO AND IRRADIATION INDUCED CROSSLINKING

by

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A thesis submitted in fulfillment of the requirements for the degree of Master of Science (Materials Engineering)

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2017

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**LIST OF SYMBOLS**

| | |
|---|---|
| $^{o}C$ | Degree Celsius |
| % | Percentage |
| µm | Micrometer |

**Kajian Terhadap Pengubahsuaian Termoplastik Kanji Ubi Kayu melalui Kimia, Cahaya dan Radiasi Mendorong Pembentukan Taut Silang**

## ABSTRAK

Pencirian terhadap pengubahsuaian termoplastik kanji (TPS) dikaji melalui sifat mekanikal, sifat terma, mikroskop imbasan elektron (SEM), spektroskopi transformer Fourier inframerah, kromatografi cecair berprestasi tinggi dan ujian biodegradasi. Sebelum melakukan proses pengubahsuaian, TPS disediakan melalui proses pemplastikan 65% kanji ubi kayu dengan 35% gliserol. Kemudian, TPS disediakan dengan menggunakan mesin penggelek panas pada 150 $^{o}$C selama 10 minit. Jenis pengubahsuaian yang berlainan, iaitu radiasi cahaya, radiasi elektron, dan asid karbosilik telah digunakan untuk mengubahsuai TPS. Dalam taut silang cahaya, TPS disinarkan di bawah lampu pada masa penyinaran yang berbeza, dari 30 minit hingga 480 minit. Sementara itu, dos sebanyak 25 kGy hingga 100 kGy dikenakan dalam proses taut silang radiasi elektron. Taut silang TPS dengan menggunakan cahaya dan sinar elektron menunjukkan perbaikan dalam sifat termal dan mekanikal, masing-masing 2.70 MPa dan 3.18 MPa. Peningkatan nilai pembentukan gel (NGM) sehingga 22.98 mg/cm$^2$ dan 19.28 mg/cm$^2$, bagi tempoh penyinaran cahaya dan dos elektron membuktikan pembentukan taut silang berlaku di dalam TPS. Walau bagaimanapun, penyinaran yang berlebihan menyebabkan degradasi kepada TPS, seterusnya mengurangkan pembentukan taut silang. Asid sitrik dan asid askorbik diperkenalkan dalam proses pengubahsuaian TPS secara kimia. Penambahan asid karbosilik divariasi pada kuantiti dari 1% - 4%, dan 10% - 50%. Berdasarkan analisis SEM, penambahan asid karbosilik memberikan permukaan pematahan yang lebih sekata. Peningkatan di dalam kuantiti asid karbosilik juga merangsang pembentukan taut silang. Nilai NGM meningkat sehingga 49.00 mg/cm$^2$ dan 57.43 mg/cm$^2$, bagi kuantiti asid sitrik dan asid askorbik yang tinggi. Hasilnya, nilai tegangan pada 40% meningkat sehingga 6.25 MPa berbanding TPS yang tidak terubah suai. Analisis penyerapan lembapan juga menunjukkan kadar kerintangan kelembapan yang lebih baik berbanding dengan TPS yang tidak terubah suai. Ujian biodegradasi yang dilakukan menunjukkan pengubahsuaian TPS dengan asid memberikan kadar biodegradasi yang rendah berbanding dengan TPS yang tidak terubah suai. Ini kerana ia mempunyai kadar kerintangan kelembapan yang lebih baik, menyebabkan pengurangkan kebolehtelapan air ke dalam struktur TPS.

