COMPOUNDING OF HIGH HEAT DISTORTION TEMPERATURE POLY(LACTIC ACID)

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การเตรียมพอลิ (แลคติก แอซิด) ผสมที่ให้ค่าอุณหภูมิการบิดงอสูง

นางสาวภวิษย์พร เกตษา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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COMPOUNDING OF HIGH HEAT DISTORTION TEMPERATURE POLY(LACTIC ACID)

Suranaree University of Technology has approved this thesis submitted in partial fulfillments of the requirement for a Master's Degree.

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ภวิษย์พร เกตษา : การเตรียมพอลิ (แลคติก แอซิด) ผสมที่ให้ค่าอุณหภูมิการบิดงอสูง (COMPOUNDING OF HIGH HEAT DISTORTION TEMPERATURE POLY(LACTIC ACID)) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.อุทัย มีคำ, 205 หน้า.

การศึกษาเบื้องต้นโดยใช้วิธีการเชิงสถิติ ที่เรียกว่าการทดลองแบบพหุคูณ(2^k) พบว่า ไซเลน พอลิออล และ กลีเซอรอล ทำให้ได้อัตราส่วนสูตรพอลิแลคติกแอซิดผสมที่เหมาะสม จากการทดลองเพิ่มเติมโดยการเติมไอโซไซยาเนตในพอลิแลคติกแอซิดผสมพบว่า คุณสมบัติเชิงความร้อน และ คุณสมบัติเชิงกลของพอลิเมอร์ผสมดีขึ้นเล็กน้อย การใช้ระบบสารก่อร่างแหระหว่างไวนิลไซเลน กับ ไดคิวมิลเปอร์ออกไซด์ในพอลิแลคติกแอซิดผสมจะพบว่า ความสามารถทางการไหลของพอลิเมอร์ผสมแบบร่างแหที่ได้มีค่าต่ำลงกับปริมาณสารไดคิวมิวเปอร์ออกไซด์ที่เติมลงไป ส่วนค่าอุณหภูมิการบิดงอ ค่าการทดสอบแรงดึง และ ค่าการทดสอบแรงกระแทกจะเพิ่มขึ้น การใช้ผงทาล์คัมเป็นสารตัวเติมในพอลิเมอร์ผสมแบบร่างแห พบว่าค่าอุณหภูมิการบิดงอของพอลิแลคติกแอซิดผสมที่เตรียมได้มีค่าสูงขึ้น ตามปริมาณของผงสารตัวเติม

การศึกษาคุณสมบัติของพอลิเมอร์ผสมระหว่างพอลิแลคติกแอซิดกับพอลิยูรีเทนที่เกิดจากปฏิกิริยาระหว่าง พอลิออล และ ไอโซไซยาเนต จะพบว่าค่าดัชนีการไหล ค่าอุณหภูมิการบิดงอ และ ค่าการทดสอบแรงดึง มีค่าลดลง แต่ ค่าการทดสอบแรงกระแทกมีค่าเพิ่มขึ้น ตามปริมาณสัดส่วนของพอลิยูรีเทนที่ผสมกับพอลิแลคติกแอซิด การศึกษาการอบแห้งชิ้นงานที่ผ่านการอบบ่มไอน้ำในตู้อบสุญญากาศ ของพอลิแลคติกแอซิดผสมพอลิยูเรเทน จะพบว่าการกำจัดความชื้นทั้งหมดออกจากชิ้นงานส่งผลให้ค่าดัชนีการไหลมีค่าลดลง ค่าอุณหภูมิการบิดงอมีค่าสูงขึ้น ส่วนค่าคุณสมบัติเชิงกลมีค่าลดลงเล็กน้อย ตามปริมาณพอลิยูรีเทนที่เพิ่มขึ้น สุดท้ายผลสรุปจากการศึกษาวิจัยพบว่า อุณหภูมิการบิดงอของ พอลิเมอร์ผสมระหว่างพอลิแลคติกแอซิด กับ พอลิออล ที่ใช้ระบบร่างแหของ เปอร์ออกไซด์ กับ ไซเลน ที่ผ่านการอบไล่ความชื้นชิ้นงานที่ผ่านการอบซาวน่ามาก่อนแล้ว มีค่าเท่ากับ 106°C โดยที่ผลการทดสอบค่าคุณสมบัติเชิงกลต่างๆ ไม่ได้ด้อยลงกว่าพอลิแลคติกแอซิด

สาขาวิชา วิศวกรรมพอลิเมอร์ ลายมือชื่อนักศึกษา ____________________
ปีการศึกษา 2555 ลายมือชื่ออาจารย์ที่ปรึกษา ____________________

PHAWITPHON KATESA : COMPOUNDING OF HIGH HEAT DISTORTION TEMPERATURE POLY(LACTIC ACID). THESIS ADVISOR : ASST. PROF. UTAI MEEKUM, Ph.D., 205 PP.

COMPOUNDING OF HIGH HEAT DISTORTION TEMPERATURE POLY(LACTIC ACID)

By using the statistical approach, 2^k factorial design of experiment (DOE), the optimization of silane, polyols and glycerol in PLA compound formula was found. Further exploring, glycerol was evidenced to enhance the flow ability and tensile properties of the compound when compare with neat PLA and the compound without glycerol PLA. Adding the reactive polymerization of poly(urethane) system; isocyanate, polyols and glycerol, in the PLA compound found that thermal properties was slightly increased with inferiority in mechanical properties. The vinyl silane/peroxide crosslink system was also investigated. It was found that the MFI was decreased but HDT, tensile and impact properties were increased with increasing the DCP concentration. In the talc filled PLA compound exploration, it experienced that higher heat resistance PLA compound was achieved by the addition of talc filler.

In the study of PLA/PU compound, the results reviewed that lower in MFI, HDT and tensile properties but fractionally higher in impact strengths when the amount of polyols in PLA/PU system was increased. Vacuum drying to remove the moisture residual derived from the sauna treatment of the samples showed the positive effect to MFI and HDT of the material at the given PU content. But it had the negative effect to the mechanical properties. Final verdict of the study concluded that the vacuum dried of the silane/DCP induced crosslinked PLA blended with polyols manifested the outstanding HDT at 106°C with no scarifying of other properties.

School of Polymer Engineering Student's Signature__________________

Academic Year 2012 Advisor's Signature__________________

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Phawitphon Katesa

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SYMBOLS AND ABBREVIATIONS

% = Percent

^{o}C = Degree celsius

mol = Mole

wt% = Percent by weight

phr = Part per hundred of rubber

rpm = Revolution per minute

hrs = Hours

min = Minute

wt/wt = Weight by weight

wt/v = Weight by volume

mm = Millimeter

g = Gram

kg = Kilogram

cm^3 = Cubic centrimeter

MPa = Mega pascal

GPa = Giga pacal

J = Joule

kN = Kilo newton

kJ/m^2 = Kilo joule per meter square

CHAPTER I

INTRODUCTION

1.1 General Introduction

Natural polymers, biopolymers, and synthetic polymers based on annually renewable resources are the basis for the twenty-first-century portfolio of sustainable, eco-efficient plastics. These biosourced materials will gradually replace the currently existing family of petroleum based polymers as they become cost wise and performance wise competitive. Polylactide or poly(lactic acid) (PLA) is the front runner in the emerging bioplastics market with the best availability and the most attractive cost structure. The production of the aliphatic polyester from lactic acid, a naturally occurring acid and bulk produced food additive, is relatively straightforward. PLA is a thermoplastic material with rigidity and clarity similar to polystyrene (PS) or poly(ethylene terephthalate) (PET). End used of PLA are in rigid packaging, flexible film packaging, cold drink cups, cutlery, apparel and staple fibre, bottles, injection molded products, extrusion coating, and so on. PLA is bio based, recyclable, and biodegradable under industrial composting conditions, in Figure 1.1 summarize the green life cycle of PLA.

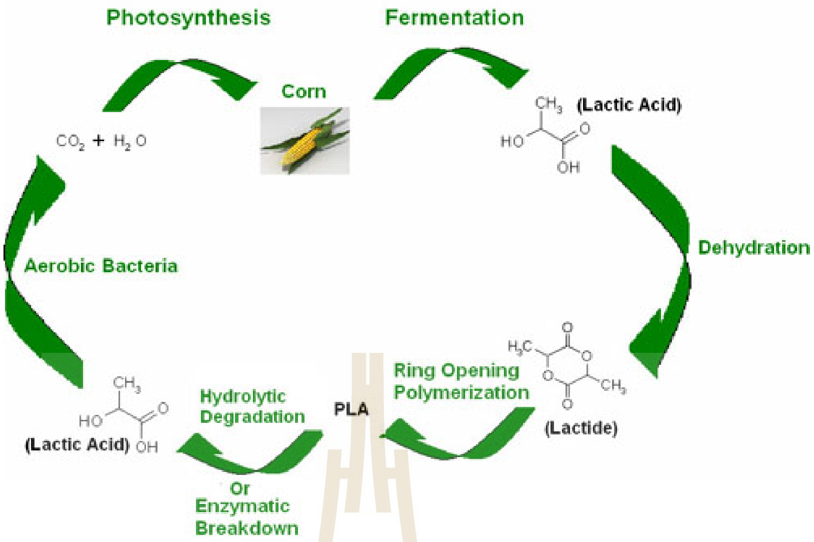
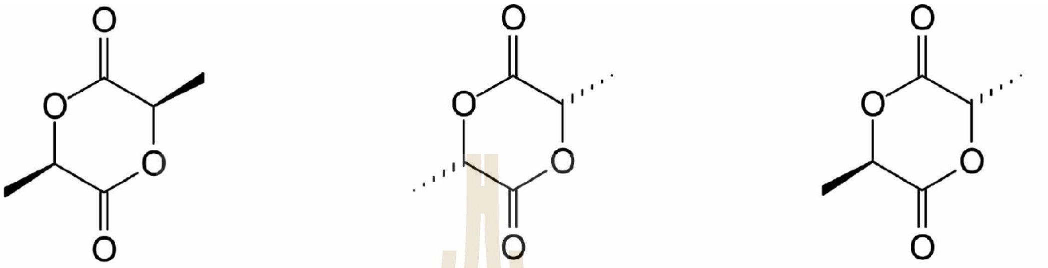


Figure 1.1 The PLA life cycle.

PLA can be produced by condensation polymerization from its basic building block lactic acid, which is derived by fermentation of sugars from carbohydrate sources such as corn, sugarcane, or tapioca. Processing, crystallization, and degradation behavior of PLA all depend on the structure and composition of the micro polymer chains, in particular the ratio of the L- to the D-isomer of lactic acid. This stereochemical structure of PLA can be modified by copolymerization of mixtures of L-lactide and meso-, D-, or rac-lactide resulting in high molecular weight amorphous or semicrystalline polymers with a melting point in the range from 130 to 185°C.

The dehydrated, cyclic dimer of lactic acid is commonly called lactide (3,6-dimethyl-1,4-dioxane-2,5-dione). Due to the two asymmetric carbon atoms in the molecule, lactide exists in three different forms as shown in Figure 1.2. In addition to the three diastereomeric structures mentioned below, also a racemate of D-lactide and L-lactide exists; rac-lactide or DL-lactide.



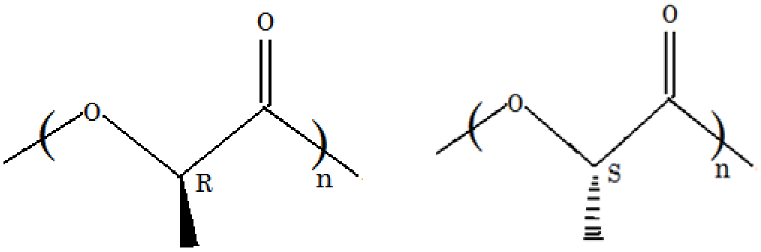
(*R*,*R*)-Lactide
or D-lactide

(*S*,*S*)-Lactide
or L-lactide

(*R*,*S*)-Lactide
or *meso*-lactide

Figure 1.2 The three diastereomeric structures of lactide (3,6-dimethyl-1,4-dioxane- 2,5-dione).

Isotactic PLLA homopolymer comprising L-lactide only is a semicrystalline material with the highest melting point, while PLA copolymers with higher D-isomer content exhibit lower melting points and dramatically slower crystallization behavior, until they finally become amorphous at D-form contents higher than 12–15%. PDLA and PLLA form a highly regular *trans* stereocomplex with increased crystallinity. PDLA acts as a nucleating agent, thereby increasing the crystallization rate. PDLA has the useful property of being optically transparent, Figure 1.3 shown the structure of PDLA and PLLA (ChemVista.net).



Poly(D-Lactide): (PDLA) Structure
(semicrystalline)

Poly(L-Lactide): (PLLA) Structure
(semicrystalline)

Figure 1.3 The structure of Poly(D-Lactide) and Poly(L-Lactide).

However, PLA is poor heat stability and mechanical properties that have limited its range of applications. Also, PLA is easily degraded under high humidity condition. Due to this easy hydrolysis of PLA under high humidity conditions, the thermo mechanical properties of PLA are easily degraded, which limits its usefulness in many applications.

1.2 Properties Improvement of PLA

Many technologies, such as annealing, adding nucleating agents, forming composite with fibre or nanofillers, chain extending and introducing crosslink structure were effectively proved for enhancing the heat stability or mechanical properties of PLA materials (Yang, Wu, Yang, & Yang, 2008). Crosslinking is a widely used method for the modification of polymer properties. This process involves the formation of three dimensional structures or gels that cause substantial changes in material properties. Crosslinked PLA is one of significant interests as well. By introducing crosslinked chains into PLA structures, physical properties such as rheological, crystallinity and thermal properties, e.g., melting temperature, and certain mechanical properties; the modulus, tensile strength and elongation at break, will be affected. Furthermore, the creep resistance and high temperature dimensional stability are in general improved by introducing the network structure. The characteristics of biodegradation and hydrolytic degradation will also be influenced. These properties are very important in actual applications. The crosslinked structure of PLA can be initiated either in the melt via thermal decomposition of peroxides or in the solid state through high energy irradiation. Chemical crosslinking was also introduced via chemical treatment of the melt by adding small amounts of crosslinking agent.

The crosslink structures of PLA can be formed by irradiation and chemical crosslinking as shown in Figure 1.4. In irradiation processes of PLA materials such as electron beam exposure, gamma-radiation, or UV light, the radiation apparatus is normally expensive and the PLA products must be in the form of thin plates so as to get enough energy from the radiation to initiate the networking reactions, which significantly limits the practical application of this method.

Chemical crosslinking is another possible way to introduce the web structures for PLA. Some chemical reactions between the crosslinking agent and the polymer chains can be initiated by chemical treatments without irradiation (Yang et al., 2008). Among the crosslinking method, Silane grafting and then water condensation have received much attention in recent years, not only for industrial applications but also in fundamental research. Because of its various advantages include easy processing, low capital investment, and favorable properties in the processed materials. Silane/water crosslinking is considered as a good candidate for chemically modified the PLLA to give a better thermo mechanical properties and hydrolysis resistance without sacrificing its valuable biodegradation properties.

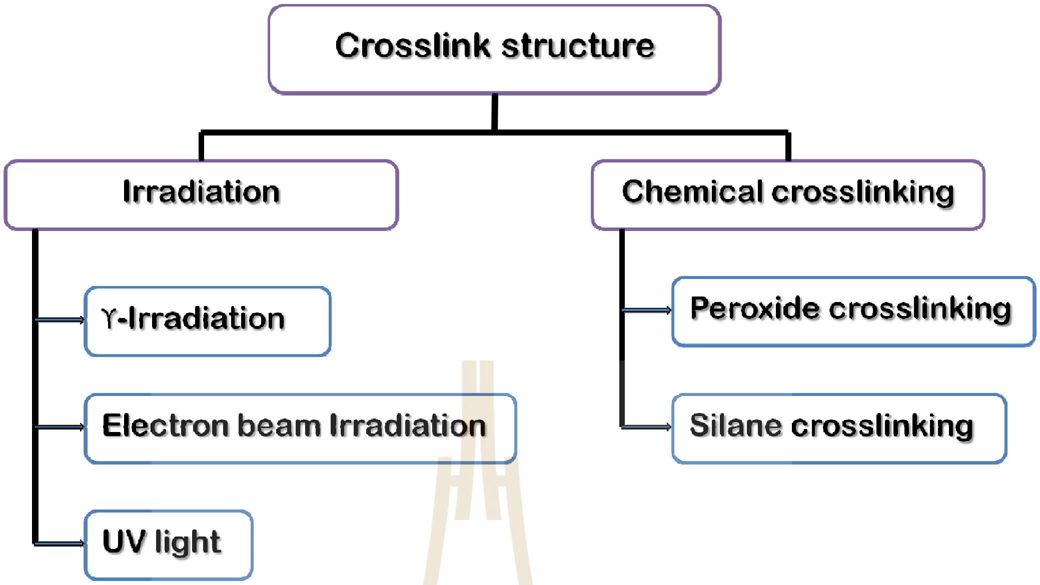


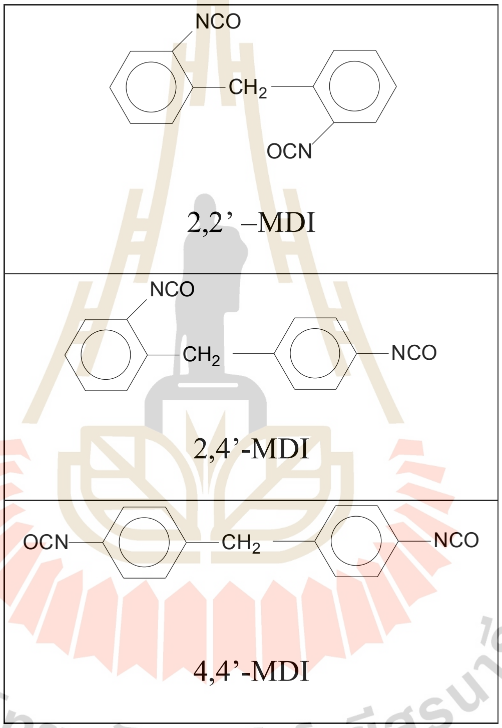
Figure 1.4 Techniques used for crosslinking of PLA.

Plasticizers are widely used to improve the processability, flexibility and ductility of glassy polymer. In this present, polyester polyols together with glycerol were studied as plasticizer in PLA compounding system. Methylene diphenyl diisocyanate (MDI) was added as chain extending and talc was employed as filler. In polymer chemistry, polyols are compounds with multiple hydroxyl functional groups available for organic reactions such as esterification with acid.

Glycerol or glycerin is a simple polyols compound. It is a colorless, odorless, low viscous liquid. It has low molecular weight of 92.1 g/mol and melting point of 17.8°C. It is commonly lower the glass transition temperature, T_g, of PLA.

Talc is a mineral clay composed of the hydrated magnesium silicate with the chemical formula as $H_2Mg_3(SiO_3)_4$ or $Mg_3Si_4O_{10}(OH)_2$.

Methylene diphenyl diisocyanate (MDI) is an aromatic diisocyanate which is less toxic than toluene diisocyanate (TDI). It exists in three isomers, 2,2'-, 2,4'-, and 4,4'- forms, but the 4,4' isomer is most widely used because the group at the 4-position is approximately four times more reactive than the group at the 2-position. The three structure isomer of MDI as shown in Figure 1.6.



Molecular formula : $C_{15}H_{10}N_2O_2$

Figure 1.5 The structures of methylene diphenyl diisocyanate (MDI).

1.3 Research Objectives

The prime objective of this research is to modify PLA through chemical approach and material compounding for improving the polymer properties especially thermal resistance by mean of HDT. The statistical method by mean of the experiment design was also used. The main objectives of the research work could be classified as follow;

(1) To study the influence of the composition parameters on the properties of non free radical initiated crosslinked PLA compound.

(2) To investigate the effect of compound ingredient on the properties of free radical initiated crosslinked PLA compound.

1.4 Scope and Limitation of the Study

There are two main itineraries of study in this research work; non free radical and free radical initiated crosslinked PLA compound that aim for manufacturing the plastic product with high heat resistance and dimensional stability via injection molding process. Dicumyl peroxide (DCP) was employed as free radical initiator. The number of silanes were used as coupling agent and also acted as post processed crosslink agent via the silane/water condensation reaction through sauna incubation. Polyester polyols and glycerol were added into compound ingredient as active plasticizers. Methylene diphenyl diisocyanate (MDI) as chain extender and talc as filler for cost reduction and mechanical and thermal improver were incorporated in PLA compound. The mechanical properties by means of tensile, impact, heat distortion temperature (HDT) testing and morphological investigation of the compound were also revealed.

CHAPTER II

LITERATURE REVIEW

2.1 General Background

PLA is one of the most promising biodegradable polymers and is expected to substitute some of the non-biodegradable engineering plastics. However, the poor thermal stability and mechanical properties limited its applications. Many technologies, such as annealing, adding nucleating agents, forming composite with fibre or nanoparticles, chain extending and introducing crosslink structure were effectively proved for enhancing the thermal stability or mechanical properties of PLA materials (Yang, Wu, Yang, & Yang, 2008).

In this chapter, the previous works related to the properties improvement of PLA are briefly discussed

2.2 Basic Principle of Polymer Crosslink Reaction

Crosslinking is one of the widely used methods for the modification of polymer properties. The process involves the formation of three dimensional structures or gels causing substantial changes in material properties. The most common examples of the crosslinking applications involve polyolefin and thermosetting resins (Han et al.). Crosslinking provides an important method to improve the thermal and chemical resistance of polyolefins. Three crosslinking methods; irradiation, peroxide and silane crosslinking, are commonly employed.

Among the networking processes, silane induction is cost effective and easily to operate. In production of silane crosslinked polyolefins, peroxide, silane (eg vinyltrialkoxy silane) and polyolefins are mixed by a melt process. During the process, the silane is grafted onto the backbones of polyolefins via free radicals reaction. The silane grafted polymers are then hydrolyzed and crosslinked by forming Si–O–Si linkages (Wang, Wu, Gui, Hu, & Fan, 2005).

Wang, Wu, Gui, Hu and Fan (2005) studied silane crosslinked polypropylene (PP). Starting from grafting of silane onto the PP backbone via melt process and then the chain were crosslinked in warm water. The reaction mechanism of silane grafted and crosslinked PP is shown in Figure 2.1. The effects of type and concentration of silane and peroxide on the silane grafting on PP were investigated. The thermal behavior of the silane crosslinked PP was studied by thermogravimetric (TGA). The results show that PP prepared via silane crosslinking increased its thermal stability greatly. DSC measurements the crystallization temperatures indicated that the onset temperature and peak temperature of the exotherm of the silane crosslinked PP was increased when compared with those of the pure PP. The silane crosslinking hardly changes the degree crystallinity of PP (Wang et al., 2005).

