



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

by

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TABLE OF CONTENT

	PAGE
THESIS DECLARATION	i
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	viii
LIST OF FIGURES	x
LIST OF ABBREVIATIONS	xvii
LIST OF SYMBOLS	xviii
ABSTRAK	xix
ABSTRACT	xx
CHAPTER 1 INTRODUCTION	
1.1 Background of study	1
1.2 Problem statements	5
1.3 Objective of research	8
1.4 Scope of study	8
CHAPTER 2 LITERATURE REVIEW	
2.1 Biopolymer	11
2.2 Starch	13
2.2.1 Cassava starch	17
2.2.1.1 Properties of Cassava starch	18

2.3 Thermoplastic starch	19
2.3.1 The role of plasticizer on TPS	22
2.4 Thermoplastic starch (TPS) modifications	24
2.4.1 Photo-induced crosslinking	26
2.4.1.1 Sodium benzoate as photo-initiator	28
2.4.2 Irradiation-induced crosslinking	30
2.4.3 Carboxylic acid modification	
2.4.3.1 Effect of low carboxylic acid concentration	31
2.4.3.2 Effect on high carboxylic acid concentration	34
2.4.3.3 Citric acid	35
2.4.3.4 Ascorbic acid	37
2.5 Biodegradation	38
CHAPTER 3 RESEARCH METHODOLOGY	
3.1 Introduction	40
3.2 Raw materials	41
3.3 Sample preparation	43
3.4 Polymer testing	53
CHAPTER 4 RESULT AND DISCUSSION	
4.1 Introduction	59
4.2 Preliminary study of Thermoplastic cassava starch (TPS)	
4.2.1 Fourier Transform Infrared (FTIR) Spectroscopy	60

4.2.2 High Performance Liquid Chromatography (HPLC)	61
4.2.3 Mechanical properties of Thermoplastic cassava starch (TPS)	63
4.2.4 Morphology analysis	65
4.3 Photo-induced crosslinking of Thermoplastic cassava starch (TPS)	
4.3.1 Fourier Transform Infrared (FTIR) Spectroscopy	66
4.3.2 Crosslinking density properties	70
4.3.3 Moisture absorption test	72
4.3.4 Effect on mechanical properties	74
4.3.5 Effect on morphology analysis	77
4.3.6 Effect on thermal analysis using TGA	79
4.4 Electron beam irradiation-induced crosslinking of Thermoplastic cassava starch (TPS)	
4.4.1 Fourier Transform Infrared (FTIR) Spectroscopy	83
4.4.2 Crosslinking density analysis	86
4.4.3 Moisture absorption test	88
4.4.4 Effect on mechanical properties	89
4.4.5 Effect on morphology analysis	92
4.4.6 Effect on thermal analysis using TGA	95
4.5 Chemical modification of Thermoplastic cassava starch (TPS)	
4.5.1 Fourier Transform Infrared (FTIR) Spectroscopy	98
4.5.2 Degree of substitution	101

4.5.3 High Performance Liquid Chromatography (HPLC)	103
4.5.4 Effect on mechanical properties	105
4.5.5 Effect on morphological analysis	108
4.5.6 Effect on thermal analysis using TGA	109
4.6 Acid induced crosslinking of Thermoplastic cassava starch (TPS)	
4.6.1 Fourier Transform Infrared (FTIR) Spectroscopy	114
4.6.2 Degree of substitution	119
4.6.3 Crosslinking density analysis	120
4.6.4 High Performance Liquid Chromatography (HPLC)	122
4.6.5 Effect on mechanical properties	124
4.6.6 Effect on morphology of Thermoplastic cassava starch (TPS)	127
4.6.7 Effect on thermal properties using TGA	128
4.7 Biodegradability performance on carboxylic acid modification Thermoplastic cassava starch (TPS)	
4.7.1 Moisture absorption test	133
4.7.2 Soil burial test	
4.7.2.1 Percentage of weight loss (% wl)	135
4.7.2.2 Optical microscopy	137
4.7.2.3 Fourier Transform Infrared (FTIR) Spectroscopy	140
4.7.2.4 High Performance Liquid Chromatography (HPLC)	143

CHAPTER 5	
5.1 Conclusion	147
5.2 Suggestion	149
REFERENCES	150
LIST OF PUBLICATIONS	162