**Study on Thermoplastic Cassava Starch Modifications via Chemical, Photo and Irradiation Induced Crosslinking**

## ABSTRACT

The characterization of modified thermoplastic starch (TPS) was investigated by means of mechanical properties, thermal properties, scanning electron microscope (SEM), Fourier transform infrared spectroscopy, high performance liquid chromatography and biodegradability test. Before performing the modification, the TPS was prepared by plasticized 65 % of native cassava starch with 35 % of glycerol. The TPS was prepared by using heated two roll mill at the 150 $^{o}$C for 10 minutes. Different type of modification, which photo radiation, electron beam radiation crosslinking, and carboxylic acid modification was prepared on TPS sheets. In photo crosslinking, TPS were irradiated under lamps at different irradiation time, from 30 minutes to 480 minutes. Meanwhile, dosage ranging from 25 kGy to 100 kGy were introduced in electron beam radiation crosslinking process. Crosslinking of TPS using photo radiation and electron beam radiation showed improved thermal properties and mechanical properties, which 2.70 MPa and 3.18 MPa respectively. The gel mass (NGM) value increases up to 22.98 mg/cm$^2$ and 19.28 mg/cm$^2$, respected to the photo irradiation time and electron dose range proved the formation of crosslinking in the TPS. However, excessive irradiation caused further degradation of the TPS, thus reduce the crosslinking formation. Citric acid and ascorbic acid were introduced into the chemical modification process of TPS. Addition of carboxylic acid were varied from 1% - 4%, and 10% - 50%. Based on SEM analysis, the addition of carboxylic acid gives a smoother fracture surface. Further increment in carboxylic acid content led to the crosslinking formation. The NGM value was increase until 49.00 mg/cm$^2$ and 57.43 mg/cm$^2$, respected to increases of citric acid and ascorbic acid content. As a resulted, the tensile value at 40% was increased up to 6.25 MPa compared to unmodified TPS. Moisture absorption analysis also showed improved moisture resistivity as compared to unmodified TPS. Biodegradability test performed resulted acid modification TPS give low degradation rate compared to unmodified TPS. These was due to their improved moisture resistivity, resulted reduce in the water permeability into the TPS structure.

# CHAPTER 1: INTRODUCTION

## 1.1 Background of study

Advances in petroleum-based plastic have benefited mankind in numerous ways. Plastic is versatile, lightweight, flexible, moisture resistant, strong and relatively inexpensive. Petroleum-based plastic has now been a regular materials that is being used on a daily basis, which it can be disposable and highly durable, depending on their composition and specific application. However, petroleum-based plastic is recognized as a long-lasting material, which it difficult to degrade in the natural environment. In addition, global climate change, caused in part by carbon dioxide released by the process of plastic combustion, has become an increasingly important problem. Plastic waste, which the disposal of items made of petroleum-based plastic, such as fast-food utensils, packaging containers and trash bag becomes serious sanitary problem. Others than the environmental problem, it also exposed the community to illness such as diarrhea, amebiasis and parasitosis (Vilpoux and Averous, 2004). Therefore, it is necessary to find an alternative ways to secure sustainable world development. To improve petroleum-based plastic degradation, some researchers have proposed partial degradable plastic. The logic in degradable mechanism proposed by Chandra and Rustgi (1998), and Hamza et al. (2009) stated that the removal of biodegradable components present in petroleum-based plastic in the waste disposal environment will slowly disintegrate and disappear. An experiment conducted showed the biodegradability of LDPE blend with 15% of starch give low degradation rate. The weight loss of the LDPE blend reduced 0.18%, compared to the degradability of pure LDPE, define that it is partially biodegradable polymer (Hamza et al., 2009).

Interest in biodegradable polymers has continued to increase significantly in recent years because of the problems associated with their disposal and effects on the environment. The research of biodegradable polymer is growing intense as continuing growing concern towards the application of green product in worldwide. Current utilization of natural polymers in packaging, semi-structural and structural application, in which synthetic polymer has been used, is a wide revival of interest for researcher and industrialists (Kumar and Singh, 2008). Biodegradable materials can be classes in four groups, which; (i) agricultural origin, (ii) microbial origin, (iii) biotechnological origin and (iv) petrol-by product origin (Vilpoux and Averous, 2004). Usage of biopolymer, such as polylactide acid (PLA), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polycaprolactone (PCL) and polyhydroxyalkanoates (PHA) in industrial processing is costly due to the expensive price of the polymers. One approach in reducing the overall cost of materials is incorporating with other bio-materials. However, incorporation of another bio-materials are limited to 30 % loading. The blend of PLA/TPS performed by Teixeira et al. (2012) resulted diminished in tensile strength of neat PLA as the TPS content increased. Similar trend also reported by Ramaraj (2007), which the tensile strength, tear resistance and burst strength of PVA decrease when the starch loading increased from 10% to 50% due to the stiffening effect and the nature of the starch granules. Since the addition of others bio-materials are limited, thus the reduction in raw material cost is less.