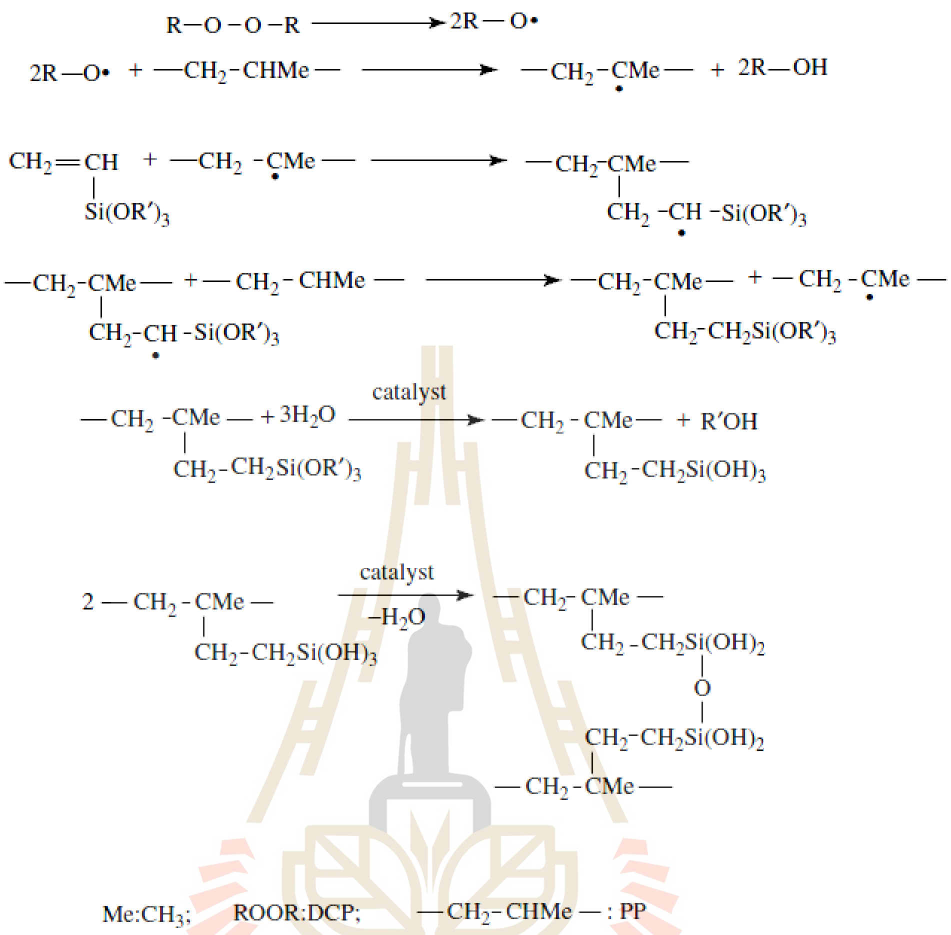


Figure 2.1 Reaction scheme of the silane-grafted and crosslinked PP, R-O-O-R represents DCP, so R represents $–C(CH_3)_2C_6H_5$ (Wang et al., 2005).

Hu, Wang, Qu, & Hu (2006) investigated free radical grafting of vinyltrimethoxysilane (VTMS) onto isotatic polypropylene (*i*-PP) in vapour phase. Its degree of grafting increased with increasing DCP and monomer concentration. The grafting of VTMS inhibited the degradation of PP to some extent in comparison with the DCP modified PP. But when the initiator concentration was high, the inhibition became minor. The thermogravimetric (TG) results showed that the thermal stability of the silane crosslinked PP increased and the stability of the DCP modified PP decreased in comparison with that of the pure PP (Hu, Wang, Qu, & Hu, 2006)

Han et al. (2007) reported that poly (ε-caprolactone) (PCL) was chemically crosslinked with various amounts of benzoyl peroxide (BPO) by two step method; first evenly dispersing the BPO into the PCL matrix and then crosslinked at elevated temperature. The gel fraction increased with an increase in BPO content. The melting temperature and crystallinity decreased with an increase in BPO content, and the crystallization temperature increased after crosslinking. Dynamic mechanical analysis results showed a decreased in the glass transition temperature as a result of chemical crosslinking of PCL. This was explained by the reduction in crystallinity and the increase in free volume due to restrictions in chain packing. Moreover, Young's modulus and elongation at break generally decreased with an increase in BPO content, but the tensile strength first increased with BPO content up to 1.0 wt%, reached a maximum, and then decreased.

Bengtsson & Oksman (2006) researched to produce silane crosslinked wood plastic composites in a compounding process. Silane induced crosslink structure is one way to improve the mechanical and long term properties of wood plastic composites. Silane crosslinked composites with different amounts of vinyltrimethoxy silane were produced in a compounding process using a co-rotating twin-screw extruder. The composites were stored in a sauna and at room temperature to study the effect of humidity on the degree of crosslink. Gel content and swelling experiments showed that the highest degree of crosslink was found in the composites stored in a sauna. The crosslinked composites showed toughness, impact strength and creep properties superior to those composites which no silane was added. The flexural modulus, on the other hand, was lower in the crosslinked samples than in the non-crosslinked ones. Differential scanning calorimetry measurements of the composites showed a lower crystallinity in the crosslinked samples than in the non-crosslinked. Processing of the crosslinked composites was found to be more difficult than processing of the non-crosslinked composites. At a higher level of silane addition, edge tearing became a problem and the extruded profiles got a rougher surface. The degree of crosslink in the composites was significantly increased after curing in a high humidity sauna at 90°C. An addition of at least 4% w/w silane solution during processing was necessary to fully crosslink the composites in the sauna within 48 h. Flexural testing showed that the toughness of the silane crosslinked composites was significantly higher than for the non-crosslinked composites. The flexural strength of the crosslinked composites reached a maximum between 2% and 3% w/w of added silane and then decreased with further addition of silane. The flexural modulus was lower in the crosslinked composites than in the non-crosslinked ones. This was explained as a result of the lower crystallinity of the polyethylene matrix in the crosslinked wood. Impact testing showed that the impact strength of the crosslinked sample was considerable higher than the non-crosslinked composites. Moreover, short term creep analysis showed that creep response in the crosslinked composites was significantly lower than in the non-crosslinked composites. There was a good correlation between the creep response and the degree of crosslinking in the composites where a higher degree of crosslinking in the composites corresponded to a lower creep response. This study provides a basis for proposing that an addition of 4% w/w or more of silane solution during processing is necessary to fully crosslink the composites in a high humidity sauna. Considering the flexural strength and stiffness of the composites, an optimum addition of silane solution is in the range of 2–3% w/w. On the other hand, if a low creep response in the composites is of the first priority, an addition of silane solution at 4% w/w is preferable.

2.3 Crosslinking of PLA

2.3.1 Radiation crosslinking

The radiation induced crosslinking of PLLA in the presence of triallyl isocyanurate (TAIC) as a crosslinking co-agent was first investigated by Jin et al. Crosslinking of PLLA started at low TAIC contents and low γ-ray dosage. DSC and dynamic mechanical thermal analysis revealed that PLLA was completely crosslinked at high weight ratios of TAIC and high γ-ray doses (Jin, Hyon, Iwata, & Tsutsumi, 2002).

Mitomo, Kaneda, Quynh, Nagasawa and Yoshii (2005) confirmed the radiation induced crosslinking of PLLA in the presence of TAIC and at the same time reported an improvement of the thermal stability and retarded enzymatic degradation of PLLA with radiation induced crosslinking.

Jia et al. (2009) enhanced the stability of plasticized poly (L-lactic acid) (PLLA) with poly(ethylene glycol) (PEG) as it is necessary for its practical application. In that study, plasticized PLLA at PLLA/PEG 80/20 wt/wt was crosslinked under γ-ray (Co^{60}) in the presence of triallyl isocyanurate (TAIC) as crosslinking agent. Experimental results indicated that the crystallization behaviors of both PEG and PLLA in the blends were restrained after irradiation. Mechanical properties of the plasticized PLLA were strengthened through crosslinking. Both yield strength and elastic modulus of the samples increased after crosslinking. Elongation at break of the crosslinked plasticized PLLA decreased with the increase of crosslinking density but remained a high value over 200%. SEM images of fracture surfaces confirmed that the ductile fracture behavior of plasticized PLLA was sustained after suitable crosslink reaction.

2.3.2 Peroxide crosslinking

The peroxide crosslinking of PLLA with dicumyl peroxide (DCP) can be prepared. At high peroxide concentration (13–25 wt%) and high curing temperatures (192^{o}C), a gel fraction equal to 1 could be determined gravimetrically (Nijenhuis, Grijpma, & Pennings, 1996).

Yang, Wu, Yang and Yang (2008) published chemical crosslinking of PLLA via chemical treatment of the melt by adding small amounts of crosslinking agent triallyl isocyanurate (TAIC) and DCP. The results showed that the crosslinked PLLA resulted in a decrease of crystallinity and a significant improve of the thermal degradation initiation and completion temperatures.

2.3.3 Silane crosslinking

Han et al. studied a silane grafting and water crosslinking approach to develop the crosslinked poly(L-lactide) (PLLA) by grafting vinylalkoxysilane onto PLLA using dicumyl peroxide, followed by silane hydrolysis to form siloxane linkages between PLLA chains. Crosslinked PLLA films were obtained by curing of silane grafted PLLA in hot water. Various techniques were used to investigate the effect of silane/water crosslinking on the thermomechanical properties, hydrolysis resistance and biodegradation of PLLA. In addition to an improvement in thermal stability and mechanical properties, hydrolysis resistance was significantly enhanced as a result of silane/water crosslink of PLLA. Moreover, the biodegradation of silane/water crosslinked PLLA was retarded compared with neat PLLA (Han et al. 2010).

In this process, vinylalkoxysilanes are first grafted onto a polymer backbone, followed by alkoxysilane hydrolysis (–Si–OH) and then siloxane (Si–O–Si) linkages are formed between polymer chains. A proposed mechanism of the silane-grafting and water-crosslinking processes for PLLA is shown in Figure 2.2.

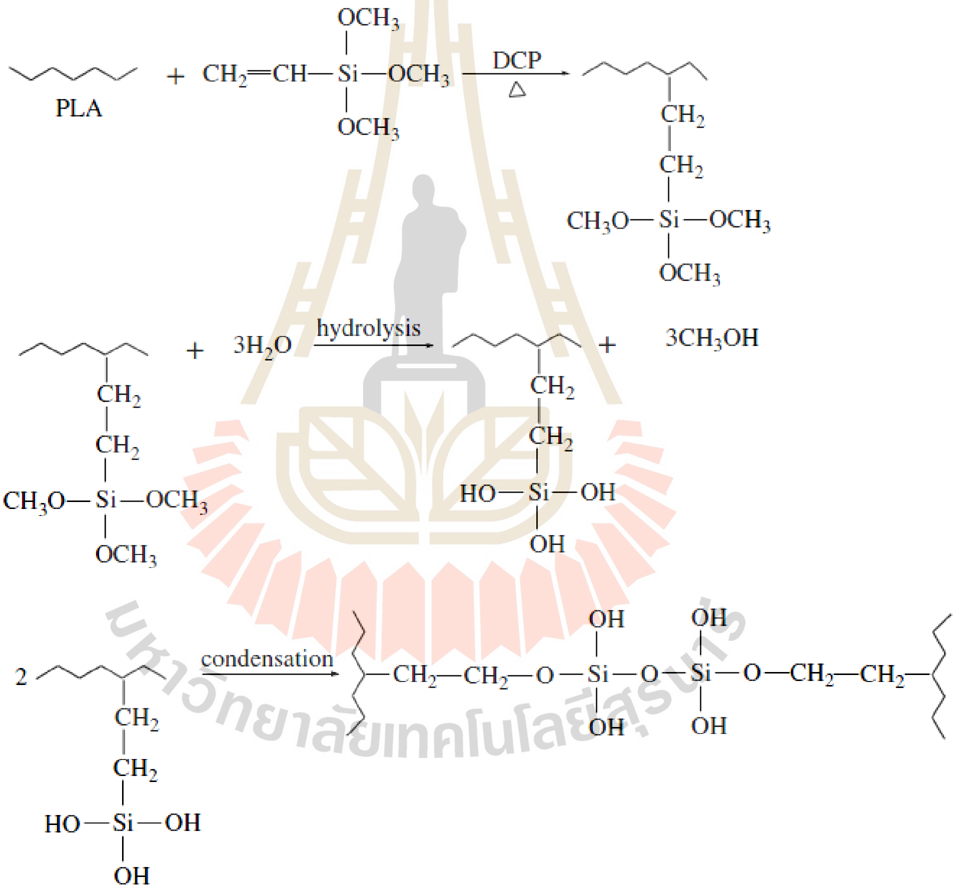


Figure 2.2 Proposed mechanism of silane grafting and water crosslinking process (Han et al., 2010).

From the works reviewed, the crosslink structure can improve properties of PLA. The crosslink structure introduced to PLA backbones by many methods. Each method had different advantages. In this study, introduction of crosslink structure by silane/moisture crosslink was explored. This method is economically advantageous because it carries out in the melt state with only low amounts of silane and no extra purification step and special apparatus is necessary.

2.4 The Effect of Plasticizer on PLA

PLA is a promising biodegradable polymer. However, because of its inherent brittle behavior, Martin & Avérous (2001) blended PLA with varies low molecular weight plasticizers. The efficiency of respective plasticizers was investigated through DSC and mechanical determinations. Glycerol was found to be the least efficient plasticizer. Thermal analysis demonstrated that oligomeric lactic acid (OLA) and the lower molecular weight polyethylene glycol (M_w = 400 g/mol, PEG400) gave the best results. The glass transition temperature decreased from 58 to 12^{o}C and 18^{o}C for 20 wt% of PEG400 and OLA, respectively. Thermal analysis also revealed the depression of the melting point temperature of about 10-15^{o}C. The elastic modulus was seen to decrease as the concentration of plasticizer increased. In the meantime, elongation at break reached up to 200% in the rage of concentration tested, 10 and 20 wt%.

Baiardo et al. (2003) studied Acetyl tri-n-butyl citrate (ATBC) and poly-(ethyleneglycol) (PEGs) with different molecular weights, from 400 to 10000, were used to plasticize poly(L-lactic acid) (PLA). Both ATBC and PEG were effective in lowering the glass transition (T_g) of PLA up to a given concentration, where the plasticizer reaches its solubility limit in the polymer, 50 wt % in the case of ATBC; 15–30 wt %, depending on molecular weight, in the case of PEG. The range of applicability of PEGs as PLA plasticizers was given in terms of PEG molecular weight and concentration. The mechanical properties of plasticized PLA change with increasing plasticizer concentration. The elongation at break drastically increased, whereas tensile strength and modulus decreased. This behavior was occurred at a plasticizer concentration that depends on the T_g-depressing efficiency of the plasticizer.

Ljungberg & Wesslén, (2002) investigated poly(lactic acid) (PLA) blended with five plasticizers; triacetine, tributyl citrate, acetyl tributyl citrate, triethyl citrate, and acetyl triethyl citrate, respectively, in a batchwise mixer and pressed into films. Triacetine and tributyl citrate were proved to be effective as plasticizers when blended with PLA. The glass transition temperature of PLA decreased linearly as the plasticizer content was increased. Both plasticizers were miscible with PLA to an extent of approx. 25 wt %. At this point, the PLA seemed to be saturated with plasticizer and the blends tended to phase separate when more plasticizer was added. There were also signs of phase separation occurring in the samples heated at 35, 50, and 80°C, most likely because of the material undergoing crystallization. The presence of the plasticizers induced an increased in crystallinity by enhancing the molecular mobility.

The tensile strength and thermal stability of polylactide (PLA) were significantly improved through chemical crosslink. However, it became much more rigid and brittle. To obtain a material with good thermal stability and enhanced ability to plastic deformation, Yang, Wu, Meng, & Yang, (2009) studied chemical crosslinked PLA with 0.5 wt % triallyl isocyanurate and 0.5 wt % dicumyl peroxide by blending with different contents of dioctyl phthalate (DOP). The advantage of using DOP is that it does not crystallize, has low glass transition temperature, and is miscible with PLA. The results showed that the DOP was an effective plasticizer for the chemical crosslinked PLA, resulting in a significantly decreased in T_g, lower yield stress, and improved elongation at break. The plasticization effect was enhanced by adding higher DOP content. In addition, the DOP enhanced the crystallinity of crosslinked PLA, and all the crosslinked samples showed better thermal stability than neat PLA. The apparent viscosity of the blends decreased with the increase of DOP content and a phase separation occurred when the content of DOP exceeded 12.5 wt %.

2.5 The Effect of MDI as Chain Extender on PLA

Li & Yang (2006) studied the thermal and mechanical properties of biodegradable poly(L-lactic acid) (PLA). The properties of the polymer were improved by reacting with 4,4-methylene diphenyl diisocyanate (MDI). The results showed that when the molar ratio of –NCO of MDI to –OH of PLA was 2:1, the T_g value can be increased to 64°C from the original of 55°C, and the tensile strength increased from 4.9 to 5.8 MPa. It demonstrated that by reacting PLA with MDI at an appropriate portion, both the thermal and mechanical performance of PLA can be increased.

Methylenediphenyl diisocyanate (MDI) was used as the chain extender for low molecular weight poly(lactic acid) (PLA) to produce high molecular weight biodegradable polymer material with a better heat resistance. Zhong et al. (1999)

reported that PLA prepolymer with a number average molecular weight (M_n) of 5800 and a weight average molecular weight (M_w) of 9800 was produced by direct polycondensation using stannous octoate as the catalyst. After 40 min of chain extension at 175°C, the resulting polymer had a M_n of 15,000 and a M_w of 57,000. The glass transition temperature (T_g) of the low molecular weight PLA prepolymer was 48.6°C. After chain extension, the T_g of the resulting polymer was raised to 67.9°C, as determined by DSC. DMA results also indicate that the heat resistance was improved by the chain extension. The DSC and X-ray diffraction pattern of annealed samples showed that both the crystallinity and rate of crystallization of PLA were lowered by chain extension reaction due to the formation of branched molecular structure.

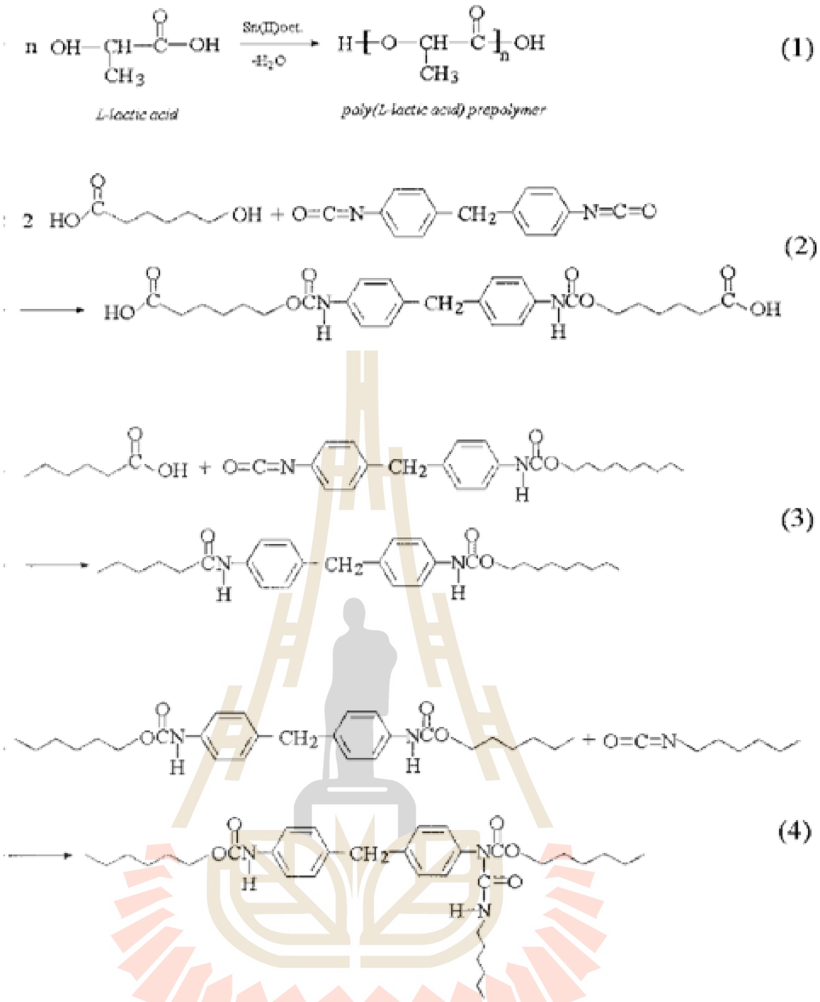


Figure 2.3 The synthesis scheme of the PLA prepolymer and the PLA chain extended with MDI (Zhong et al., 1999).

The PLA prepolymer was synthesized using stannous octoate as the catalyst according to reaction (1) shown in Figure 2.3. After chain extending at 175°C for 40 min, the reaction product was collected and analyzed. It suggested that diisocyanate can connect the hydroxyl end groups of PLA molecules through urethane bonds so as to double the molecular weight as shown in reaction (2) of Figure 2.3. The excess amount of the isocyanate group may also react with the other end of PLA molecule

(—COOH) to form amide linkage according to reaction (3) of Figure 2.3 or react with the urethane group known as an allophanate reaction to cause chain branching or crosslink reaction (4).

2.6 The Effect of Fillers on PLA

Harris & Lee (2008) investigated the overall crystallization rate and final crystallinity of PLA. They found that the crystallinity was controlled by the addition of physical nucleating agents as well as optimization of injection molding processing conditions. Talc as a nucleating agents showed dramatic increases in crystallization rate and final crystalline content as indicated by isothermal and nonisothermal crystallization measurements. Isothermal crystallization halftimes were found to decrease nearly 65 folds by addition of only 2% talc. Process changes also had a significant effect on the final crystallinity of the molded neat PLA, which was shown to increase from 5 to 42%. The combination of nucleating agents and process optimization not only resulted in an increase in final injection molded crystallinity level, but also allowed for a decrease in processing time. An increase of over 30^{o}C in the heat distortion temperature and improved strength and modulus by upwards of 25% were achieved through these material and process changes.

Li & Huneault 2007) investigated different strategies to promote PLA crystallization with the objective of increasing the crystalline content under typical polymer processing conditions. The effect of heterogeneous nucleation was assessed by adding talc, sodium stearate and calcium lactate as potential nucleating agents. The PLA chain mobility was increased by adding up to 10 wt% acetyl triethyl citrate and polyethylene glycol as plasticizers. The crystallization kinetics was studied using

DSC analysis under both isothermal and non isothermal conditions. The isothermal data showed that talc was highly effective in nucleating the PLA in the 80-120^{o}C temperature range. The non isothermal data showed that the combination of nucleant and plasticizer was necessary to develop significant crystallinity at high cooling rates. The nucleated and/or plasticized PLA samples were injection molded and the effect of mold temperature on crystallinity was determined. It was possible to mold the PLA formulations using mold temperatures either below 40^{o}C or greater than 60^{o}C. At low temperature, the molded parts were nearly amorphous while at high mold temperatures, the PLA formulation with proper nucleation and plasticization was shown to achieve crystallinity levels up to 40%, close to the maximum crystalline content of the material. Talc was an effective nucleating agent while calcium lactate and sodium stearate had little or no nucleating ability. Polyethylene glycol (PEG) and acetyl triethyl citrate (ATC) were shown to be efficient plasticizers that increased the achieved crystallinity even at high cooling rates when used in combination with talc. The room temperature tensile mechanical properties were only slightly affected by plasticizer content and crystalline content when 0, 2, 5% plasticizer was used. In fully crystallized formulation that contained 10% plasticizer, the ductility of the material increased dramatically. This effect was explained by a high plasticizer concentration in the amorphous phase. In all cases, the crystallized PLA formulations showed higher temperature resistance than the unmodified PLA controls.

Fowlks & Narayan worked on poly(lactic acid) (PLA) talc composites which were reactively compatibilized using maleic anhydride functionalized PLA (MAPLA) as an interfacial additive. The incorporation of MAPLA contributed to an increase in the crystallinity of PLA in the composites, and when added in an optimal concentration, it showed the improvement of tensile strength. Thermo mechanical measurements indicated the reinforcement effect of the talc and the coupling effect of the MAPLA inclusion. Overall, that investigation provided experimental evidence of enhanced adhesion at the interface, which was believed to be due to the MAPLA addition. A maleic anhydride grafted PLA was employed as an interfacial modifier in PLA/talc composites. Investigation of the mechanical and morphological properties of the composites provided experimental evidence of increased adhesion at the interface between the PLA matrix and the talc filler. That data indicated the existence of a critical value, beyond which no more improvements occurred, as reflected by a sudden decrease in tensile strength. Thermo mechanical properties confirmed this critical value to be at 5% MAPLA. In spite of the improved interfacial coupling with the maleated PLA addition, the elongation at break remained very low, due to the inherent behavior of PLA and the increased in crystallinity of the matrix.