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LIST OF TABLES

NO.		PAGE
2.1	Amylose content and granule size of starch	16
2.2	Composition of cassava starch powder	18
2.3	Physiochemical properties of glycerol at 20°C	23
3.1	Properties of glycerol	41
3.2	Properties of citric acid	42
3.3	Properties of ascorbic acid	42
3.4	Properties of sodium benzoate (SB)	43
3.5	Preparation of TPS with different of glycerol	44
3.6	Irradiation time of thermoplastic starch (TPS) under UV light	46
3.7	Dose range (kGy) for electron beam radiation thermoplastic starch (TPS)	49
3.8	Composition of thermoplastic starch (TPS) with citric acid (CA) and ascorbic acid (AA) at different content	51
4.1	Chromatogram data on thermoplastic cassava starch (TPS)	63
4.2	Thermal properties of photo-irradiated TPS under different irradiation time	80

4.3	Thermal properties of electron beam irradiation under different dose range	95
4.4	The value of substitution and degree substitution (DS) for modified TPS	101
4.5	Data from HPLC analysis with modified-TPS	103
4.6	TGA analysis data of chemical modification of TPS	110
4.7	The value of % of substitution and degree of substitution (DS)	120
4.8	The chromatogram data of acid induced crosslinking	123
4.9	Thermogravimetric analysis of acid induced crosslinking of TPS at different concentration	130
4.10	Chromatogram data on soil burial test	143

LIST OF FIGURES

NO.		PAGE
2.1	Structure of starch granule	14
2.2	Single helix of linear amylose chain	15
2.3	Chemical structure of branching amylopectin chain	15
2.4	Flow process of cassava starch production	17
2.5	Disruption of starch granules under heat and shear mechanism	20
2.6	Stages involve in the processing of thermoplastic starch	21
2.7	Structure of glycerol	23
2.8	Structure of sodium benzoate	29
2.9	Schematic representation of starch granule at different structural level	32
2.10	Structure of citric acid	36
2.11	Structure of ascorbic acid	37
3.1	Flow process of thermoplastic starch (TPS) preparation	45
3.2	Schematic of photo irradiation box	47
3.3	Flow process of photo-induced crosslinking of thermoplastic starch (TPS)	48

3.4	Flow process of irradiation induced crosslinking of thermoplastic starch (TPS)	50
3.5	Flow process of thermoplastic starch (TPS) modification via chemical modification	52
4.1	The FTIR spectrum of cassava starch granule and plasticized cassava starch (TPS)	61
4.2	Chromatogram of thermoplastic cassava starch (TPS)	62
4.3	The effect different plasticizer content on; (a) tensile strength, and (b) elongation at break of TPS	64
4.4	SEM micrograph of; (a) cassava starch granule and (b) thermoplastic cassava starch (TPS) with 35% glycerol	65
4.5	FTIR of photo-induced crosslinking at different irradiation time	67
4.6	Spectrum analysis of COO^- and C-C=C band	67
4.7	The formation of reactive radicals in sodium benzoate	68
4.8	The mechanism involves in photo initiated TPS	69
4.9	The relationship between the carboxylate group and irradiation time for TPS	70
4.10	Swelling degree of photo-irradiated TPS	72
4.11	Rate of moisture absorption for photo-induced crosslinking TPS	73
4.12	Effect of photo-irradiation time on; (a) tensile strength and (b) elongation at break (%) of TPS	76

4.13	SEM micrograph of TPS photo-irradiation at; (a) 0 min, (b) 30 min, (c) 60 min, (d) 120 min, (e) 240 min, (f) 360 min and (g) 480 min	79
4.14	Thermal analysis of; (a) thermogravimetric analysis and (b) derivative thermal analysis of TPS under different photo-irradiation time	82
4.15	FTIR spectrum of electron beam irradiated TPS at different dose range	84
4.16	FTIR spectra at corresponding peaks bands	84
4.17	Schematic structural in electron beam irradiation induced crosslinking	86
4.18	Swelling degree of electron beam irradiation TPS at different dose range	87
4.19	Rate of moisture absorption of electron beam irradiation TPS at different dose range	89
4.20	Effect of electron beam irradiation on; (a) tensile strength, and (b) elongation at break of TPS with different dose range	91
4.21	SEM micrograph of TPS irradiated under; (a) 0 kGy, (b) 25 kGy (c) 50 kGy, (d) 75 kGy, and (e) 100 kGy	94
4.22	Thermal analysis of; (a) thermogravimetric analysis, and (b) derivative thermal analysis, of TPS at different electron beam dose range	97
4.23	FTIR spectrum of TPS, CA2TPS and AA2TPS	99
4.24	Schematic hydrolysis mechanism at α -1,6-glycosidic linkage	99
4.25	FTIR spectrometry of corresponding peaks	100