Starch is a carbohydrate polymer that can be purified from various sources. Corn, wheat, sorghum, tapioca and potato are all major resources, containing about 70 – 80 % starches. These starches have been used in the food industries, as well as in the paper and other non-food industries. This number is expected to increase in the near future with the development of biopolymer, such as poly(lactic acid) (PLA), as substitutes for petroleum-based plastic. Starch is widely used as a viable alternative to making biodegradable plastic due to cheap, renewable and fully biodegradable. Furthermore, it easily degrades when exposed to the environment and compost organisms. Starch usually exists in granular state, which it composed of semi-crystalline polymer structure.

Starch can be process like thermoplastic polymer in the presence of plasticizer via the aid of heat and shear mechanism. The native starch granules are converted into a homogeneous melt under controlled pressure and temperature in order to disrupt the starch granular structure. The obtained continuous phase of viscous starch melt was known as thermoplastic starch (TPS), which has properties alike conventional thermoplastic polymer. Later, it can be processed with existing plastic processing, such as injection molding, compression, extrusion and blow molding (Zhou et.al, 2008).



Disruption of starch granules and their supramolecular, dissociation of complexes with lipids and melting of crystals with the assistance of added water or plasticizer induced to the formation of soluble starch or thermoplastic starch. Although thermoplastic starch (TPS) exhibit thermoplastic-like properties, it lacks in several properties than conventional thermoplastic, like low mechanical strength and have the tendency to absorb moisture. High water content and thermal degradation due to the chain cleavage are the limitations in TPS processing. Retrogradation process, caused by evaporation of water or plasticizer leads to the loss of film clarity and embrittlement. In order to overcome it, several approaches such as structural modifications have been tried to mitigate the shortcomings.

Most of modified starches are produced by chemical substitutions of the hydroxyl group attached to the starch molecules. Starch modifications, will greatly affect the characteristic of the final modified starch and consequently, product quality. Starch modification achieved through derivatization, such as etherification, esterification, cross-linking and grafting of starch. These modifications alter starch gelatinization, pasting and retrogradation behavior (Zhang et al., 2014). Starch modification by pre-gelatinization, such as the disintegration of the crystalline starch granules by heat, high pH or shear force to obtain water-soluble amorphous products. Modification of starch using carboxylic acid, such as malic acid, citric acid and ascorbic acid induced to acetylation process. Acetyl group reduced the hydrogen bonding formation between hydroxyl group of starch and water molecules, thus improved the water resistivity of the starch blends. According to Reddy and Yang (2010), citric acid also can act as crosslinker in starch film and improve the tensile strength of starch film approximately 150% higher as compared to non-crosslinking starch film. Filler either mineral filler or fiber, are also used as another approach to reinforce thermoplastic starch (TPS). The TPS/ fiber composite has shown great improvement in mechanical properties, gas barrier, water resistance and thermal stability. Others approach also performed to improve properties of thermoplastic starch (TPS) like chemical hydrolysis, surface treatment and additives.

Technically, various modification approaches can be performed onto TPS. Detduangchan and Wittaya (2011) had performed the study of photo-crosslinking on TPS. Addition of sodium benzoate as photo-initiator improved the tensile strength of the rice starch film. In addition, it improved the water vapour permeability, resulted in the crosslinking formation. Delville et al. (2003) and Detduangchan and Wittaya (2011) suggested the crosslinking process occurs due to the radical formation from the decomposition of sodium benzoate that initiated the radical formation of the starch backbone. Interest involved TPS modification without using additional initiator are increasing every year. Influence of ionizing radiation on the TPS properties was clearly stated by Henry et al. (2010), respectively. The solubility of native starch increase as increasing the dose range of the electron beam irradiation, directly resulted from the break of starch macromolecular chain. Increase in starch solubility improved the quality of the starch film formation as it decreases the irregularities formation in film thickness (Henry et al., 2010; Nagasawa et al., 2004). The analysis performed by Singh et al. (2011) and Shinshonok et al. (2007) showed that the crystallinity of starch granule decrease with the increase in irradiation dose. From the x-ray diffraction (XRD) analysis, the intensity of the peaks decreased due to decrease in the relative crystallinity of the starch granule. This results from the cleavage of amylopectin molecules, induced the free radical formation (Khandal et al., 2013; Singh et al., 2011; Henry et al., 2010).