Huda, Drzal, Mohanty, & Misra (2007) evaluated the effect of the addition of silane treated and untreated talc as the fillers on the mechanical and physic mechanical properties of poly(lactic acid) (PLA)/recycled newspaper cellulose fibers (RNCF)/talc hybrid composites. For that purpose, 10 wt% of a talc with and without silane treatment were incorporated into PLA/RNCF at 60wt%/30 wt% composites that were processed by a micro-compounding and molding system. In that work, the flexural and impact properties of PLA/RNCF composites improved significantly with the addition of 10 wt% talc. The flexural and impact strength of these hybrid composites were found to be significantly higher than that made from either PLA/RNCF. The hybrid composites showed improved properties such as flexural strength of 132 MPa and flexural modulus of 15.3 GPa, while the unhybridized

PLA/RNCF based composites exhibited flexural strength and modulus values of 77 MPa and 6.7 GPa, respectively. The DMA storage modulus and the loss modulus of the PLA/RNCF hybrid composites were found to increase, whereas the mechanical loss factor , tan δ, was found to decrease. The storage modulus increased with the addition of talc, because the talc generated a stiffer interface in the polymer matrix. Differential scanning calorimetry (DSC) thermograms of neat PLA and of the hybrid composites showed nearly similar glass transition temperatures and melting temperatures. Scanning electron microscopy (SEM) micrographs of the fracture surface of notched Izod impact specimen of 10wt% talc filled PLA/RNCF composite showed well filler particle dispersion in the matrix and no large aggregates are present. The comparison data of mechanical properties among samples filled with silane treated and untreated talc fillers showed that the hybrid composites filled with silane treated talc displayed the better mechanical prosperities relative to the other hybrid composites.

As the review of the publications for improvement of PLA properties by any means, there is no evidence that the thermal properties by mean of HDT of PLA and/or PLA compound can exceed the temperature above 100°C. Going to this temperature boundary with retaining the mechanical properties can broaden the applications of this polymer such as high temperature resistance packaging. In accordance, the prime goal for this research work will be the exploring of the possibility of fabricating the PLA/compound that can retain its properties at temperature above 100°C where hot filling and packing can be accomplished.

CHAPTER III

EXPERIMENTAL METHODOLOGY

3.1 Materials

Table 3.1 summarizes the reagents used and their function on compounding process in this study. The extrusion grad poly(lactic acid) (PLA), 2002D, with a density of 1.24 g/ml was purchased from Nature Works®. The silanes, *gamma*-aminopropyltriethoxysilane, Silquest A-1100, APS, and Vinyltrimethoxysilane, A-171, VTMS, manufactured from Crompton Corporation was individually used as coupling agent. Aliphatic polyester polyols, Rayelast A 8770 is available from IRPC Polyol Co., Ltd, and used as processing aid and plasticizer. Commercial grad glycerol was employed as plasticizer. Methylene diphenyl diisocyanate (MDI), Suprasec® 2020, as a chain extender from Huntsman Polyurethanes was added into compound ingredient. Dicumyl peroxide (DCP) was employed as initiator in free radical initiated process. Talc, JetFine 3CA , particle size of 1.1 µm was engaged as filler and manufactured by Luzenac company. The solid blend between Tris(2,4-ditert-butylphenyl) phosphate, Irgafos 168, and Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, Inganox 1076, at weight ratio of 1:1 was incorporated as heat/processing stabilizer. They were supplied from Ciba Specialty Chemicals Corporation. The structure and properties given by manufacturer of the chemicals used in this research work are shown in Figures 3.1-3.3 and Tables 3.2-3.7, respectively.

Table 3.1 The summarization of the reagents and their function in PLA compound.

Chemical Name	**Trade name**	**Function**
3-aminopropyltriethoxysilane (APS)	A-1100	Coupling agents
Vinyltrimethoxysilane (VTMS)	A-171	Coupling agents
Polyester polyols	Rayelast® A 8770	Processing aids and plasticizer
Glycerol	-	Plasticizer
Methylene diphenyl diisocyanate (MDI)	Suprasec® 2020	Chain extender
Dicumyl peroxide (DCP)	-	Free radical initiator
Tris(2,4-di-tert-butylphenyl) phosphate	Irgafos 168	Heat/processing stabilizer
Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate	Inganox 1076	Heat/processing stabilizer
Talc	JetFine 3CA	Filler

Table 3.2 The properties of the commercial poly(lactic acid), PLA2002D.

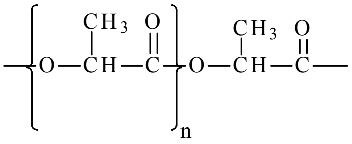
Properties	Value
Chemical structure	 $-\left[O-\overset{CH_3}{CH}-\overset{O}{C}\right]_n-O-\overset{CH_3}{CH}-\overset{O}{C}-$
Specific Gravity	1.24
Melt Index, g/10 min at 190/2.16	4 - 8
Tensile Strength@Break, psi (MPa)	7,700 (53)
Tensile Yield Strength, psi (MPa)	8,700 (60)
Tensile Modulus, kpsi (GPa)	500 (3.5)
Tensile Elongation, %	6.0
Notched Izod Impact, ft-lb/in (J/m)	0.24 (12.81)

Table 3.3 The properties of Gamma-Aminopropyltriethoxysilane (Silquest A-1100, APS) and Vinyltrimethoxysilane (A-171, VTMS).

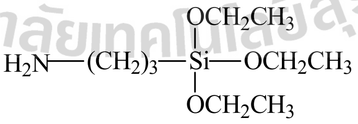
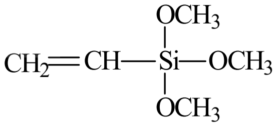
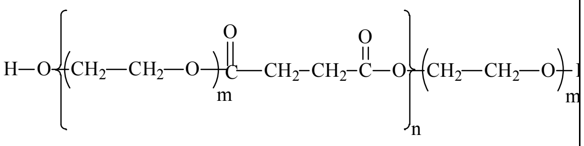
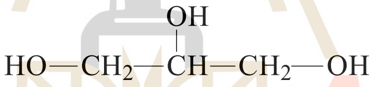
Properties	A-1100	A-171
Chemical name	*gamma*-aminopropyl triethoxysilane (APS)	Vinyltrimethoxysilane (VTMS)
Structure	 $H_2N-(CH_2)_3-\overset{OCH_2CH_3}{\underset{OCH_2CH_3}{Si}}-OCH_2CH_3$	 $CH_2{=}CH-\overset{OCH_3}{\underset{OCH_3}{Si}}-OCH_3$
Appearance	Clear, colorless	Clear, colorless
Specific Gravity@25°C	0.95	0.97
Flash point (°C)	96	28
Boiling point (°C)	220	122

Table 3.4 The properties of Polyester polyols (Rayelast A 8770).

Properties	Value
Structure	 $H-O\left[\left(CH_2-CH_2-O\right)_m\overset{O}{\overset{\Vert}{C}}-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-O\right]_n\left(CH_2-CH_2-O\right)_m$
Appearance	Light yellow liquid
Viscosity @60^{o}C, cps	1500 - 1800
Hydroxyl value, mg KOH/g	54 - 60
Acid number, mg KOH/gm (max.)	1.2 - 1.6
Water Content, % (max.)	0.05
Color, Pt-Co (max.)	150



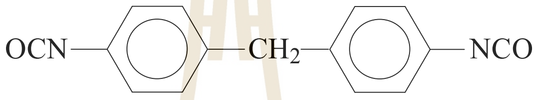
$HO-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2-OH$

$C_3H_5(OH)_3$

Figure 3.1 The structure of glycerol.

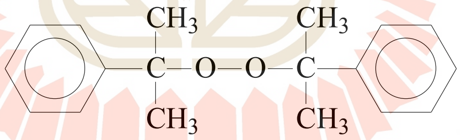
Table 3.5 The properties of methylene diphenyl diisocyanate (MDI), Suprasec® 2020.

Properties	Value
%NCO	29.5
Viscosity@25°C, mPa.s	40
Functionality	2.1



$C_{15}H_{10}N_2O_2$

Figure 3.2 The structure of methylene diphenyl diisocyanate (MDI).



$C_{18}H_{22}O_2$

Figure 3.3 The molecular structure of dicumyl peroxide (DCP).

Table 3.6 The properties of Tris(2,4-ditert-butylphenyl) phosphate , Irgafos 168.

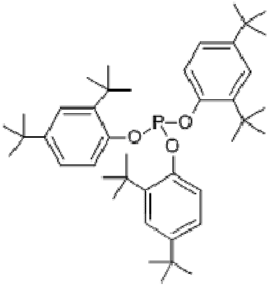
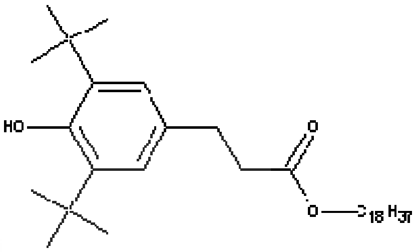
Properties	**Value**
Structure	
Appearance	White powder
Purity	99.0% min
Melting point	183-187°C
Volatility	0.3%
Clarity of solution	Clear
Acid Value (mgKOH/g)	0.3% max
Anti-hydrolyze (90°C,water,14hrs)	Qualified
Transmittance	(425nm) 98% min; (500nm) 98%min
Applications	IRGAFOS 168 is a hydrolytically stable phosphite processing stabilizer. It reacts during processing with hydro peroxides formed by autoxidation of polymers preventing process induced degradation and extending the performance of primary antioxidants.

Table 3.7 The properties of octadecyl 3-(3,5-di-tert-butyl-4-hydroxypheny propionate, Irganox 1076.

Specifications	**Value**
Structure	
Appearance	White crystal powder
Purity	98.0% min
Melting point	50-55°C
Volatility	0.5%max
Flash point	110°C
Ash	0.1% max
Transmittance	(425nm) 96% min; (500nm) 98%min
Applications	IRGANOX 1076, a sterically hindered phenolic antioxidant, is highly efficient, non discoloring stabilizer for organic substrates such as plastics. It protects these substrates against thermo oxidative degradation.

3.2 Test Samples Preparation

The PLA compounds explored in this work were classified into two main systems; (*i*) crosslink without free radical initiation and (*ii*) with free radical initiator, DCP. For the compounding process without DCP, PLA pellets and Talc underwent dehumidified treatment in a vacuum oven at 80°C for at least 2 hrs to remove the excess moisture. The assigned amounts of silane, viscous polyester polyols, glycerol and MDI were manually and vigorously premixed using mechanical mixer in the container. The dried PLA pellet was then coated with the liquids mixture. To achieve the evenly and throughoutly coating onto the pellet, paddle driven by electric mixer was employed to assist the mechanical stirring phenomenon. Finally, talc and thermal/processing stabilizer solid powder was added and again vigorously stirred. Eventually, the ingredient was ready for melt compounding in the co-rotating twin screw extruder.

For the compound crosslinked by DCP free radical initiator, the pre dehumidified PLA was warmed at approx. 50^{o}C for about 10 minutes in closed container before adding the DCP onto the pellet. Allow the free radical initiator to completely liquidified, then the mixture was vigorously stirred for a few minutes. Consequently, the DCP coated PLA was mixed with the other ingredient in the exact manner as previously described.

The well premixed ingredient was melt compounded by co-rotating intermeshing twin screw extruders, Brabender Model PL2100, having the screws diameter of 25 mm with L/D ratio of 20. The screw is consisted of 3 kneader zones. The mixing was achieved at 10 rpm screw speed and the electrically controlled barrel temperature profile at 180, 190, 200, 210, 220^{o}C from feed to die zones, respectively. The extruded strand was allowed to cool down under atmospheric condition. The compound was granulated by pelletizer.

The pellet was dried under vacuum oven at 80°C for at least 2 hrs to remove residual moisture before injection molding. Injection molding used for test specimen preparation in this research study was reciprocating type machine from Tederic, model TRX60c. The barrel temperature was electronically controlled at 180, 185, 185 and 190^{o}C, from feed zone to nozzle for the crosslinked compound system without DCP initiation. However, for adding the DCP initiator onto PLA compound it was found that the melt flow index of the compound was much lower, very high viscosity, than the system without DCP. Therefore, the temperature profile was raised to 190, 200, 200 and 210°C, respectively. Increasing the profile to much higher temperature, it was observed that the compound degradation was evidenced. The mold temperature was constantly maintained at 30^{o}C and the cooling time was set at 30 seconds.

The molded specimens were equally divided into two sets of sample. The first set was allowed to anneal at room temperature for overnight. This sample was assigned as original sample. The other series of sample was incubated at 60^{o}C in sealed and moisture saturated oven for 12 hrs. The incubation process was conducted in order to accelerate the competition of silane/water crosslink condensation reaction. This type of sample was again assigned as sauna cured or cured sample. The schematic diagram illustrated in Figure 3.4 summarizes the complete experimental procedure for preparing the PLA compounding test specimen.

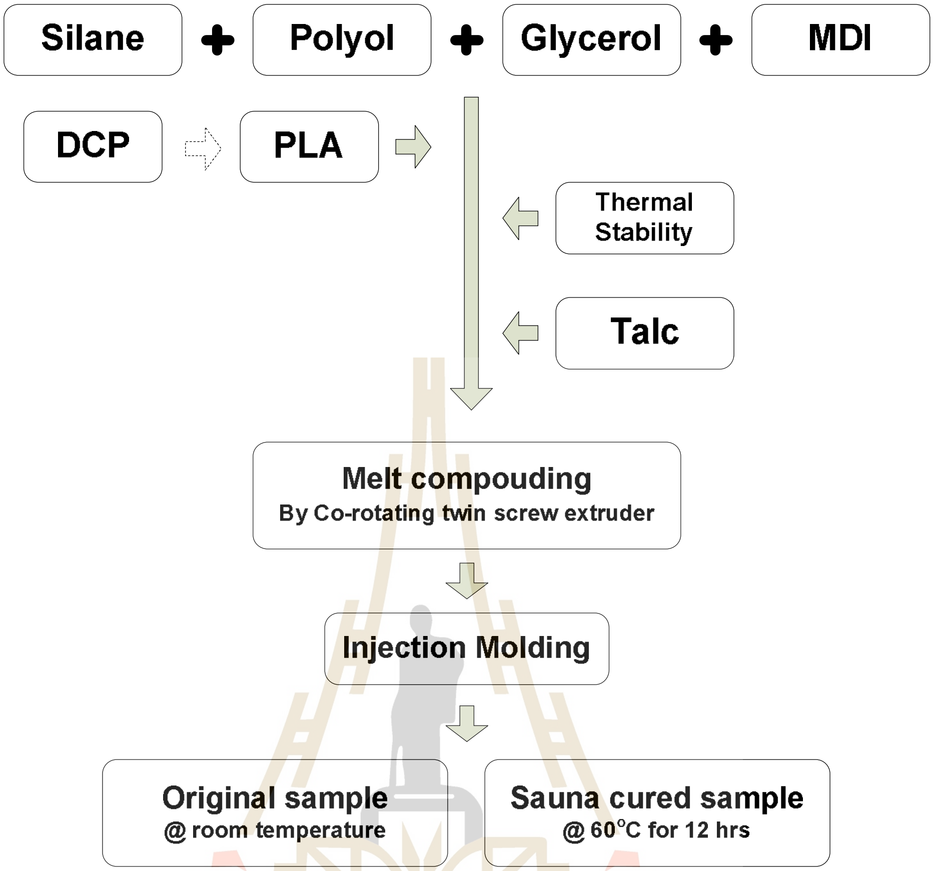


Figure 3.4 Flow chart for preparation of PLA compound test specimen.

3.3 Characterization and Testing

3.3.1 Heat distortion temperature (HDT) measurement

In according to ASTM D648, heat distortion temperature (HDT) was examined using Atlas Testing Machine, Model HDV1. The heating rate used was 2±0.2°C/min, rate A. The samples were raised from ambient temperature to the observed value by using silicone oil as heating transfer media. The injected rectangular cross section specimen with approx. 127 mm in length, 12.9 mm in depth, and 3.2 mm in width were tested. Three specimens were immersed and three point bended, at span length of 100 mm, with the calculated loading weight at the assigned standard load at 0.455 MPa. The HDT was directly read from the thermometer when the specimen had been deflected to 0.25 mm or 0.010 in. The HDT of the sample was recorded as average value from 3 tested specimens.

3.3.2 Tensile testing

For determining tensile properties of the PLA compound, the standard test ASTM D638 was followed. The Instron^{TM} universal testing machine, model 5565, was used. The constant strain rate of cross head speed was set at 50 mm/min. The dimension of dumbbell shaped specimens at 12.9 mm in width at narrow section, 20 mm in overall width, 60 mm in gauge length, 165 mm in overall length, and 3.2 mm in thickness prepared by injection molding was elongated. The distance between the ends of the grips and the final gauge length were adjusted at 120 mm and 50 mm, respectively. Commonly, five samples were conducted and averaged for each set of sample. The tensile properties; tensile strength, % strain at break, and Young's modulus (E), were reported.

3.3.3 Izod impact testing

Impact tests were conducted in according to ASTM D256 using the Atlas Basic Pendulum Impact tester Model BPI impact testing machine. The test specimens with 12.9 mm in thickness, 64 mm in length, and 3.2 mm in width. For the notched impact testing, the specimen was V-notched by using standard notch machine. The impact resistances testing for both notched and unnotched modes were performed at the striking pendulum having the impact energy of 2.7 and 5.4 J, respectively. The impact resistance was calculated as the impact strength, kJ/m^2, that was obtained by dividing the failure energy with the cross section area of the sample.

3.3.4 Gel fraction determination

The gel fraction of the crosslink fraction was determined by nondissolved content remaining after dissolving the sample in suitable solvent using the following Equation 3.1.

$$\text{Gel fraction} = (W_g/W_o) \times 100 \tag{3.1}$$

Where W_o is the original weight (dry) of the PLA compound.

W_g is the calculated nondissolved content of the PLA compound.

The accurately weighed, 0.10 – 0.12 g, pellet sample was tightly enveloped into filter paper No. 42. Virgin PLA and empty envelope were used as reference and blank, respectively. The envelopes were placed in 500 ml round bottom flask filled with approx. 300 ml of chloroform. The samples were refluxed at 50°C for 3 hrs. After allowing the reflux test equipment to cool down to room temperature, the sample envelopes were removed and vacuum dried at 65°C for 3 hrs. Then, the packages were precisely weighed to calculate the remaining gel content.

3.3.5 Biodegradability

The biodegradability testing of sample were conducted by using simulated landfill chamber. Within chamber, it was filled with composted soil at 60°C. The aerobic atmosphere was imitated by constantly feeding of oxygen gas or pumping the fresh air into the compost. The test specimens were immersed in water overnight and pre weighing before test. They were then buried in the soil at approximately 2 inches in depth. The samples were removed to monitor the weight loss every 2 weeks. The weight loss percentage was calculated by the following Equation 3.2.

$$\text{Weight loss } (\%) = (W_o - W_t) \times 100 / W_o \tag{3.2}$$

Where W_0 is Weight of test sample before burial

W_t is Weight of test sample after burial for given buried time(t)

3.3.6 Scanning electron microscopy (SEM)

The morphology of fractured surface of the compound specimens taken from notched Izod impact testing were examined using scanning electron microscope (SEM) model JSM 6400. The specimens were cut at the thickness of 5 mm below the fractured surface. It was placed on the sample holder and coated with silver paint. Fracture surface was again coated with gold by ion sputtering for 5 min. Finally, scanning electron photograph was taken.

3.4 DOE Analysis Using Design Expert^{TM}

The design of experimental (DOE) by mean statistical approach conducted in this research was 2^k factorial method. The ***k*** components are the interested design parameters. Each parameter (***k***) for each test is divided into two levels and arbitrarily called “low” and “high”. In this study, mostly 3 parameter factors that was “2^3”

factorial was designed. Then, the totals of 8 conditions of experiment were conducted. Table 3.8 shows the example of the design matrix for k = 3. One or more responds are needed for analysis.

Table 3.8 The 2^3 factorial design.

Conditions	**Factor**			**Interaction**				**Response**
	A	**B**	**C**	**AB**	**AC**	**BC**	**ABC**	**Y**
1	+	+	+	+	+	+	+	
2	+	+	−	+	−	−	−	
3	+	−	+	−	+	−	−	
4	+	−	−	−	−	+	+	
5	−	+	+	−	−	+	−	
6	−	+	−	−	+	−	+	
7	−	−	+	+	−	−	+	
8	−	−	−	+	+	+	−	

An alternative to the normal probability plot of factor effects is the half-normal plot. This is a plot of the absolute value of the effect estimates against their cumulative normal probabilities. The straight line on half normal plot always passes through the origin and should also pass close to fiftieth percentile data value.

The degree of significant (α) was given at 95% confidential for this study. The calculation of significant level of the experimental data was verified by using Design

Expert^{TM} version 7.0.0, which is the commercial statistical software analysis to assist the statistical figures calculation. The significant effects from half-normal plot can be also confirmed by ANOVA testing using this computer program. If *p*-value less than 0.05 indicates that the calculated effect (s) is/are significantly affected by the design parameter (s).

The effects of factors were calculated by averaging the responses of each factor at the high or plus (+) level and subtracting the average at the low or minus (-) level for same factor as shown in Equation 3.3. Then, the calculated effects were ranked, ***i***, from minimum to maximum. The *p*-value is area under the normal distribution. According to the design of experiment method, *p*-value is calculated from Equation 3.4 where *i* is the rank of effect *i* ($E_{f,i}$). Accordingly, Z-value as cumulative probability, as shown in Figure 3.5, is obtained from the conversion of *p*-value as summarized in Table A-1 and A-2 in the appendix A.

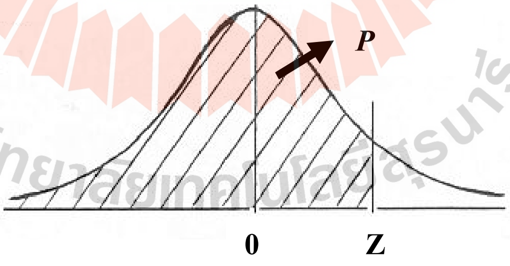


Figure 3.5 Normal distribution curve.

$$E_{f,i} = \bar{F}_{i(+)} - \bar{F}_{i(-)} \tag{3.3}$$

$$p = \frac{i-0.5}{2^{k}-1} \tag{3.4}$$

Where $E_{f,i}$ = The effect value of respond *i*

$\bar{F}_{i(+)}$ = Average response at high level setting of a factor

$$\frac{\sum Y(+E_{f,i})}{n/2}$$

$\bar{F}_{i(-)}$ = Average response at low level setting of a factor

$$\frac{\sum Y(-E_{f,i})}{n/2}$$

p = Probability

$\boldsymbol{k}$ = Number of factor was study

i = Rank number of the effect, that order by followed effect value (E_f)

Table 3.9 Statistical value of factors.

Rank (*i*)	**Effect value ($E_{f,i}$)**	***p*-value**	**Z-value**
1	$E_{f,1}$	$\frac{1-0.5}{2^k-1}$	
2	$E_{f,2}$	$\frac{2-0.5}{2^k-1}$	
3	$E_{f,3}$	$\frac{3-0.5}{2^k-1}$	
…	…	…	
…	…	…	
…	…	…	
2^k-1	$E_{f,2^k-1}$	$\frac{(2^k-1)-0.5}{2^k-1}$	

The computer software calculation, the most effect at the right side in a half-normal plot should be selected before analysis. Keep selecting from right to left until the straight line is matched with the majority of the effects near zero. Notice that the Design Expert adjusts the line to exclude the chosen effects. At the point where the process should be end, this line jumps up, leaving a noticeable gap. The effect factors and/or their interactions that lie along the line are negligible and the rest of the effects are significant effects. The trivial effects that have no influence, fall on the straight line near zero effect level, are used to estimate the experimental error.

Pareto chart may help to visualize the magnitude of the chosen effects by displaying them on an ordered bar chart. The vertical axis shows the *t*-value of the absolute effects. This is dimensionless statistic scales in terms of standard deviations. In this case, it makes no difference to the appearance of the half-normal plot. The effects that fall below the bottom limit are non significant effects. For the effects that fall above the limit are significant effects.