4.26	Schematic esterification reaction of modification TPS, which R* exhibit for CA or AA group	101
4.27	The HPLC chromatogram of TPS, CA2TPS and AA2TPS	105
4.28	The effect of chemical modification on; (a) tensile strength, and (b) elongation at break of modified TPS	106
4.29	The SEM micrograph of; (a) TPS, (b) CA2TPS and (c) AA2TPS	109
4.30	The thermogram of; (a) TGA, and (b) DTG for TPS and acid modified-TPS	113
4.31	FTIR spectrum of acid induced crosslinking	115
4.32	FTIR spectrum in the peak range of 1600 cm ⁻¹ for acid induced crosslinking	115
4.33	Schematic structure of acid induced crosslinking of TPS	117
4.34	Relationship between carbonyl group with crosslinking formation	118
4.35	Normalized gel mass (NGM) of acid induced crosslinking TPS	121
4.36	Normalized swelling degree (NSD) of acid induced crosslinking TPS	122
4.37	The chromatogram of acid induced crosslinking modified-TPS	124
4.38	The effect of acid induced crosslinking of TPS on; (a) tensile strength, and (b) elongation at break at different acid concentration	125
4.39	SEM micrograph of acid induced crosslinking for; (a) 30% CA, (b) 40% CA, (c) 30% AA, and (d) 40% AA	128

4.40	The thermogram of; (a) TGA, and (b) DTG of acid induced crosslinking of modified-TPS	132
4.41	Rate of moisture absorption of TPS with chemical modification under RH=100%	134
4.42	Representative weight loss curve of TPS with modification TPS at different concentration and carboxylic acid	135
4.43	Biodegradation of; (a) and (b) TPS, CA modified TPS; (c) 2%, (d) 4%, (e) 30% and (f) 40%, and AA modified TPS; (g) 2%, (h) 4%, (i) 30% and (j) 40%, after 30 days	139
4.44	The FTIR spectrum of; (a) CA modified TPS, and (b) AA modified TPS after 30 days of biodegradation test	142
4.45	Carbonyl index of TPS and modified-TPS before and after 30 days of degradation process	142
4.46	The chromatogram of; (a) CA modified TPS, and (b) AA modified TPS after 30 days of degradation	146

LIST OF SYMBOLS

°C	Degree Celsius
%	Percentage
μm	Micrometer

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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 °C selama 10 minit. Jenis pengubahsuaian yang berlainan, iaitu radiasi cahaya, radiasi elektron, dan asid karbosilik telah digunakan untuk mengubahsuaikan 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/cm² dan 19.28 mg/cm², 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 divariasikan pada kuantiti dari 1% - 4%, dan 10% - 50%. Berdasarkan analisis SEM, penambahan asid karbosilik memberikan permukaan pematangan yang lebih sekata. Peningkatan di dalam kuantiti asid karbosilik juga merangsang pembentukan taut silang. Nilai NGM meningkat sehingga 49.00 mg/cm² dan 57.43 mg/cm², bagi kuantiti asid sitrik dan asid askorbik yang tinggi. Hasilnya, nilai tegangan pada 40% meningkat sehingga 6.25 MPa berbanding TPS yang tidak berubah suai. Analisis penyerapan lembapan juga menunjukkan kadar kerintangan kelembapan yang lebih baik berbanding dengan TPS yang tidak berubah suai. Ujian biodegradasi yang dilakukan menunjukkan pengubahsuaian TPS dengan asid memberikan kadar biodegradasi yang rendah berbanding dengan TPS yang tidak berubah suai. Ini kerana ia mempunyai kadar kerintangan kelembapan yang lebih baik, menyebabkan pengurangan 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 °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/cm² and 19.28 mg/cm², 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/cm² and 57.43 mg/cm², 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 different physicochemical, 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.