## 1.2 Problem statements

Usage of conventional plastic induced to plastic waste. Conventional plastic difficult to dispose and it takes longer time to degrade. Awareness of plastic disposal induced to the further research in usage of biodegradable polymer. Starch becomes one of the promising biodegradable materials. Among varies type of starch, cassava starch was selected in this study due to large production and cheaper. Therefore in order to compromise the full usage of starch replacing the synthetic polymer, the cassava starch needs to undergo plasticization process. The plasticization process performed under the influence of plasticizer, such as glycerol, incorporated with cassava starch granule. The plasticizer acts as a lubricant, which induce facilitating the movement of starch macromolecule. Therefore, under controlled shear and temperature, the granular starch structure was disrupted and turn into a continuous melt phase. Based on Zhang et al. (2014), the addition of plasticizer allowed the property's transformation of the native starch granule either in physical or thermal properties. The amount of plasticizer influences the properties given to the thermoplastic starch (TPS), which neither the plasticization effect, nor antiplasticization effect to occur (Zhang and Han, 2010). Therefore, an extensive studies need to perform to clearly understand the effect of plasticizer on thermoplastic starch (TPS).



Generally, native starch exhibits strong hydrophilic properties, which mitigate the low mechanical properties of the thermoplastic starch (TPS). Nevertheless, strong intermolecular and intramolecular interaction between amylose and amylopectin cause the brittleness of the thermoplastic starch (TPS). Thus, it limits the full usage of thermoplastic starch in the general applications. Furthermore, the water absorption results in reduction of the thermoplastic starch (TPS) shelf-life and induce retrogradation of the TPS (Niazi and Broekhuis, 2015). In an attempt to overcome it, numerous studies had been performed. Influence of radiation, such as photo radiation and electron beam radiation, performed in the thermoplastic starch (TPS). In the study of photo radiation performed by Detduangchan and Wittaya (2011), and Zhou et al. (2008), showed the crosslinking formation in the thermoplastic starch (TPS) were influenced by the amount of photoinitiator and the irradiation energy. Moreover, at a different electron beam dose range, it gives differ physiocochemical, morphological and pasting properties of the irradiated starch (Nemtanu et al., 2007; Gani et al., 2013). In the recent review, the effect of the radiation treatments was focused more on the granular starch (Bhat and Karim, 2009). Therefore, less exposure on the properties of irradiated thermoplastic starch (TPS) is performed. In order to pertaining properties of irradiated thermoplastic starch (TPS), further research need to execute.

Apart from the radiation treatment, the other modification is chemical modifications. Chemical modification, involved the reaction of starch with chemical reagent, that induces to either hydrolysis nor crosslinking process (Zhu, 2015; Lewicka et al., 2015). This is due to the tendency of acid in hydrolyzing, promotes starch granules fragmentation and dissolution (Jiugao et al., 2005; Carvalho et al., 2005). Research perform by Reddy and Yang (2010) resulted in low acid concentration it provided relatively low improvement in mechanical properties compared to high concentration. It is stated that at low concentrations, there is a relatively low crosslinking formation. Meanwhile, at high concentration the tendency of crosslinking formation is higher. In order to fully understand the mechanism occurs between different acid concentration onto the starch, an extensive studies need to perform.

## 1.3 Objective of Research

This study was focused on the improvement in the properties of thermoplastic starch (TPS) by using physical and chemical modification. The specific objectives of this research are stated as following goals:

1) To characterize the properties of thermoplastic starch (TPS) in the presence of glycerol as plasticizer.

2) To investigate the effect of photo and radiation induced crosslinking on the mechanical and thermal properties of thermoplastic starch (TPS).

3) To analyse the effect of carboxylic acid treatment on the structural changes and mechanical properties of thermoplastic starch (TPS).

4) To analyse the biodegradability performance on acid modified thermoplastic starch (TPS).

## 1.4 Scope of study

This study has been divided into three stages as following:

Stage I involved modification of TPS via photo-induced crosslinking process, by using sodium benzoate (SB) as photo-initiator. This stage was focused on the photo irradiation time on the extent of the crosslinking process. To study the effect of TPS on the crosslinking mechanism, tensile test and TGA are performed to analyze the improved mechanical and thermal properties. Swelling test by using dimethyl sulfoxide (DMSO) is