The significant effects from half-normal plot can be also confirmed in ANOVA results. By check the probability or “*p*-value” for the effects which were selected. If the *p*-value less than 0.05 based on the statistical analysis by the ANOVA, it indicates that the effects are significant effects. As the result, the effect of the assigned parameters on the desired respond can be concluded.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Design of Experiment#1: Effect of Silane, Polyols and Glycerol

The main target of this research work is to obtain the PLA compound that has extinguish in high service temperature where HDT is above 100°C with no scarify the mechanical properties. Hence, the influence of silane, polyols and glycerol on the properties of PLA compound was statistically investigated by mean of design of experiment(DOE). Those chemical ingredients were assigned as parameters A, B and C, respectively. According to the 2^k factorial design, $2^3= 8$, the design matrix was established as shown in Table 4.1. The experimental respond properties by mean of MFI, HDT, tensile and impact tests were obtained and summarized in Table 4.1. General observation and within the standard deviation of the test obtained, it is seen that the properties are slightly, but noticeable, differences in the measured values between original and sauna cured samples. This could be influenced by silane/water condensation reaction during the incubation process. The reaction probably gives rise to the branch or network structure or perhaps the crystallinity changes in the PLA sample. However, HDT of the compound does not increase to the target level at 100°C.

4.1.1 The MFI analysis

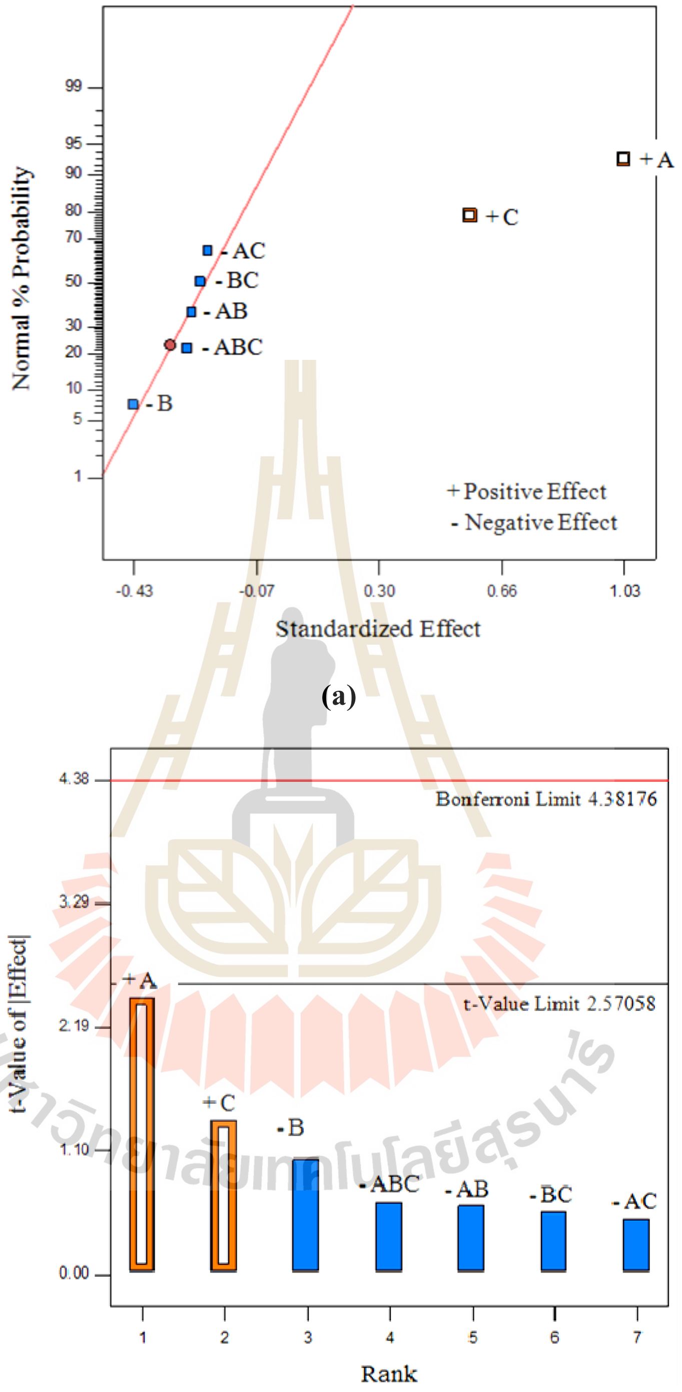
Rheological properties by mean of the melt flow index obtained at 190/2.16 from run no. 1 to no. 8 are illustrated in Table 4.1. The MFI of the PLA compound, it is seen that the MFI of the compounds are higher than virgin PLA. It means that the viscosity of PLA compound was decreased by adding those chemicals. It might be due to the fact that addition of very low viscosity polyols and glycerol into the compound and hence they increase the flow ability of the compound. Additionally, the PLA chains might be undergone glycolysis by glycerol during the compound process in twin screw extruder. The phenomenon leads to the shortening of chain and hence lowering in viscosity.

Applying the statistical analysis by mean of DOE for the MFI respond, the calculation of the standard effects of the individual parameter and also the interacted parameters by assisting of the Design Expert^{TM} are done and converted into standard normal probability. Consequently, the plot of the normal % probability with the effects is shown in Figure 4.1 (**a**). Based on the plot, it is seen that amount of silane (+A) content and glycerol (+C) content, which are positive effect, are obviously out of the linear trend line. It indicates that these two parameters have the tendency to be significantly affected on the melt flow index of PLA compound. However, the pareto chart that is constructed from the *t*-value of the effects and their rank shown in Figure 4.1 (**b**). The chart indicates that A and C are below the critical *t*-value. It reviews that these two parameters have no significant effect on the MFI of the designed PLA compound. To confirm this proposition and the design model, the ANOVA testing is taken into account and the test results are given Table 4.2.

ANOVA results are concluded that the designed model, the given parameters and their levels, used to manufacture the PLA compound in this present experiment has no significantly affected on MFI as it is indicated by the calculated *p*-value, 0.0817, of the model more than the assigned critical value, 0.05 (95% of confidential).

Table 4.1 Respond data of original and cured samples.

Runs	Composition (phr)			MFI (g/10min)	HDT (^{o}C)		Tensile strength (MPa)		Young's modulus (GPa)		Strain at break (%)		Notched impact (kJ/m^2)		Unnotched impact (kJ/m^2)	
	Silane (A)	Polyols (B)	Glycerol (C)		original	cured	original	cured	original	cured	original	cured	original	cured	original	cured
PLA	0	0	0	3.35±0.04	53.1±0.83	53.1±1.51	24.17± 0.87	26.28±0.79	1.21±0.08	1.23±0.02	4.49±0.78	3.99±0.48	3.36±0.39	3.16±0.21	23.56±1.21	21.34±4.86
1	(-) 0.5	(-) 0.5	(-) 0.1	5.34±0.19	51.5±0.64	51.0±0.68	24.85±1.48	25.65±1.13	1.24±0.06	1.21±0.02	3.55±0.58	3.77±0.68	3.16±0.48	3.28±0.34	19.41±2.63	21.45±2.75
2	(-) 0.5	(-) 1.0	(+) 0.3	8.21±0.11	49.1±0.95	57.3±0.50	23.75±2.08	29.63±0.95	1.24±0.05	1.19±0.04	3.73±0.56	3.75±0.17	3.56±0.97	3.60±0.37	17.67±2.03	19.98±2.29
3	(-) 1.0	(+) 1.5	(-) 0.2	7.54±0.16	50.1±0.58	49.7±0.83	23.04±1.72	25.44±1.42	1.19±0.04	1.15±0.04	3.78±0.58	3.62±0.29	2.94±0.51	2.95±0.46	19.77±1.28	21.15±5.02
4	(-) 1.0	(+) 2.0	(+) 0.4	8.99±0.34	48.3±0.31	57.9±1.14	23.36±1.13	29.13±0.46	1.19±0.03	1.17±0.03	3.68±0.34	3.51±0.14	2.75±0.35	3.91±0.63	25.73±2.96	16.76±3.33
5	(+) 1.5	(-) 1.0	(-) 0.2	9.16±0.57	48.7±0.61	53.5±0.95	23.02±2.53	25.92±2.15	1.21±0.01	1.03±0.03	4.49±1.40	3.64±0.42	2.63±0.33	2.70±0.59	23.86±4.04	20.57±2.26
6	(+) 1.5	(-) 0.5	(+) 0.3	11.63±0.58	48.7±0.76	50.4±1.25	23.11±1.96	22.88±2.34	1.20+0.05	1.12±0.07	4.13± 0.48	4.48±1.25	2.96±0.47	2.75±0.25	20.07±2.81	23.16±1.28
7	(+) 2.0	(+) 2.0	(-) 0.1	9.78±0.61	47.8±1.11	56.5±2.60	22.04±1.39	24.86±1.17	1.19±0.03	0.95± 0.05	4.14±0.89	4.00±0.34	2.47±0.23	2.41±0.46	21.40±2.02	21.59±2.54
8	(+) 2.0	(+) 1.5	(+) 0.4	9.57±0.52	48.3±0.70	58.1±1.79	22.29±1.7	27.62±1.3	1.16±0.01	1.16±0.03	4.01±1.04	3.65±0.36	2.20±0.51	2.28±0.30	18.22±2.31	16.07±1.18



(a)

(b)

Figure 4.1 Response analysis of MFI; (**a**) Normal plot and (**b**) Pareto chart.

Table 4.2 ANOVA results of MFI.

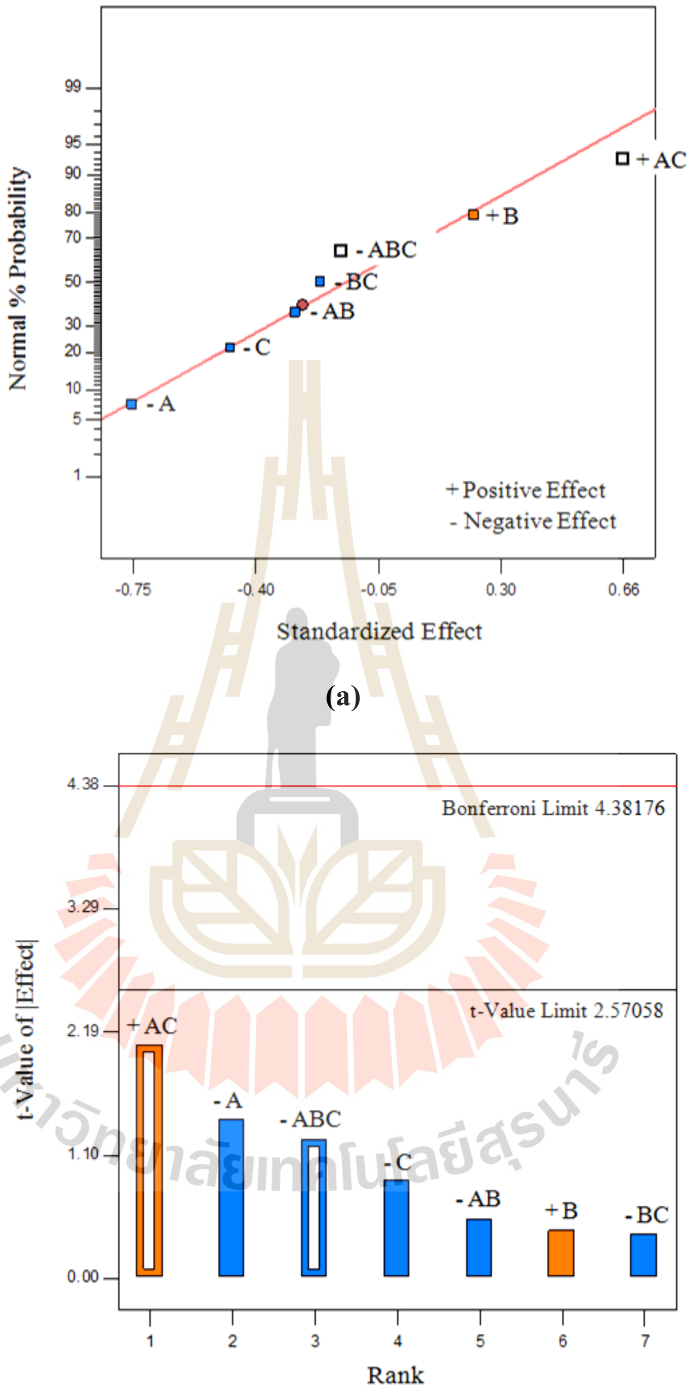
Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F
Model	14.95	2	7.47	4.31	0.0817
A-Silane	10.41	1	10.41	6.00	0.0579
C-Glycerol	3.23	1	3.23	1.86	0.2308
Residual	8.67	5	1.73		
Cor Total	23.62	7			

4.1.2 Analysis of HDT

The heat distortion temperature (HDT) as it is prime interest of this research. The target value of HDT for PLA compound at above100°C in order to expanded the applications of the biopolymer into hot food/drink packaging industries. However, from the first experiment results, shown in Table 4.1, found that the HDT of PLA compounds is obviously lower than the HDT of virgin PLA but the test values slightly increased after the sauna cured process. The maximum HDT of the compound is 58°C at Run#4 and Run#8 after the curing process. This maximum value is still much lower than desired value at 100°C. The increasing in HDT after curing reaction is might be due to the occurring of crosslink network via silane/moisture condensation reaction. Increasing in crystallinity of PLA compound while annealing the samples at temperature at 80°C for 12 hours might be another explanation for this elevating. Prolonging polymer, especially semicrystalline ones, at above its T_g generally increased in the ordering of chains and hence the mechanical and thermal properties are increased (T. Norraprateep & U. Meekum, 2011).

Using the Design Expert^{TM}, the statistical analysis of the HDT responds were performed. The normal % probability against the standardized effects is elected and shown in Figure 4.2 (**a**) for the sample without moisture incubation.

The plot shows that all of the calculated effects are well fitted on the straight line only the interaction between silane and glycerol (+AC) and interaction of all parameters (-ABC), which are positive and negative effect, respectively, that are slightly excluded from the rest. It indicates that these two parameters have the tendency to be significantly affected on the HDT of PLA compound. However, the pareto chart that is constructed from the *t*-value of the effects and their rank shown in Figure 4.2(**b**). It is illustrated that the calculated *t*-values of +AC and -ABC are below the critical *t*-value. It reviews that these two parameters have no significant effect on the HDT of the designed PLA compound. To confirm this statement and the designed model, the ANOVA analysis at 95% of confidential is taken into account and the test results are given in Table 4.3. The test results conclude that the designed model and the given parameters and their levels, used to prepare the PLA compound in this research experiment has no significant affect on HDT. As seen by the calculated *p*-value, 0.1768, of the designed model higher than the assigned critical value at 0.05.



(a)

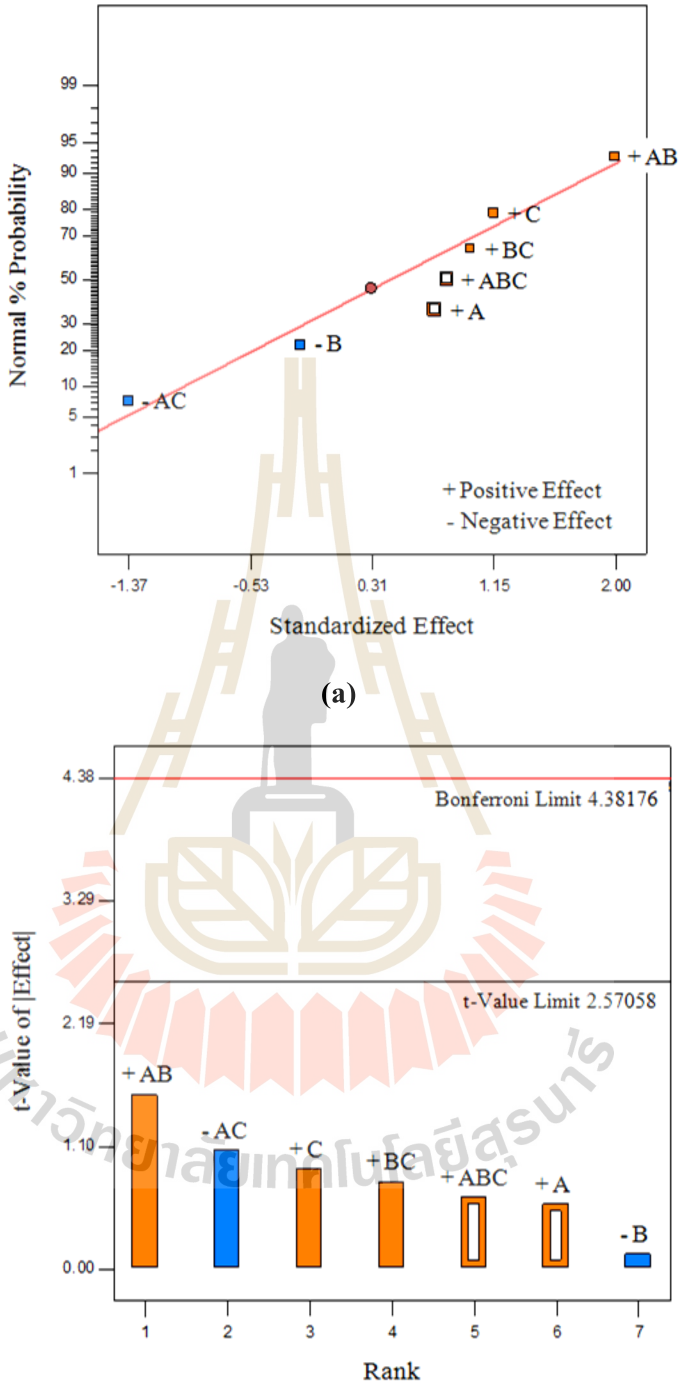
(b)

Figure 4.2 Response analysis of HDT for the original PLA compound; (**a**) Normal plot and (**b**) Pareto chart.

Table 4.3 ANOVA results of HDT for the original PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	5.138	2	2.569	2.500	0.1768
AC	4.441	1	4.441	4.322	0.0922
ABC	1.580	1	1.580	1.537	0.2700
Residual	5.138	5	1.028		
Cor Total	10.276	7			

Exact manner was performed on the HDT of sauna cured specimen, Figure 4.3(**a**) presents the normal % probability shows that amount of silane (+A) and interaction of silane, polyols and glycerol (+ABC) out of a straight line. Both are positive effect (+) on the HDT of the sauna cured sample. It is indicated that these two parameters have probably significant effect on the HDT of the PLA compound after sauna curing. Not only the normal plot is employed to conclude the effect of the parameters on the HDT of the PLA compound but also the pareto chart is also presented in Figure 4.3 (**b**). The chart confirms that the calculated *t*-values derived from parameters A and ABC are lower than the critical *t*-value. It means that these two factors are not significant effect to the HDT of the sauna cured PLA compound. Confirmation by ANOVA testing shown in Table 4.4 the calculated *p*-value of this designed model is 0.8202, it is higher than confidential value at 0.05. It concludes that there is no significant effect of silane, polyester polyols and glycerol contents on the HDT of sauna cured PLA compound. By using these ingredients at the designed level of contents, the possibility of having PLA compound with the HDT close to 100^{o}C is null.



(a)

(b)

Figure 4.3 (**a**) Normal plot and (**b**) Pareto chart of the HDT respond for the sauna cured samples.

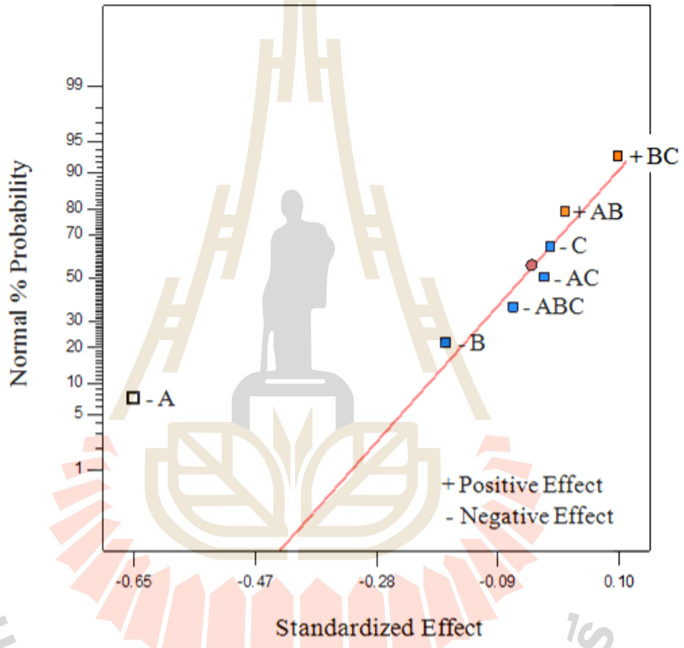
Table 4.4 ANOVA results of HDT for the sauna cured samples.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	6.765	2	3.383	0.206	0.8202
A-Silane	5.017	1	5.017	0.306	0.6040
ABC	1.165	1	1.165	0.071	0.8004
Residual	81.976	5	16.395		
Cor Total	88.741	7			

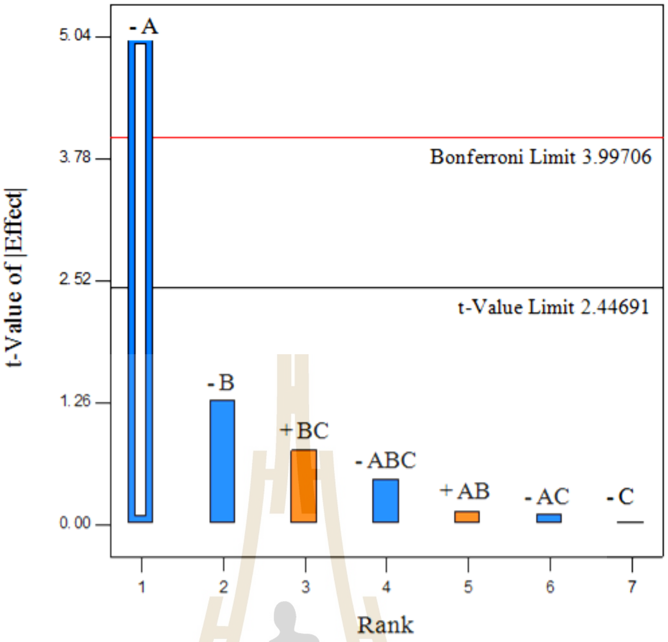
4.1.3 Tensile properties

Mechanical properties by mean of tensile test for the PLA compound were also studied. Quick scanning of the test results seen that the tensile strength of the compound are slightly lower than neat PLA but they become superior after undergo sauna treatment. The maximum values at 29.63 MPa and 29.13 MPa were found for Run#2 and Run#4, accordingly. The rigidity of the material derived from Young's modulus is also presented. Within the standard deviation of the tests, it is observed that the modulus of pure PLA more or less similar to those obtained from the PLA compounds. However, the most figures obviously drop after the sauna process. They indicate that the cured sample become inferior in toughness as noticeable by the decreasing in % strain at break after curing process.

Closely observation by the statistical methods, the normal plot and pareto plots of the tensile strength of the original specimen show in Figure 4.4 (**a**) and 4.4 (**b**), respectively. It is seen that parameter A, silane content, is absolutely excluded from the linear trend line. It is pointed out that this parameter must be the significant effect on the tensile strength of PLA compound before undergo sauna treatment. It is a negative effect (-). Figure 4.4 (**b**), the pareto chart, confirms that the calculated *t*-value of parameter A is much higher than the critical *t*-value. ANOVA testing summarized in Table 4.5 also conclude that *p*-value of the designed model and also for the parameter A is 0.0024 which is less than the confidential value at 0.05. It reinforces that the tensile strength will be decreased if increasing silane content (+A) vice versa the strength increase if compounding the polymer using low level of silane content.



(a)



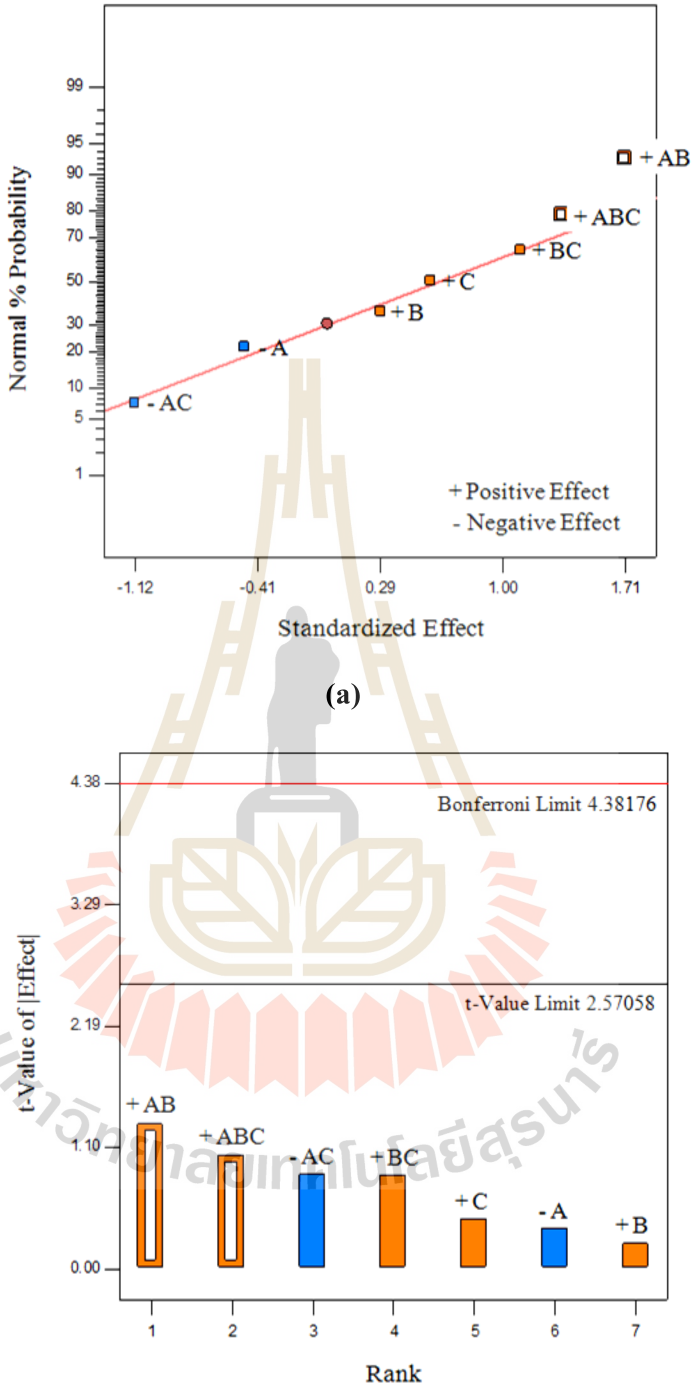
(b)

Figure 4.4 (**a**) Normal plot and (**b**) Pareto chart of the tensile strength of the original PLA compound.

Table 4.5 ANOVA results of the tensile strength of the original PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	***p*-value Prob > F**
Model	4.277	1	4.277	25.389	0.0024
A-Silane	4.277	1	4.277	25.389	0.0024
Residual	1.011	6	0.168		
Cor Total	5.288	7			

In case of sauna cured samples, the statistical analysis of tensile strength by the normal plot and pareto chart are shown in Figure 4.5 (**a**) and 4.5 (**b**), respectively. The normal plot indicates that exposed the interacted responds between silane and polyols (+AB) and interacted of all parameters (+ABC) are positive effect on the sauna cure tensile strength, as they are slightly deviated from the liner trend line. There less tendency for becoming the significant effect on the tensile property. Accordingly, the pareto result reviews that the calculated *t*-values of both +AB and +ABC are lower than the critical one. From these two examinations it is preliminary state that the parameters have no real effect on the tensile strength cured PLA compound. To confirm this obligation, the ANOVA testing was taken into account and the test results are given Table 4.6. ANOVA results are illustrated that the designed model, the above two parameters for the experiment have no significantly effected on the tensile strength of sauna cured samples as it is indicated by the calculated *p*-value, 0.6802, of the model is more than the assigned critical value, 0.05. Also, the *p*-values of those two parameters are above the critical value. From the statistical evaluation, the conclusion can be made that and the within this experimental constrain, the parameters and their levels of parameter do not have any significant effect on the tensile strength of the sauna cured PLA compound.



(a)

(b)

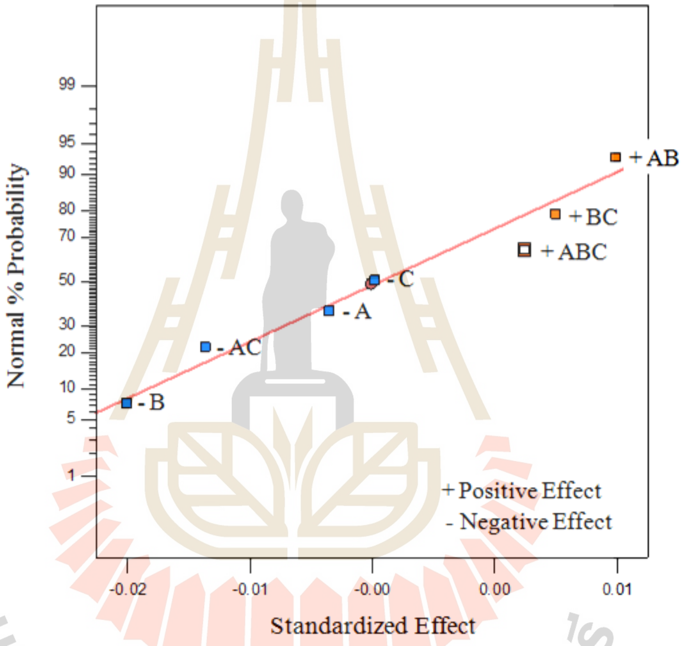
Figure 4.5 (**a**) Normal plot and (**b**) Pareto chart of the tensile strength of cured PLA compound.

Table 4.6 ANOVA results of the tensile strength of cured PLA compound.

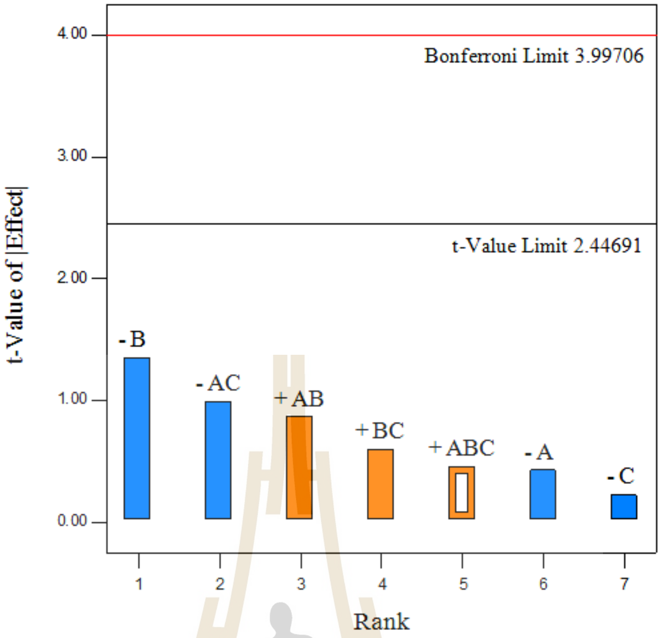
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	***p*-value Prob > F**
Model	5.122	2	2.561	0.417	0.6802
AB	1.716	1	1.716	0.279	0.6198
ABC	5.057	1	5.057	0.823	0.4059
Residual	30.728	5	6.146		
Cor Total	35.850	7			

Young's modulus of the original and cured PLA compound samples are summarized in Table 4.1. Within the standard deviation of error, the modulus of PLA compound is obviously lower than the virgin PLA. It is observed that the modulus of sauna cured was obviously decreased when compare with the original ones. Two postulations might be used to explain. Firstly, the PLA chains were scission during compounding process via glycolysis reaction. Hence, the shorter chain compound become inferior in the strength and toughness, lower in modulus. Later, chain of the compound forms the network structure as the result of silane crosslink reaction. Taken both previous tensile strength and lowering in strain at break, as will be discuss later on, it is believed that chain breakdown is most likely to respond to the lower in the modulus.

Figure 4.6 (**a**) and 4.6 (**b**) are the normal plot and pareto chart of the modulus respond for the original of PLA compound. The standard plot shows that the silane, polyols and glycerol contents (+ABC) is out of the linear trend line. It is implied to be the significant parameters for the modulus of PLA compound before sauna treatment. Observation on the pareto chart, it is shown that *t*-value of ABC is less than the critical value of the model. This demonstrate that the modulus is not significantly affected by the parameters and their levels used in the designed experiment. This testimonial is confirmed by the following ANOVA testing as concluded in Table 4.7. It is seen that the computed *p*-value of the designed model and also ABC are 0.4595 which are higher than the desired critical value at 0.05. It means that the model and also the suspected parameters have no significantly effect on the Young’s modulus of PLA compound without sauna incubation.



(a)



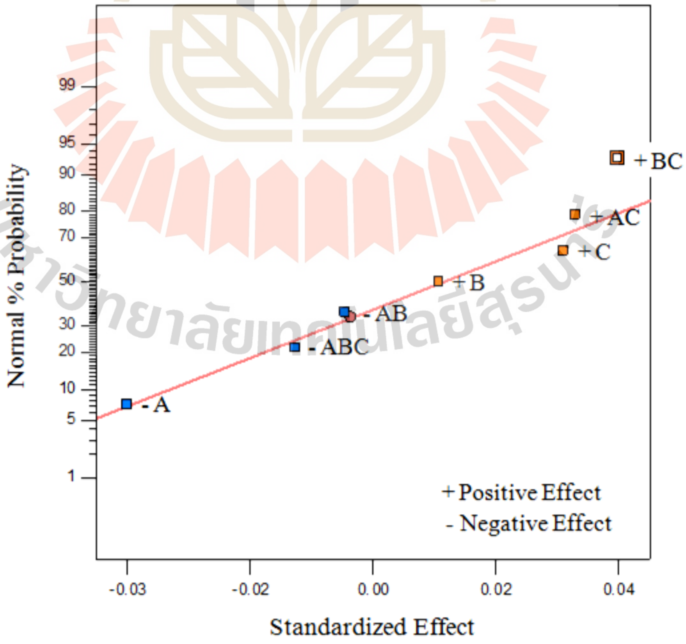
(b)

Figure 4.6 (**a**) Normal plot and (**b**) Pareto chart for the Young's modulus of the original PLA compound.

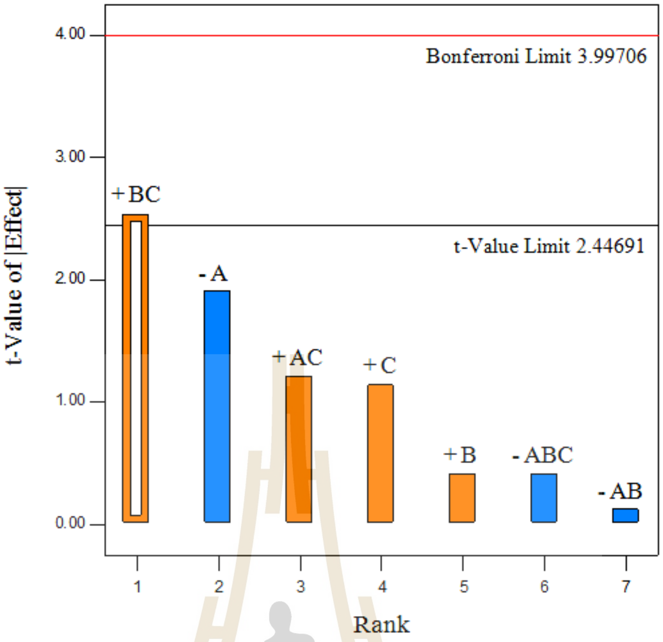
Table 4.7 ANOVA results for the Young's modulus of the original PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	***p*-value Prob > F**
Model	4.403E-004	1	4.403E-004	0.62	0.4595
ABC	4.403E-004	1	4.403E-004	0.62	0.4595
Residual	4.231E-003	6	7.051E-004		
Cor Total	4.671E-003	7			

In contrast with the Young's modulus of original sample, the sauna cured PLA compound shows the significant affected by the designed parameter. Figure 4.7 (**a**) and 4.7 (**b**) are the results of normal plot and pareto chart of the Young's modulus of the sauna cured PLA compound specimen. The plot reveals that the calculated standard effect of +BC, which is the polyols and glycerol contents, is noticeably excluded from the linear line and it is positive effect to the modulus. Similarly, the pareto chart confirms that *t*-value of +BC is just higher than the critical figure of the model. From the results, it is quite confident to say that polyols and glycerol contents have the real effect to the modulus of the compound. To strengthen this unambiguous statement, ANOVA conclusion is taken into account and reported in Table 4.8. The *p*-value of the model and also +BC is 0.0444 which is less than designed confidential 95% (α=0.05). The testing outcome means that, taking the statistical results, using both polyols and glycerol at high level of contents ((+B)x(+C)=+BC) will give rise to the high tensile modulus of the sauna cured PLA compound. Because these interacted parameter is significant effect on its modulus.



(a)



(b)

Figure 4.7 (**a**) Normal plot and (**b**) Pareto chart for the Young's modulus of cured PLA compound.

Table 4.8 ANOVA results for the Young's modulus of cured PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	***p*-value Prob > F**
Model	0.029	1	0.029	6.42	0.0444
BC	0.029	1	0.029	6.42	0.0444
Residual	0.027	6	4.446E-003		
Cor Total	0.055	7			

The deformation under tension force measured by the percentage of elongation at break of the PLA compound summarized in Table 4.1. It was observed that the strain at break of the compounds prepared in this experiment is lower than virgin PLA, especially after the sauna curing. The decreasing in the strain probably due to the change in molecular structure, from linear to branched or crosslinked chains. Another explanation is the degradation of PLA chain during the melt processing. The later was prevented by adding the thermal/processing stabilizer into the compound ingredient.   Analysis of the ingredient parameters by the statistical mean of the prepared original samples are summarized in Figure 4.8 (**a**) and 4.8 (**b**) and also in ANOVA Table 4.9, respectively. The normal plot in Figure 4.8 (**a**) reveals that only the interacted parameters between silane and glycerol content (AC) is visibly deviated from liner trend line. It is the negative effect. It is suspected to be the significant factors on the strain at break statistically respond. In contrast, the calculated *t*-value of this interaction shown in the pareto chart, Figure 4.8 (**b**), is below the critical value. It confirms that this factor is insignificant effect to the strain. The ANOVA testing conclusion at 95% confidential as shows in Table 4.9 also support that the –AC factor does not have the real influence on the strain of the PLA compound as indicated by higher calculated *p*-value than the 0.05.

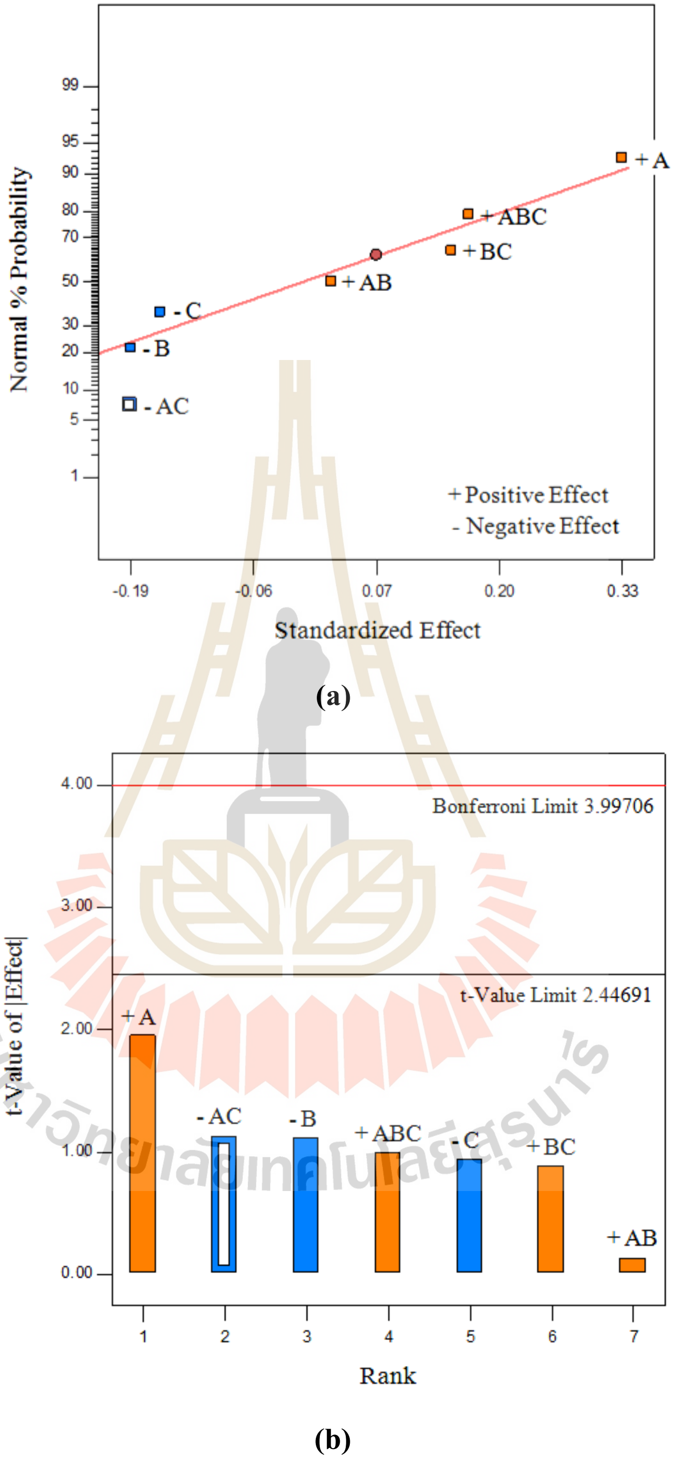
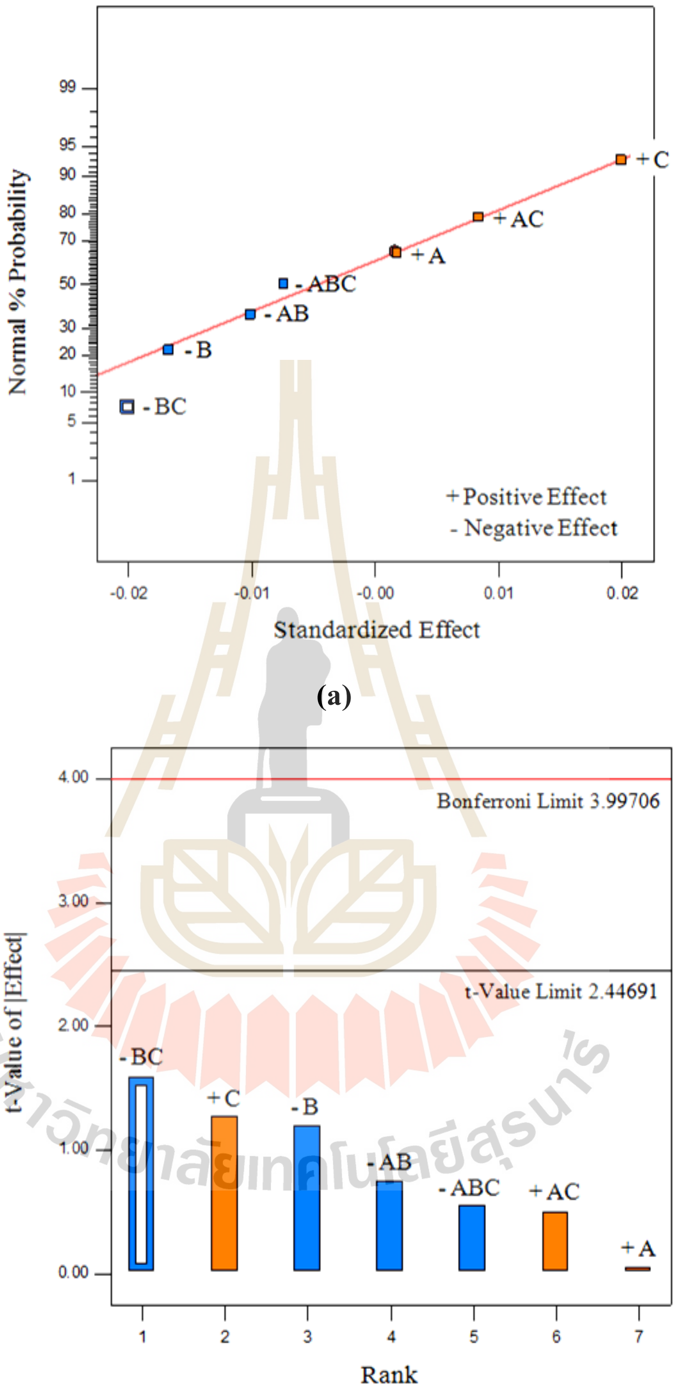


Figure 4.8 (**a**) Normal plot and (**b**) Pareto chart for the strain at break of original PLA compound.

Table 4.9 ANOVA results for the strain at break of original PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	***p*-value Prob > F**
Model	0.055	1	0.055	0.531	0.4938
AC	0.055	1	0.055	0.531	0.4938
Residual	0.618	6	0.103		
Cor Total	0.673	7			

Similarly to the original condition, the statistical evaluation of the strain at break of the sauna cured PLA compound reported in Figure 4.9 (**a**), Figure 4.9 (**b**) and Table 4.10, respectively. The normal % probability plot shows that the interacted factors between polyols and glycerol (BC) is slightly far beyond the linear regression line. It is implied that this negative effect is likely and tendency to be a significant influence on the strain at break. Combining with the *t*-value found in the pareto chart, Figure 4.9 (**b**), it is manifested that the *t*-value is below the critical one. So this factor does not have any significant to the strain of the PLA compound after undergoing sauna treatment. Moreover, the ANOVA conclusion given in Table 4.10 also reconfirms that the calculate *p*-values of the designed model and of the –BC, both are equal to 0.1638, are well below the set critical value. It means that the given parameters and the levels of contents used in the experimental design do not have real effect to the strain at break of the PLA compound.



(a)

(b)

Figure 4.9 (**a**) Normal plot and (**b**) Pareto chart for the strain at break of cured PLA compound.

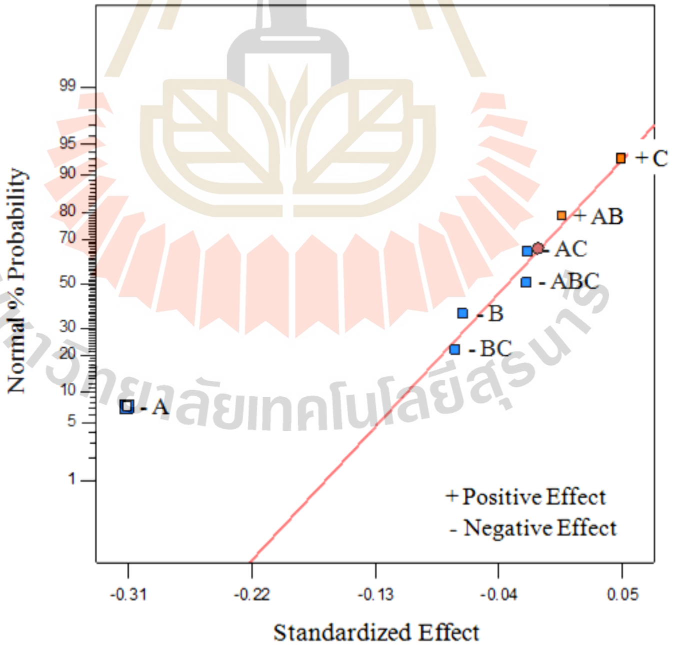
Table 4.10 ANOVA results for the strain at break of cured PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	***p*-value Prob > F**
Model	0.198	1	0.198	2.516	0.1638
BC	0.198	1	0.198	2.516	0.1638
Residual	0.472	6	0.079		
Cor Total	0.670	7			

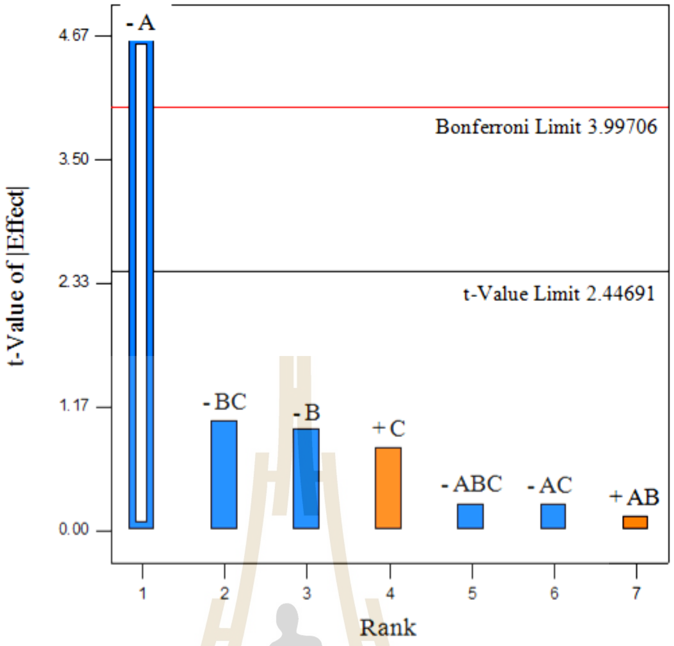
4.1.4 Impact strength of compound

Impact tests both notched and unnotched modes are used to study the fracture toughness of PLA compound. The ability of material to absorb energy during plastic fracture deformation refers to the impact strength and at the same time the durability of sample. Brittle materials have low toughness means they have low plastic deformation. In Table 4.1 summarize the impact strengths of PLA compound obtained from the design experimental. Within the standard error of the test, the results show that most of notched and unnotched impact strengths obtained from the sauna cured samples are mostly and marginally higher than the original samples. But the differences are ambiguous. However, it is not too over estimation to give the hypothesis that the increasing in the impact test values are trustworthy by silane/moisture reaction via the sauna cure. It is somewhat enhance bonding strength of the intermolecular interaction and hence improve the toughness of the material.

Exactly the same manner as the previous discussions, the statistical measurement on the notched impact of the original sample is performed. The normal % probability, pareto chart and ANOVA conclusion are given in Figure 4.10 (**a**), Figure 4.10 (**b**) and Table 4.11, consequently. The normal plot manifests that only silane content (-**A**) is excluded from the others in the regression line. It means that the significant effect of this factor could be concluded. Together with the calculated *t*-value taken from the pareto chart, Figure 4.10 (**b**), it is also strengthen the above conclusion is correct. Because the *t*-value of factor A higher than the critical *t*-value of the model. The ANOVA conclusion given in Table 4.11 also emphasis that the designed model and the level of silane contents (**-A**) has significant effects on the notched impact respond of PLA compound sample before undergoing sauna treatment. Taken only this the statistical conclusion, it may be written that superior notched impact strength of the PLA compound can be achieved by compounding at low level of silane, 1.0 phr. Adding silane above 1.0 phr would give rise to the more brittle compound.



(a)



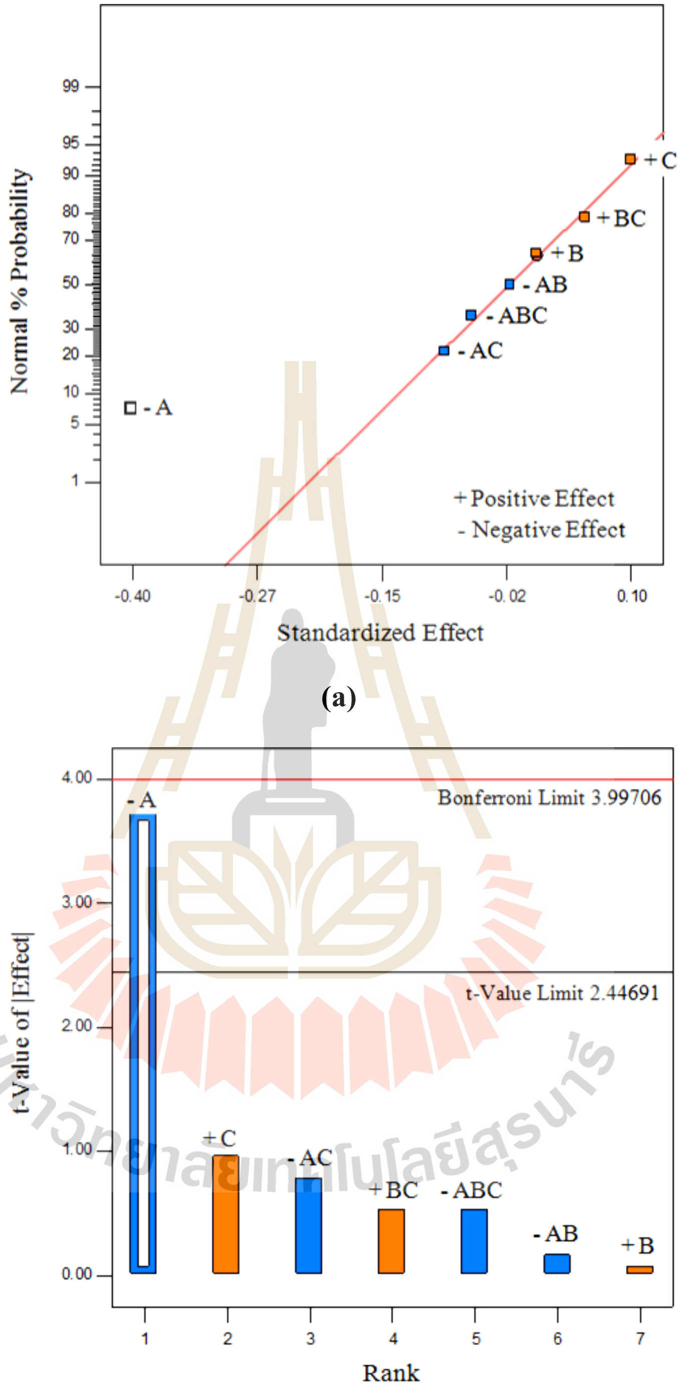
(b)

Figure 4.10 (**a**) Normal plot and (**b**) Pareto chart for the notched impact strength of original PLA compound

Table 4.11 ANOVA results for the notched impact strength of original PLA compound.

Source	Sum of Squares	df	Mean Square	F Value	*p*-value Prob > F
Model	0.979	1	0.979	21.804	0.0034
A-Silane	0.979	1	0.979	21.804	0.0034
Residual	0.269	6	0.045		
Cor Total	1.248	7			

Similar observations to those original specimens are also observed for the moisture incubated samples. Figure 4.11 (**a**), 4.11 (**b**) and Table 4.12 are the statistical evaluation of cured PLA compound, respectively. The normal plot as presented in Figure 4.11 (**a**) manifest that only silane content (+**A**), which is negative effect, is far beyond the linear trend line. It has the tendency to be the pronounce effect to the notched impact strength of sauna cured sample. Furthermore, the pareto chart constructed from the calculated *t*-value of the effects and their ranks shown in Figure 4.11 (**b**) confirms that the calculated value of parameter **A** is greater than the critical value. From both plots, it can state that **A** has significant effect on the impact strength of the notched PLA compound that undergone sauna cure. The confirmation of this proposition is tighten by the ANOVA analysis as given Table 4.12. The results are concluded that *p*-values of the experimental model and also the silane content are 0.0098 which is undoubtedly below the desired degree of confidential. So, resulting from the statistical mean it can be said that the given parameters and their levels used in the DOE have the significant effect to the notched impact of PLA compound. Adding the silane at low level, below 1.0 phr, will have a significantly increase in the notched impact strength of the compound that using high level of silane content, above 1.5 phr.



(a)

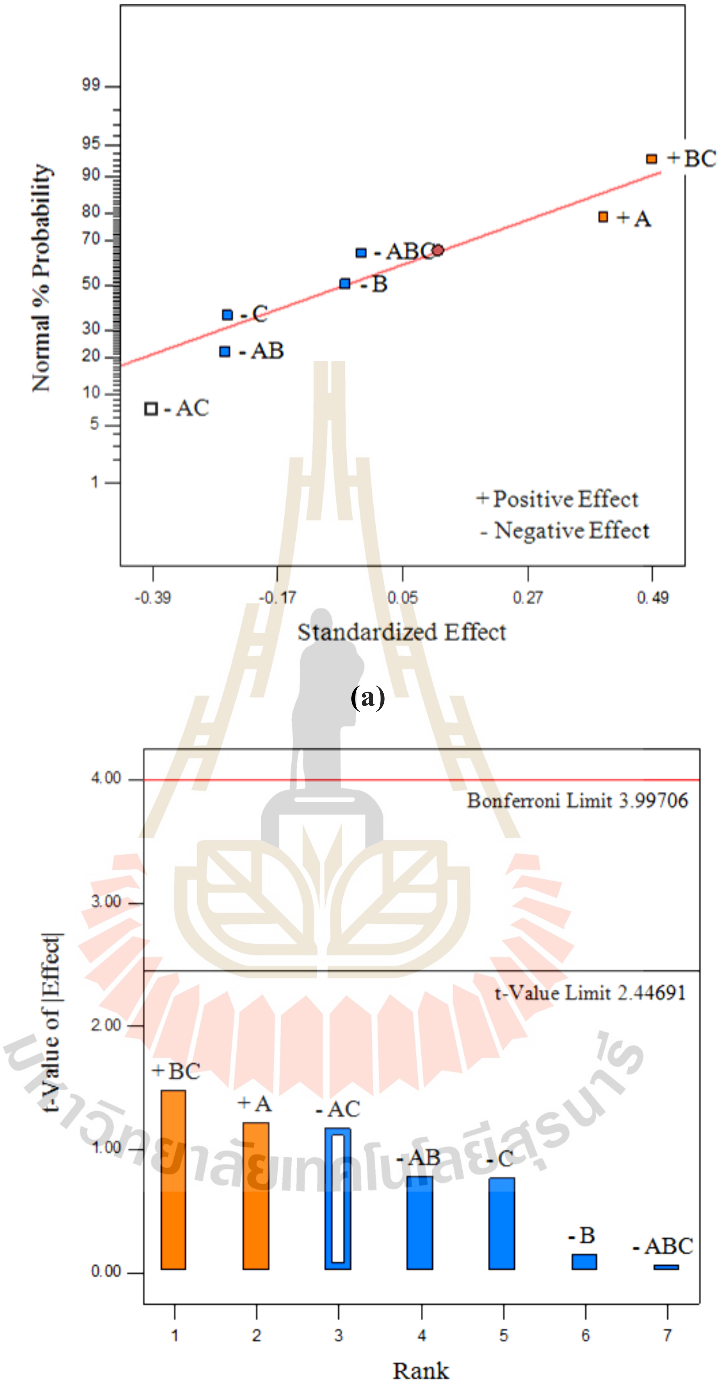
(b)

Figure 4.11 (**a**) Normal plot and (**b**) Pareto chart for the notched impact strength of cured PLA compound.

Table 4.12 ANOVA results for notched impact strength cured PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	***p*-value Prob > F**
Model	1.601	1	1.601	13.864	0.0098
A-Silane	1.601	1	1.601	13.864	0.0098
Residual	0.693	6	0.115		
Cor Total	2.294	7			

Figure 4.12 (**a**) and 4.12 (**b**) show the normal plot and pareto chart of the unnotched impact respond of the PLA compound before sauna curing, respectively. The standard plot reveals that all factors are scattered. Carefully observation, the interacted parameter between silane and glycerol (-**AC**) is most further from the regressed linear line. It indicates that this negative interacted factor is probably a significant effect to the unnotched impact of the uncured PLA compound. On the other hand, the pareto plot provided in Figure 4.12 (**b**) shows that the *t*-value of AC below the limit value. It means that the unnotched impact of the PLA compound is not significantly affected by the silane and glycerol contents. Not only the pareto analysis but also the ANOVA testing as summarized in Table 4.13 confirms that the designed model and hence -AC have no significant effect on the unnotched impact strength of PLA compound without the sauna treatment. Because of their *p*-values are higher than the critical one.



(a)

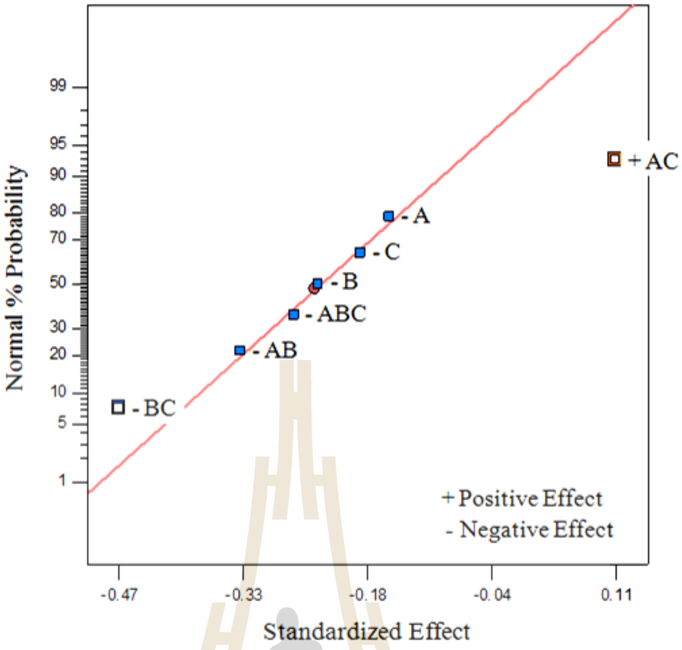
(b)

Figure 4.12 (**a**) Normal plot and (**b**) Pareto chart of the unnotched impact strength of original PLA compound.

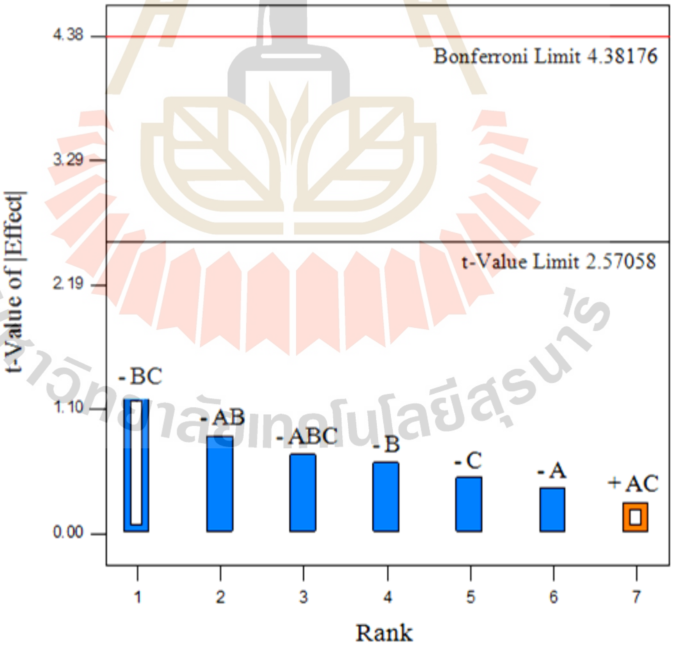
Table 4.13 ANOVA results for the unnotched impact strength of original PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	***p*-value Prob > F**
Model	10.032	1	10.032	1.369	0.2863
AC	10.032	1	10.032	1.369	0.2863
Residual	43.964	6	7.327		
Cor Total	53.997	7			

The similar outcome is observed for the unnotched impact of the sauna cured PLA compound. Figure 4.13 (**a**) and 4.13 (**b**) are the normal plot and pareto chart of the respond of effect, respectively. It is seen in the normal plot that the interaction between silane and glycerol contents (+AC) and between polyols and glycerol (-BC) have the tendency to be the real effect to the unnotched impact strength and they are positive and negative effects, respectively. These two points cannot be included into the linear regression line. Calculation of *t*-value of the factors, Figure 4.13 (**b**), they are far below the limit value. It implies that unnotched impact of sauna cured PLA compound is not significantly controlled by the suspected parameters. The ANOVA conclusion as given in Table 4.14 reinforces that the given parameters and the level of contents and also both interaction +**AC** and -BC do not have the significant influence on the unnotched impact respond of the sauna treatment PLA compound.



(a)



(b)

Figure 4.13 (**a**) Normal plot and (**b**) Pareto chart for the unnotched impact strength of cured PLA compound.

Table 4.14 ANOVA results for unnotched impact strength of cured PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	***p*-value Prob > F**
Model	11.435	2	5.718	0.931	0.4532
AC	0.463	1	0.463	0.075	0.7947
BC	9.327	1	9.327	1.519	0.2726
Residual	30.709	5	6.142		
Cor Total	42.144	7			

By converting the statistical conclusion of all the given responds, of both original and cured sample, into the regressed equations, the designed equation can be statistically resolved and summarized in Table 4.15. The predicted regression formula could be used to formulate the PLA compound into the desired properties. For example, for tensile strength of the compound without sauna curing is 23.18-0.33 (A). It means that if the maximized tensile strength of original PLA compound can be achieved by using low level of silane (-A), below 1.0 phr. The rest of the significant properties can be performed in the similar manner.

Table 4.15 The predicted regression model for the properties of PLA compound derived from the DOE analysis.

Properties	Regressed models
Original:	
Melt flow index	No significant
HDT	No significant
Tensile strength	23.18-0.33(A)
Young's modulus	No significant
% Strain at break	No significant
Notched impact	2.83-0.16(A)
Unnotched impact	No significant
Sauna Cured:	
HDT	No significant
Tensile strength	No significant
Young's modulus	1.11+0.01(BC)
% Strain at break	No significant
Notched impact	2.98-0.20(A)
Unnotched impact	No significant

4.1.5 Morphological investigation

The fractured surfaces SEM photographs of neat PLA, PLA compound from Run#2 and Run#8 are shown in Figure 4.14 (**a**) - (**d**), respectively. Figure 4.14 (**a**) illustrates the fractured surface of neat PLA. Its crake propagated residual is similar to those commonly found in the brittle polymers. On the other hand, the fractured trace for the PLA compound which low level of silane and polyester polyols, but high glycerol contents were employed, Run#2, as given in Figure 4.14 (**b**) reviews that the crake surface is smoother and has some evidence of fibril like traces. From the previous discussion, this compound formula exhibits the highest notched impact strength among the others. Also, the fractured surfaces of Run#8 for original and sauna cured sample are shown in Figure 4.14 (**c**) and 4.14 (**d**) respectively. The sample was prepared with high levels of all parameters and their notched impact test values are the lowest. It is seen that there are small droplets within the homogenous matrix phase. There is also a few of fibril like traces on the crake tip. After sauna incubation, the surface becomes rougher. From the SEM result, it might be state that the ingredients added into the PLA matrix phase at the given high level of contents cannot be completely miscible with the polymer. Small droplets of the immiscible phase can act as craze initiator and hence speed up the propagation of crack through the matrix phase. As the result, the toughness of sample becomes inferior. Competition of phase separation and crosslink bonding via silane/water condensation reaction during the sauna treatment has no pronounce enhancement of the toughness incompetency. On the other hand, it introduces the thermosetting characteristic, high brittle material, into PLA compound.

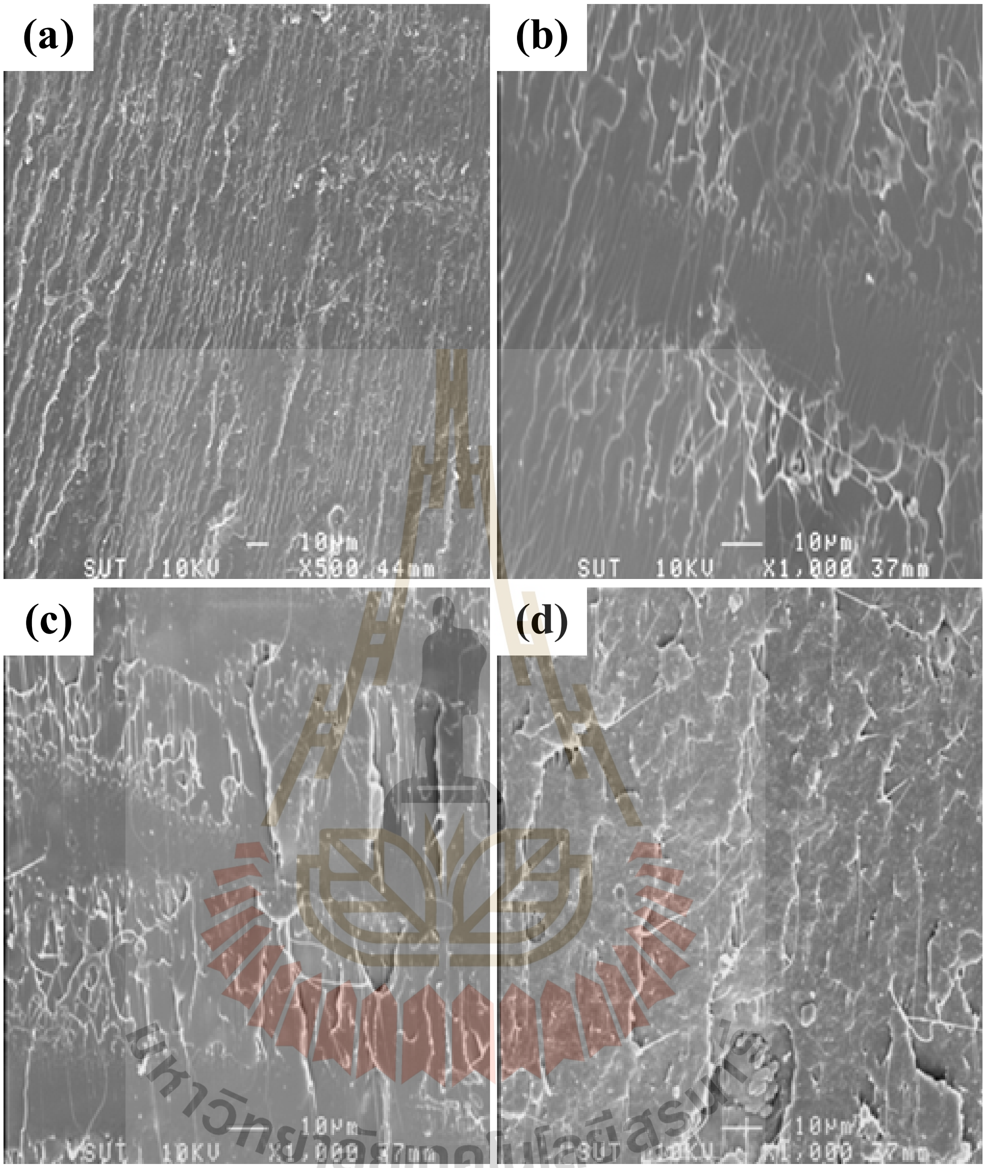


Figure 4.14 SEM micrograph of; (**a**) neat PLA(X500), (**b**) Run#2 (original), (**c**) Run#8 (original), (**d**) Run#8 (cured), respectively.

Combining between the SEM analysis with the above the statistical conclusion, it can confidently conclude that the impact strength of PLA compound manufactured from the designed parameters, silane, polyols and glycerol, at high levels of content will have the significant effect to the fracture toughness of the compound. Good ductility of PLA compound could be obtained if the silane addition is kept at low level, less than 1 phr. Other parameters, mostly, have no significant effect to the respond properties tested in this research work.

4.2 The Effect of Glycerol on PLA Compound

From the previous experiment, DOE, it was found that the impact property of the PLA compound is reversed, negative effect, with the silane content. Polyester polyols is mainly acted as either miscible plasticizer or processing aid for the PLA compound. It normally had negative effect to the HDT of the compound, especially when sauna cure taken place. Glycerol would act as chain branching agent during the moisture incubation process. As its hydroxyl groups have ability to condense with silane to form non linear polymer chain. On the way round, glycerol can also accelerate the glycolysis reaction on the PLA chain. Hence, the short chain polymers are formed and the material becomes more brittle. For the goal target to improve the properties, especially HDT, of PLA compound in this experiment, it was purely chemically interest to fine tune the precise amount of glycerol content needed in the PLA compound. Retaining the silane at low level of content, 1.0 phr, and polyols at high level of content, 2.0 phr, in the PLA compound formula, varying glycerol from 0.1 to 0.3 phr were assigned and mixed as shown in Table 4.16. The test results obtained from the design samples are shown in Table 4.17.

Table 4.16 The composition of PLA compound by varying glycerol contents.

Runs	Composition (phr)		
	Silane	Polyol	Glycerol
PLA	-	-	-
1	1.0	2.0	0
2	1.0	2.0	0.10
3	1.0	2.0	0.15
4	1.0	2.0	0.20
5	1.0	2.0	0.25
6	1.0	2.0	0.30

Table 4.17 Test results of the original and cured PLA compound at different glycerol contents.

Runs	Glycerol content (phr)	MFI (g/10min)		HDT (^{o}C)		Tensile strength (MPa)		Young's modulus (GPa)		Strain at break (%)		Notched impact (kJ/m^2)		Unnotched impact (kJ/m^2)	
		original	**cured**	**original**	**cured**	**original**	**Cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**
PLA	PLA	3.35 ± 0.04	3.82 ± 0.14	53.1 ± 0.83	53.1 ± 1.51	24.17 ± 0.87	26.28 ± 0.79	1.21 ± 0.08	1.23 ± 0.02	4.49 ± 0.78	3.99 ± 0.48	3.36 ± 0.39	3.16 ± 0.21	23.56 ± 1.21	21.34 ± 4.86
1	0	7.94 ± 0.61	10.78 ± 1.00	46.1 ± 0.31	51.9 ± 0.23	41.82 ± 2.57	50.88 ± 4.27	2.14 ± 0.01	2.19 ± 0.06	3.80 ± 0.25	3.98 ± 0.74	2.86 ± 0.25	2.42 ± 0.68	19.26 ±2.70	25.13 ± 2.00
2	0.10	7.94 ± 0.67	10.69 ± 0.61	45.9 ± 0.12	55.8 ± 1.83	44.05 ± 4.88	54.38 ± 2.56	2.15 ± 0.02	2.06 ± 0.07	3.54 ± 0.59	4.02 ± 0.54	3.14 ± 0.41	2.34 ± 0.15	23.87 ± 1.56	23.98 ± 0.30
3	0.15	7.87 ± 1.24	12.41 ± 0.11	46.1 ± 0.64	56.8 ± 1.22	43.62 ± 1.75	50.58 ± 4.52	2.32 ± 0.07	2.05 ± 0.08	3.68 ± 0.37	4.26 ± 0.43	2.96 ± 0.20	2.23 ± 0.03	25.73 ± 1.73	24.62 ± 0.92
4	0.20	8.08 ± 0.81	11.04 ± 0.45	46.0 ± 0.53	54.7 ± 2.40	43.62 ± 4.28	52.23 ± 3.07	2.21 ± 0.05	2.11 ± 0.05	4.01 ± 0.81	4.28 ± 0.36	2.80 ± 0.26	2.53 ± 0.35	25.60 ± 3.46	25.22 ± 1.77
5	0.25	8.52 ± 0.77	10.40 ± 0.07	46.0 ± 0.45	51.3 ± 1.51	46.65 ± 2.34	52.70 ± 1.55	2.30 ± 0.05	2.10 ± 0.04	3.02 ± 0.08	3.75 ± 0.13	2.54 ± 0.34	2.08 ± 0.19	21.96 ± 3.55	24.07 ± 1.69
6	0.30	6.75 ± 1.21	8.83 ± 0.43	47.6 ± 0.92	55.9 ± 0.64	49.74 ± 1.07	59.20 ± 1.60	2.14 ± 0.07	2.11 ± 0.09	3.35 ± 0.31	3.78 ±0.23	2.07 ± 0.14	4.78 ± 0.18	21.14 ± 2.78	21.37 ± 0.65

4.2.1 MFI of PLA compound

The flow ability of PLA compound by mean of the melt flow index obtained at 190/2.16 with corresponding with glycerol contents is summarized in Table 4.17 and also plotted and shown in Figure 4.15, respectively. The result shows that flow ability of the compound after sauna incubation is obviously and significantly higher than the original samples. The increasing in the flow ability is might be due to hydrolysis reaction induce by the moisture absorbed during the incubation. Because, there was no drying step of the incubated samples before conducting the MFI testing. Consequently, when the moisture saturated sample was placed into the barrel of the testing machine at 190^{o}C the chain degradation would be accelerated. Hence, the viscosity of material would be much lowered, higher in MFI. Later on, the comparison between the MFI results of the original and the vacuum dried of the sauna cured samples will be presented and deeply discussed. With respect to the increase amount of glycerol addition, it is observed that the MFI of PLA compounds are gradually increased with increasing the glycerol content until roughly at 0.20 phr. Further increase the content from 0.25 phr, the index was sharply depleted for both original and sauna cured compound. Glycerol as plasticizers in PLA compound which by definition it increase the polymer chain mobility. However, decreasing in MFI when excess glycerol was added, it perhaps the gelation occurred in the compound. Therefore, material become more viscous.

4.2.2 Heat distortion temperature (HDT)

The HDT is the main objective of this research. As presented in Table 4.17 and plotted in Figure 4.15, the test results indicate that the service temperatures are almost unchanged with respect to the glycerol contents for the original samples.

These values are much lower than the virgin PLA. However, they are slightly decreased with increasing the amount of glycerol to 0.25 phr for the sauna treated ones. But at 0.3 phr of glycerol, the test value is higher. Either chain degradation or plasticizing effect, as mentioned earlier, would responsible for the lower in HDT. At the stage gelation, the effects would become diminish. Comparing between the sample before and after moisture incubation, the HDT of sauna cured samples are much higher than original samples. The superior could be due to the silane/water condensation reaction during the incubation process. The reactions probably give rise to the branch or inter molecular network structures, hence higher in the HDT.

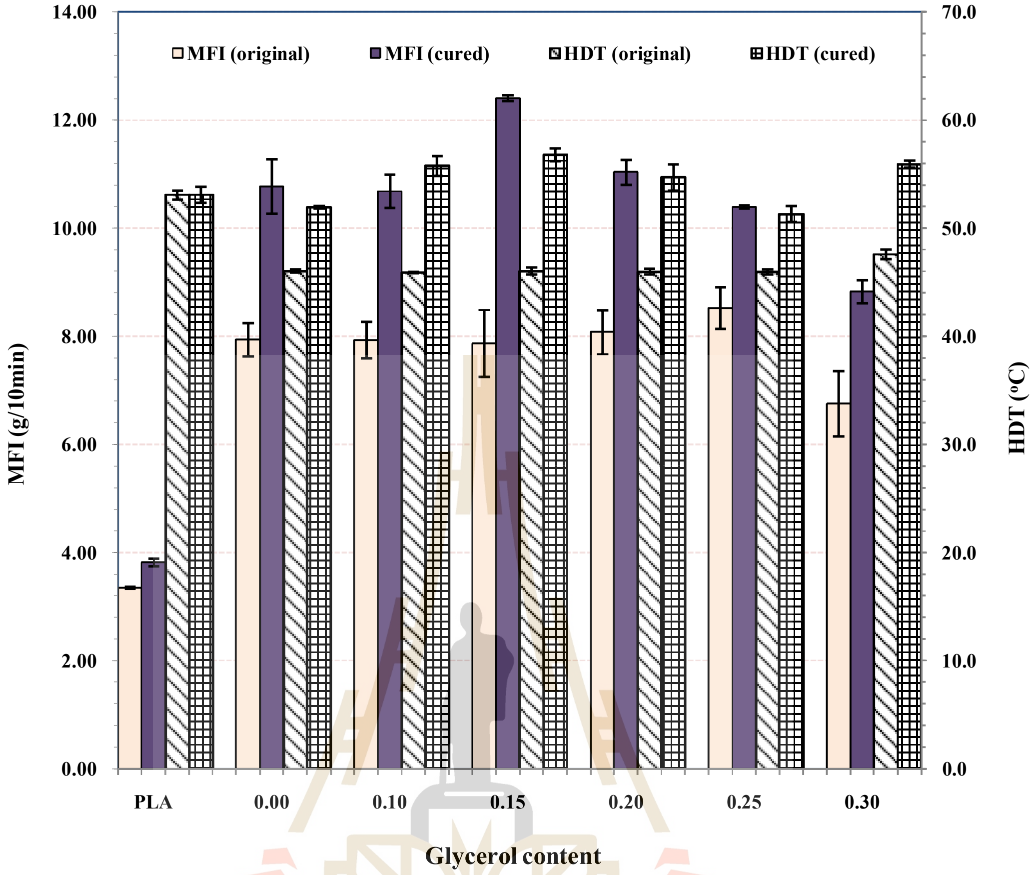


Figure 4.15 The MFI and HDT of PLA compound with glycerol contents.

4.2.3 Tensile Properties

The result of tensile properties; strength, modulus and strain at break, are summarized in Table 4.17 for both original and sauna cured sample, respectively. Considering the tensile strength and Young's modulus when they are plotted with the glycerol contents as shown in Figure 4.16. Within the statistical error, it is found that tensile strength is slowly increased when increasing the glycerol contents for both original and cured conditions. Moreover, the tensile strength of sauna cured is obviously higher than original one. The maximum tensile strength of the compounds are observed at 0.3 phr of glycerol addition. The strength of PLA compounds are much higher than the virgin PLA.

In contrast with the strength, it is observed that there is no pronounce relationship between the Young's modulus of the PLA compound and glycerol content for the specimen before and after sauna curing as also presented in Figure 4.16. Again, Young's modulus of original sample is higher than sauna cured. Closer investigation, it seems that the modulus is marginally increased with increasing the glycerol in the compound ingredient. Further using this reagent beyond 0.3 phr, the test value is inferior.

The plot of the strain at break for the samples both before and after sauna curing at different in the glycerol content is illustrated in Figure 4.17. For glycerol addition from 0 to 0.2 phr, the strain at break is slightly increased in corresponding with the amount of the chemical. Then, the ability of material deformation is reduced for further addition of the glycerol.

Combine the three parameters of the tensile properties together, it can be said that the tension strength, or material ductility, of the PLA compound using silane, polyester polyols and glycerol at the given concentration, is increased with increasing the glycerol used. Further increase this chemical addition, the property become abysmal. On the other word, brittle material would be observed by using excess glycerol in the compound ingredient. As explain earlier that the excess glycerol would become the glycolysis reagent for the PLA matrix. It would induce the chain degradation and hence lower the toughness of the compound obtained. But small optimized amount of the reagent can be used as plasticizer and enhanced the ductility of the PLA compound. From this experiment, the suitable amount of glycerol that can be used to enhance to tensile properties of the PLA compound is not more than 0.25 phr.

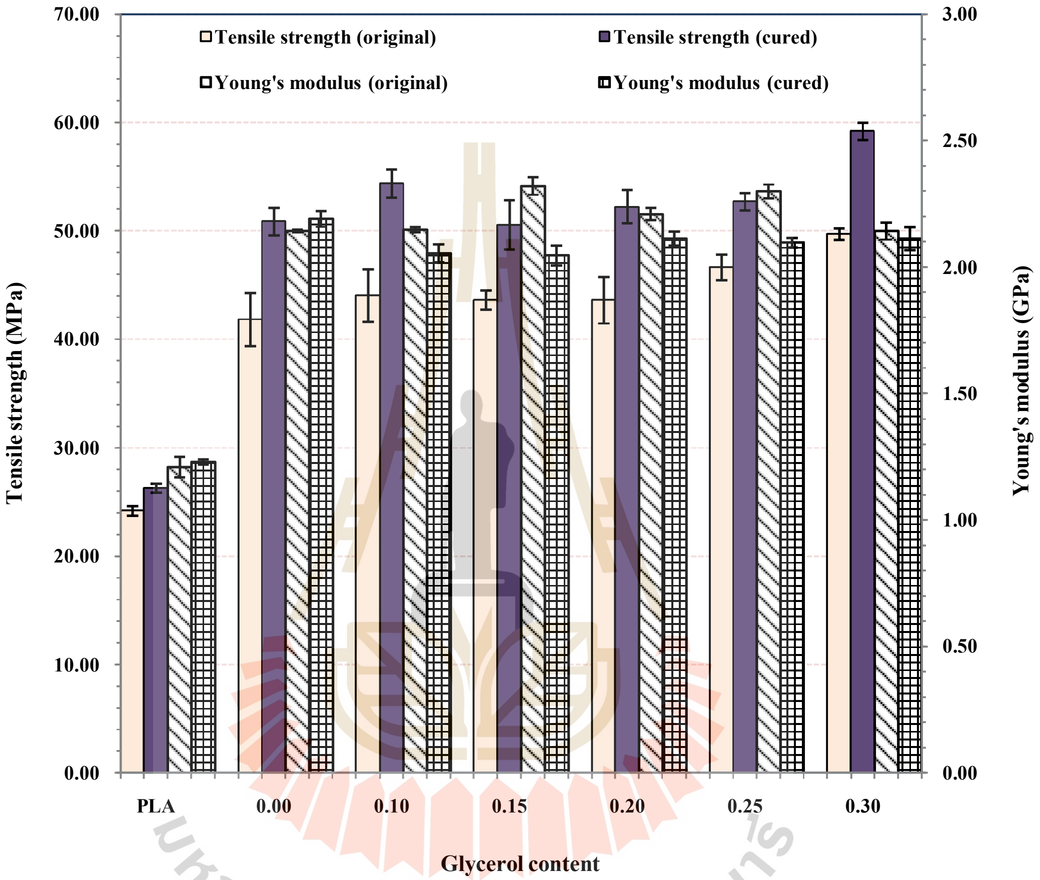


Figure 4.16 The tensile strength and modulus of PLA compound with glycerol contents.

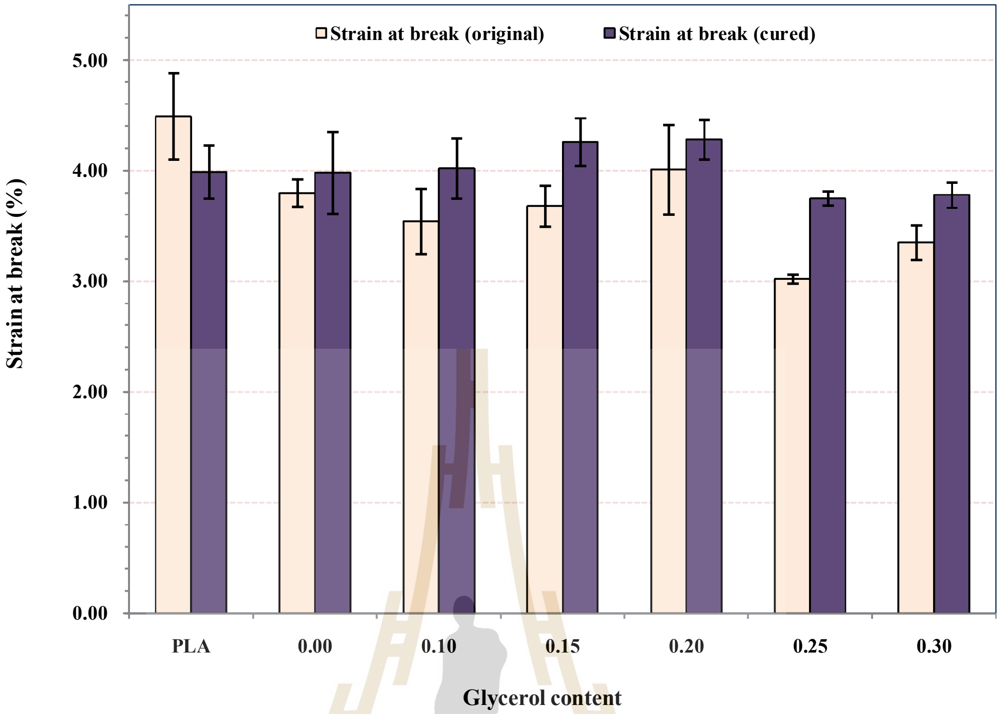


Figure 4.17 The % strain at break of PLA compound with glycerol contents.

4.2.4 Impact strengths

Figure 4.18 is the plot of notched and unnotched impact strength, summarized in Table 4.17, against the glycerol used for PLA compounding. It is seen that the fracture toughness by mean of the notched impact strength of both original and cured sample is graduately decreased with increasing the glycerol concentration except for cured condition at 0.3 phr which test value is oddly higher. Also, the impact strength of the cured sample is undoubtedly lower than the original sample. The PLA compound becomes more brittle material when increasing glycerol content.

For the unnotched mode of testing, it also noticed that the unnotched strength seem to be slightly decreased when using more glycerol especially at the content higher than 0.15 phr for both with and without sauna incubation.

The hypothesis for adding glycerol into the compound ingredient was as the plasticizer. It should improve the flow ability of the compound as concluded in the previous discussion. Adding the plasticizer normally can enhance the toughness and ductility of polymer. But from the result found in this experiment, glycerol at limited amount can enhance the mobility of the PLA chain and then improve the melt flow rate and tension ability of the compound. Further addition of glycerol, generally beyond 0.25 phr, the excess amount of the plasticizer would be reversed into the glycolysis reagent that can degrade the polymer matrix chain. As the result, the lowering in the toughness of the shorted chain polymer compound is observed. To deactivate the hydrolysis ability of this plasticizer, glycerol and isocyanate will be added to form branch chain liquid polyurethane. The effective of the reactive isocyanate will be discussed later in this report.

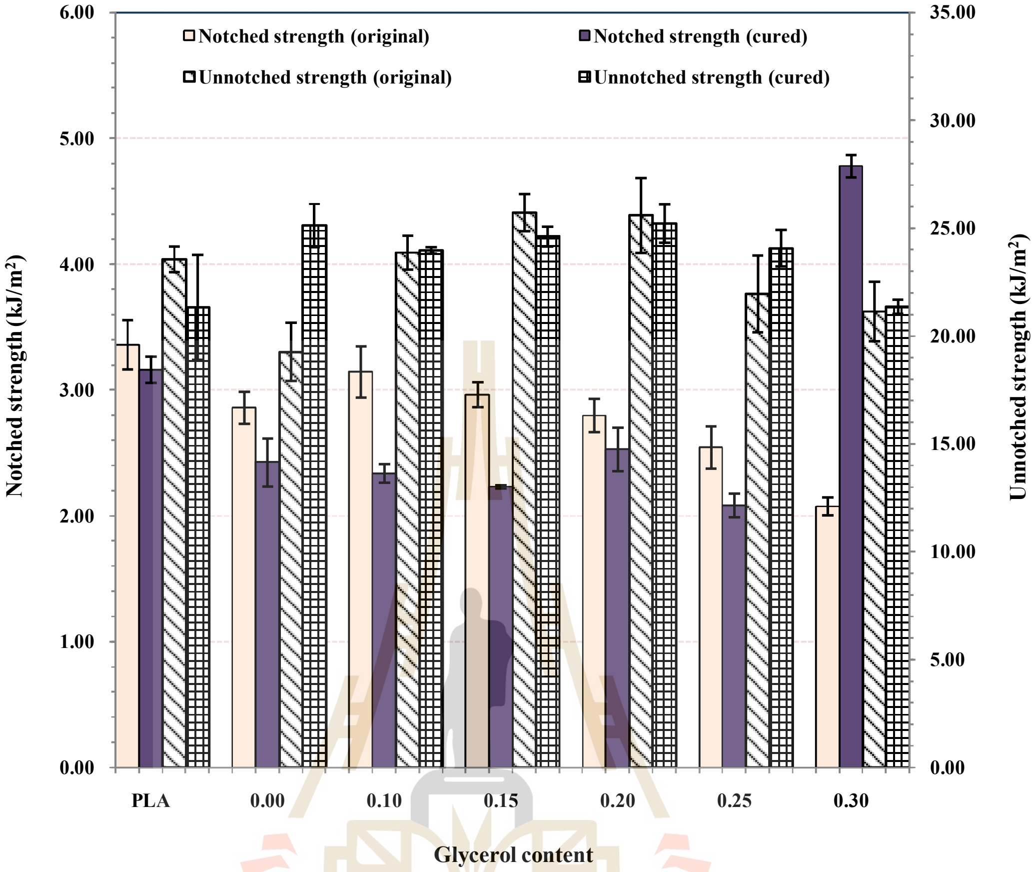


Figure 4.18 The impact testing of PLA compound with glycerol contents.

4.2.5 SEM analysis

The morphology of PLA compound by mean of scanning electron photographs of the fractured surface for the samples compounded using 0.1 and 0.3 phr of glycerol are shown in Figure 4.19. Previously, the fracture toughness of the PLA prepared was slowly increased with increasing the glycerol content from 0.1 to around 0.2 phr. Then, they were fractionally decreased on further increase in the glycerol content. They were also observed that there was a significant variation in the impact strengths of original and cured samples. In order to explain those variations, the trace of the fracture phenomena by the SEM analysis is needed. At 0.1 phr of glycerol, where it seems to have the better impact strength than the others, the SEM results of the original and cured compound are given in Figure 4.19 (**a**) and 4.19 (**b**). It is seen that the web like structure is presented on the fractured surfaces. After sauna post curing, the evidence of crack propagation is clearly seen. However, at 0.3 phr of glycerol addition, the fibrilla structure is still existed but loosely located but no evidence of crack propagated surface. The fibril structure may either come from the rubbery phase of the polyester polyols added or the product from the reaction of polyols/glycerol and amino silane to form rubbery polymer. Generally, the rubbery polymer which is immiscible blended into the brittle thermoplastics phase, it acts as crack tips dissipator. As the result, the crack propagation is stopped or slow down and high toughness material is obtained. From this experiment, it is seen by the SEM that the more glycerol loading the less in the formation of fibril structure. Consequently, impact strength is generally decreased with increasing the glycerol content.

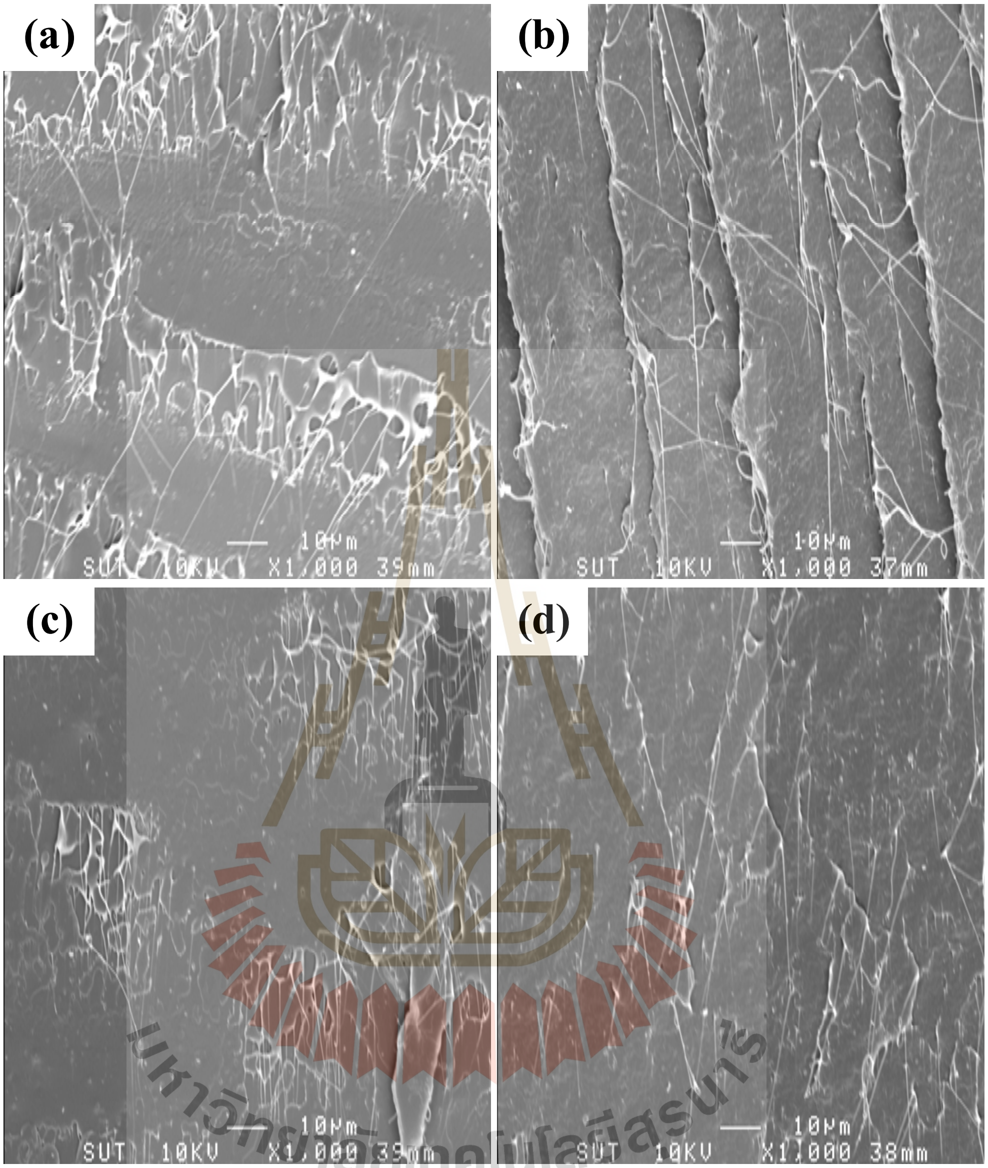


Figure 4.19 SEM micrographs for the fractured surfaces of PLA compound with glycerol contents; (**a**) original 0.1 phr; (**b**) cured 0.1 phr; (**c**) original 0.3 phr; and (**d**) cured 0.3 phr.

From the results seen in this experiment, adding glycerol as supplement plasticizer into the PLA compounding process, it generally enhances the flow ability and tensile properties of the compound when compare with pure PLA and the compound without glycerol. However, adding this plasticizer at high content, for example more than 0.2 phr, the fracture toughness properties of the PLA obtained is inferior. In next experiment, highly reactive isocyanate in conjunction with polyester polyols and glycerol to form the reactive poly(urethane) polymerization in the PLA compound process will be explored.

4.3 The Effect of Isocyanate on PLA Compound

From the previous experiment known that the optimal glycerol content was more than 0.2 phr. However the HDT of PLA compound was lower than 100°C. So that, in this experiment further improvement of the PLA compound properties, specially the HDT, is explored. In this research topic, study the effect of isocyanate; methylene diphenyl diisocyanate (MDI), as chain extender on the PLA compound is investigated. Generally, isocyanate can react with the hydroxyl end groups of glycerol, polyols and/or PLA end group to form the amino linkage, or commonly called urethane bonding between the reactants. As mentioned earlier that excess glycerol in the PLA compound ingredient would undergo glycolysis reaction on the PLA chain. It shortens the PLA chain and hence diminishing the mechanical properties. Deactivating the glycerol with isocyanate would reduce the tendency of the chemical induced chain degradation. Moreover, amino bonded chain forming between isocyanate and either from polyester polyols added or end group of PLA chain would be benefit for the toughness properties of the compound. So, improvement of the PLA compound properties by adding the isocyanate into the ingredient will be expected. In the compound formula studied, retaining the recipe content at 1.0 phr of silane, 2.0 phr of polyols and 0.3 phr of glycerol but varying the isocyanate from 0.1 to 0.3 phr is assigned as shown in Table 4.18. The compound was prepared in the twin screw extruder. The injection molded samples were tested and all the results obtained are summarized in Table 4.19.

Table 4.18 The composition of PLA compound with various isocyanate contents.

Runs	**Composition(phr)**			
	Silane	**Polyols**	**Glycerol**	**Isocyanate**
PLA	-	-	-	-
1	1.0	2.0	0.30	0
2	1.0	2.0	0.30	0.10
3	1.0	2.0	0.30	0.15
4	1.0	2.0	0.30	0.20
5	1.0	2.0	0.30	0.25
6	1.0	2.0	0.30	0.30

Table 4.19 Test results of PLA compound with various isocyanate contents.

Runs	Isocyanate content (phr)	MFI (g/10min)		HDT (^{o}C)		Tensile strength (MPa)		Young's modulus (GPa)		Strain at break (%)		Notched impact (kJ/m^{2})		Unnotched impact (kJ/m^{2})	
		original	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**
PLA	PLA	3.35 ± 0.04	3.82 ± 0.14	53.1 ± 0.83	53.1 ± 1.51	24.17 ± 0.87	26.28 ± 0.79	1.21 ± 0.08	1.23 ± 0.02	4.49 ± 0.78	3.99 ± 0.48	3.36 ± 0.39	3.16 ± 0.21	23.56 ± 1.21	21.34 ± 4.86
1	0	6.75 ± 1.21	8.83 ± 0.43	47.6 ± 0.92	55.9 ± 0.64	49.74 ± 1.07	59.20 ± 1.60	2.14 ± 0.07	2.11 ± 0.09	3.35 ± 0.31	3.78 ±0.23	2.07 ± 0.14	4.78 ± 0.18	21.14 ± 2.78	21.37 ± 0.65
2	0.10	7.36 ± 0.24	8.34 ± 0.29	45.0 ± 1.60	54.5 ± 0.50	41.20 ± 4.31	45.96 ± 2.88	2.19 ± 0.07	2.01 ± 0.13	4.65 ± 0.90	6.79 ± 1.73	2.68 ± 0.32	2.85 ± 0.20	21.68 ± 1.64	28.51 ± 4.40
3	0.15	7.44 ± 0.35	8.83 ± 0.38	44.0 ± 0.72	55.0 ± 0.92	37.54 ± 1.09	48.60 ± 4.90	2.09 ± 0.06	2.02 ± 0.17	6.60 ± 1.06	5.75 ± 0.96	2.62 ± 0.33	2.73 ± 0.22	25.78 ± 3.20	29.15 ± 3.72
4	0.20	7.53 ± 0.20	8.98 ± 0.21	45.7 ± 0.76	56.7 ± 0.50	43.08 ± 3.12	48.77 ± 1.58	2.09 ± 0.06	2.13 ± 0.11	4.71 ± 1.18	5.08 ± 0.85	2.37 ± 0.18	2.66 ± 0.25	27.89 ± 2.91	29.60 ± 2.48
5	0.25	8.70 ± 0.14	9.33 ± 0.31	43.9 ± 0.90	55.3 ± 1.01	41.07 ± 0.80	43.16 ± 4.21	2.10 ± 0.08	2.04 ± 0.05	4.61 ± 0.56	6.61 ± 1.84	2.56 ± 0.10	2.77 ± 0.19	25.01 ± 3.75	26.20 ± 0.18
6	0.30	7.65 ± 0.76	9.31 ± 0.40	44.3 ± 0.81	55.3 ± 1.67	41.08 ± 3.30	41.83 ± 3.90	2.12 ± 0.04	2.02 ± 0.07	3.94 ± 0.64	5.58 ± 0.96	2.27 ± 0.08	2.97 ± 0.31	24.82 ± 3.08	29.85 ± 1.90

4.3.1 The effect of isocyanate content on the MFI

Table 4.19 and Figure 4.20 illustrates the MFI of the compound with respect to the isocyanate added contents for both with and without sauna cured process. It is seen that the MFI of PLA compound is marginally increased with increasing the isocyanate content for both original and sample with the sauna cured. However, when compare with the virgin PLA, it is observed that the flow ability of the compound is obviously at least two folds higher. But they are relatively similar to the compound without isocyanate addition. From the rheological results, the hypothesis that adding the isocyanate into the ingredient would retard the glycolysis reaction and also extending the chains by isocyanate/hydroxy bonding, consequently the viscosity of the compound would be increased, lower the MFI, cannot be explained. But, the result suggests that the compound has lower viscosity than the virgin polymer. The chain degradation still exist during the mixing process even though the isocyanate is incorporated. This degradation phenomenon would have the great effects on the mechanical properties of the compound that will be later discussed.

4.3.2 The effect of isocyanate content on HDT

Within the statistical standard deviation, HDT of the PLA compound with increasing the isocyanate content is almost constant as observed as the numerical figures in Table 4.19 and graphical in Figure 4.20. Especially for the compound without sauna cured, HDT of PLA compound is approximately 6^{o}C below the virgin PLA. After sauna curing processing, HDT of the compound was significantly increased but not that higher than the virgin polymer. The increasing of HDT via the sauna incubation is probably arisen through the siloxane formation. Another explanation can be included in this phenomenon is that HDT can be elevated by incubation of the PLA sample at 60^{o}C, above the T_g of polymer, for 12 hrs. This is because the crystallinity of PLA or perhaps others polymer formed during the compounding process would be increased and hence the higher in HDT.

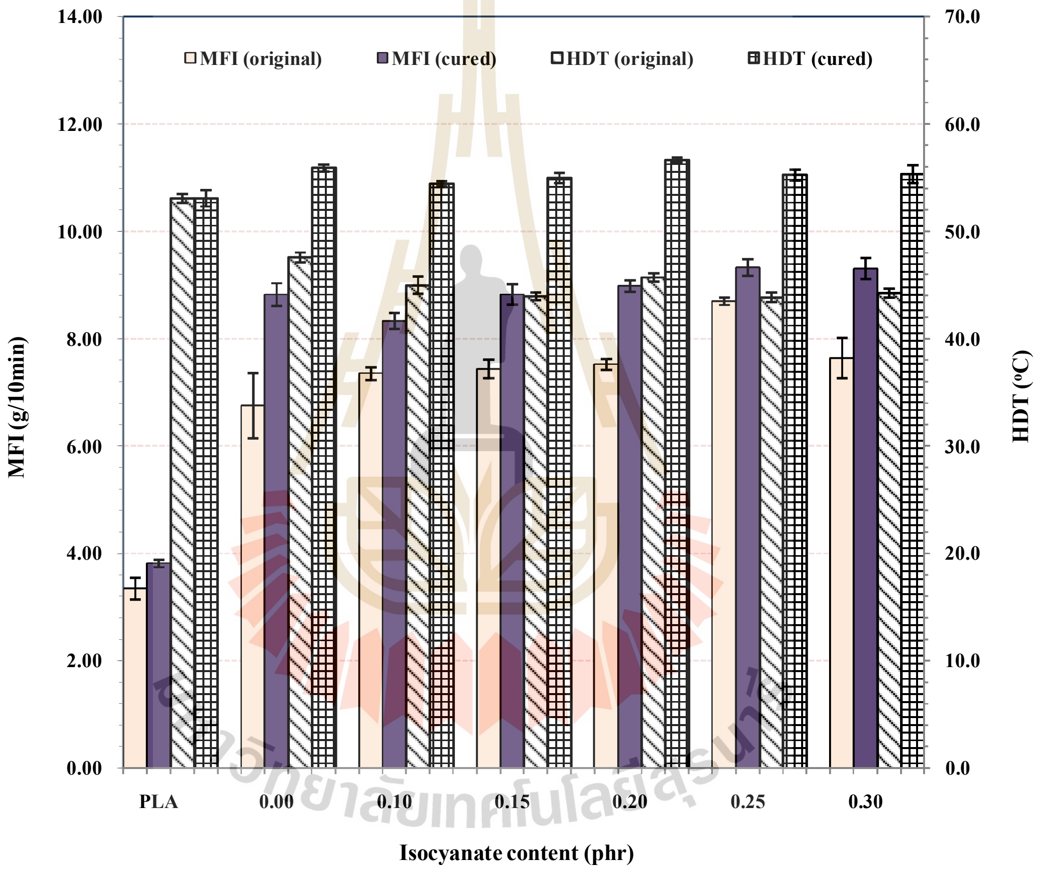


Figure 4.20 The MFI and HDT of PLA compound with isocyanate contents.

4.3.3 The tensile properties

The results of tensile testing on the PLA compound specimen before and after sauna treatment are summarized in Table 4.19. Tensile strength, Young's modulus and strain at break against the isocyanate contents are also plotted and given in Figure 4.21 and 4.22, respectively. Generally, it is indicated that the sauna incubation increases the tensile strength and strain at break but slightly decreases in modulus. Comparison with the virgin polymer, tensile strength of the compounds are much higher. But, it is seem that adding isocyanate into the compound recipe is marginally lowered the strength. The isocyanate content does not have any obvious effect on the strength as the test values are almost unchanged with the amount of isocyanate addition.

Similarly, the modulus of the compounds as shown in Figure 4.21 indicate that Young's modulus of PLA compound is again higher than neat PLA. There is slightly decreased in the modulus of PLA compound after sauna cured process. But the modulus are almost unchanged with increasing the isocyanate content. From the modulus figures, it can manifest that siloxane bridging through the moisture incubation process would increase the ductility of the compound as the tighter chain packing is formed.

For the flexibility of the compound, derived from the strain at break, with respect to the amount isocyanate addition is reported in Figure 4.22. According to the test results, it is seen that the deformability of the PLA compound is better than the PLA. Further adding the isocyanate into the compound is further enhanced the strain at break for both original and cured samples. However, it is quite ambiguous to state that there is different between the test values between original and cured specimen. But it is noticed that sauna treatment is majorly higher the % strain of the compound. Within the acceptable error and combining the tensile properties obtained, it is confidence to suggest that higher in tensile strength, modulus and strain at break of the PLA compound shows the superior in the ductility of the material. But adding isocyanate into the compound does not much enhance the property vice versa it has high possibility, with an ambiguous, to reduce the tensile loading ability.

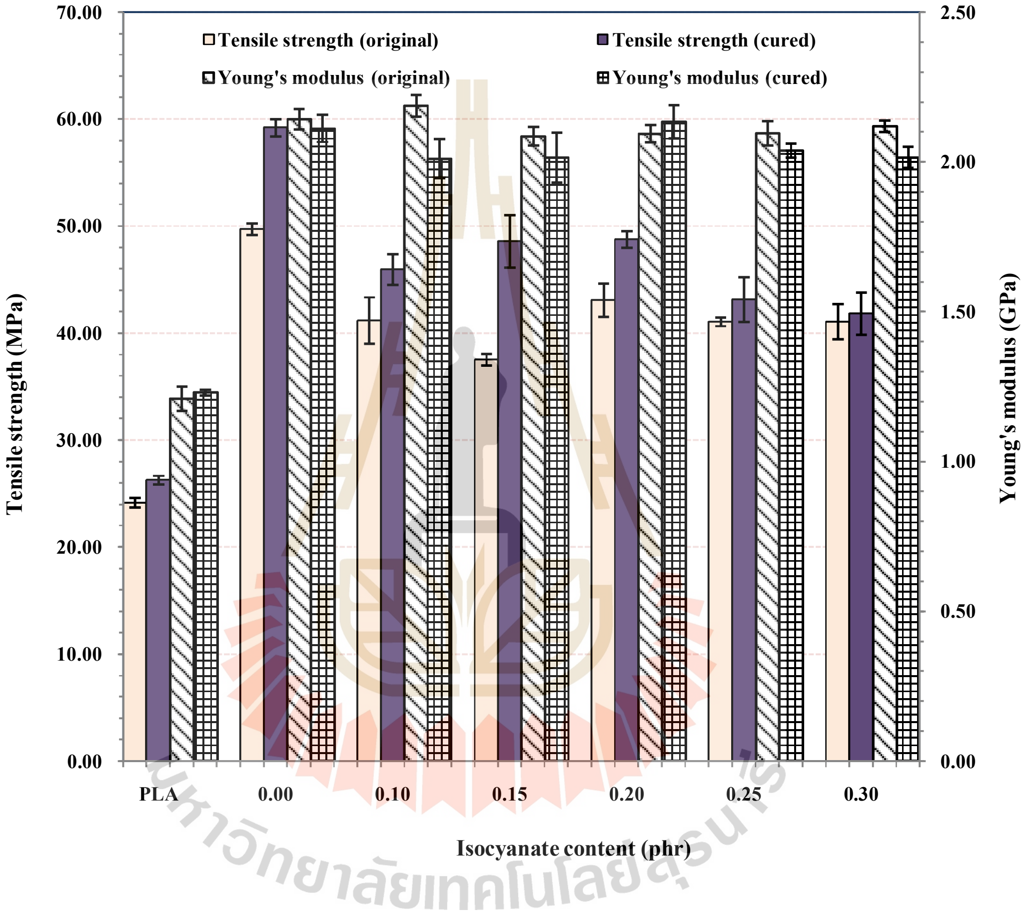


Figure 4.21 The tensile strength and modulus of PLA compound with isocyanate contents.

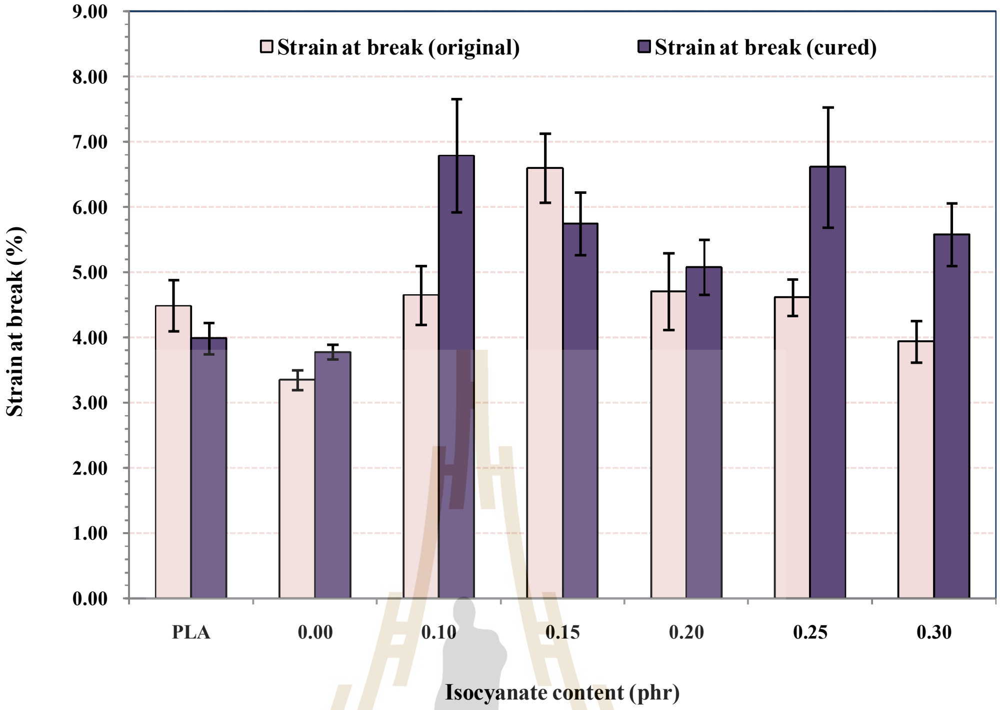


Figure 4.22 The % strain at break of PLA compound with isocyanate contents.

4.3.4 The impact strength

Taking the results of notched and unnotched impact strengths reported in Table 4.19 plot against the amount of isocyanate addition. Graph is shown in Figure 4.23. It is seen that the notched impact strength of the isocyanate added PLA compound is fractionally decreased with increasing the amount of isocyanate for both original and cured samples. Even though, the sauna incubation has slightly higher the strength. When compare with the strength of pure PLA and PLA compound without isocyanate addition, the test values are lower especially for the sauna cured specimen.

In contrast to the notched mode, the unnotched impact strength of PLA compound with addition of isocyanate content show that they are more or less independence on the chemical. The test values are much higher than the neat PLA and PLA compound without isocyanate incorporation, especially in the cured condition.

According to the results found, it scientific hypothesis can be made that adding isocyanate, which is reactive with hydroxyl group, into the PLA compound the material behave likely to be thermosetting in nature, low notched impact but high in unnotched impact. Taking only these impact testing observation, it could suspect that addition of reactive isocyanate in the compound the reaction between hydroxyl groups; from glycerol, polyester polyols or hydroxyl terminated end-group of PLA, with isocyanate to form hard and brittle segments in the matrix phase. As the result, the tough material; PLA compound with no isocyanate, turn into brittle one.

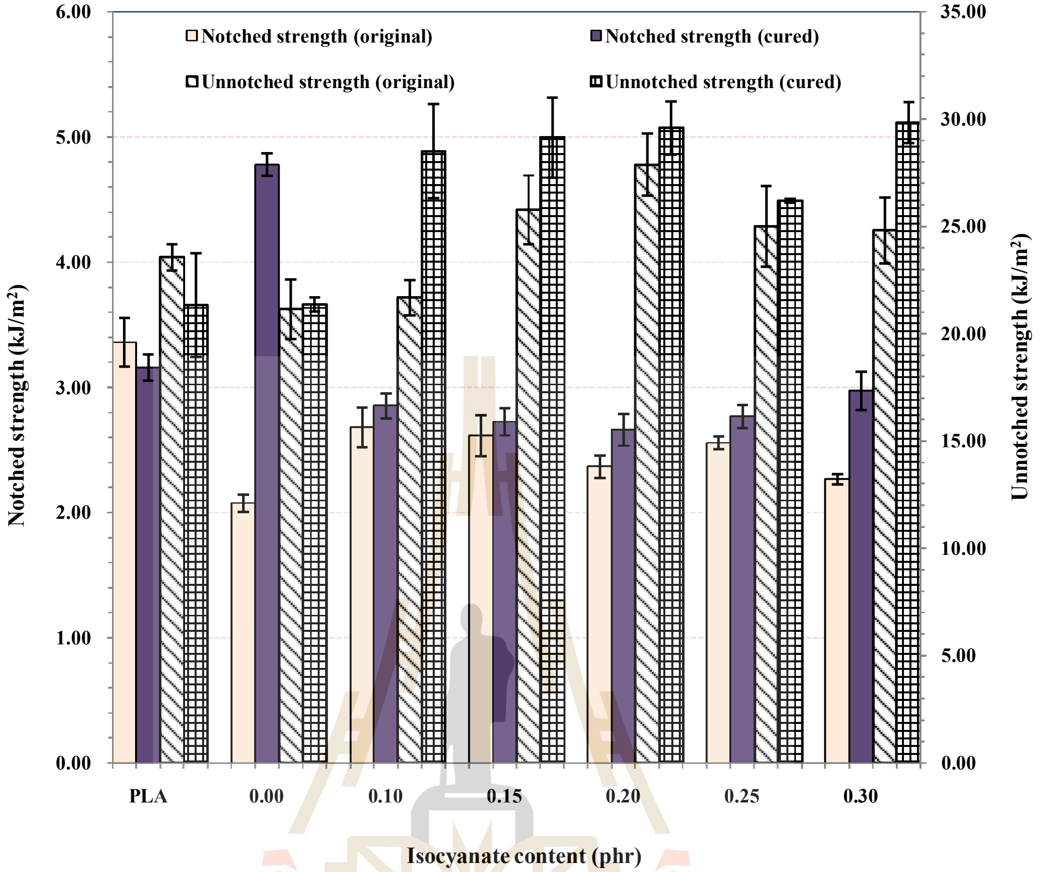


Figure 4.23 The impact strength of PLA compound with isocyanate contents.

4.3.5 Morphology of isocyanate added PLA compound

Figure 4.24 (**a**) – 4.24 (**d**) show the SEM micrographs of the fractured surfaces of PLA compound with 0.2 and 0.3 phr of isocyanate added, respectively. The common observation seen from the picture is that the fractured surface transform from relatively smooth of original one to rough traces of cured sample. Tiny dispersed drops are evidenced on the surface of the compound. Highly viscous, or rubbery, in nature of the drop on the original specimen is observed by the fibril formation during the sample break down. The diminishing of the fibril tail is seen when the sample was cured and increased the amount of isocyanate. This micro dispersed phase could be the polyester polyols. Consequently, this observation could reinforce the earlier statement made that the reaction between isocyanate with hydroxyl reagent, polyols, to form the hard segment; polyurethane, into the compound matrix. The hard particle, hence, decrease the fracture toughness of the material.

From the experiment results on the effect of isocyanate addition into the PLA compound, it can conclude that the thermal property is slightly increased but not much as the target need, 100°C. Also, the mechanical properties are inferior when compare with the compound without the isocyanate. The compound also becomes thermosetting in nature because the reaction between isocyanate group and hydroxyl group to form the dispersed hard segment.

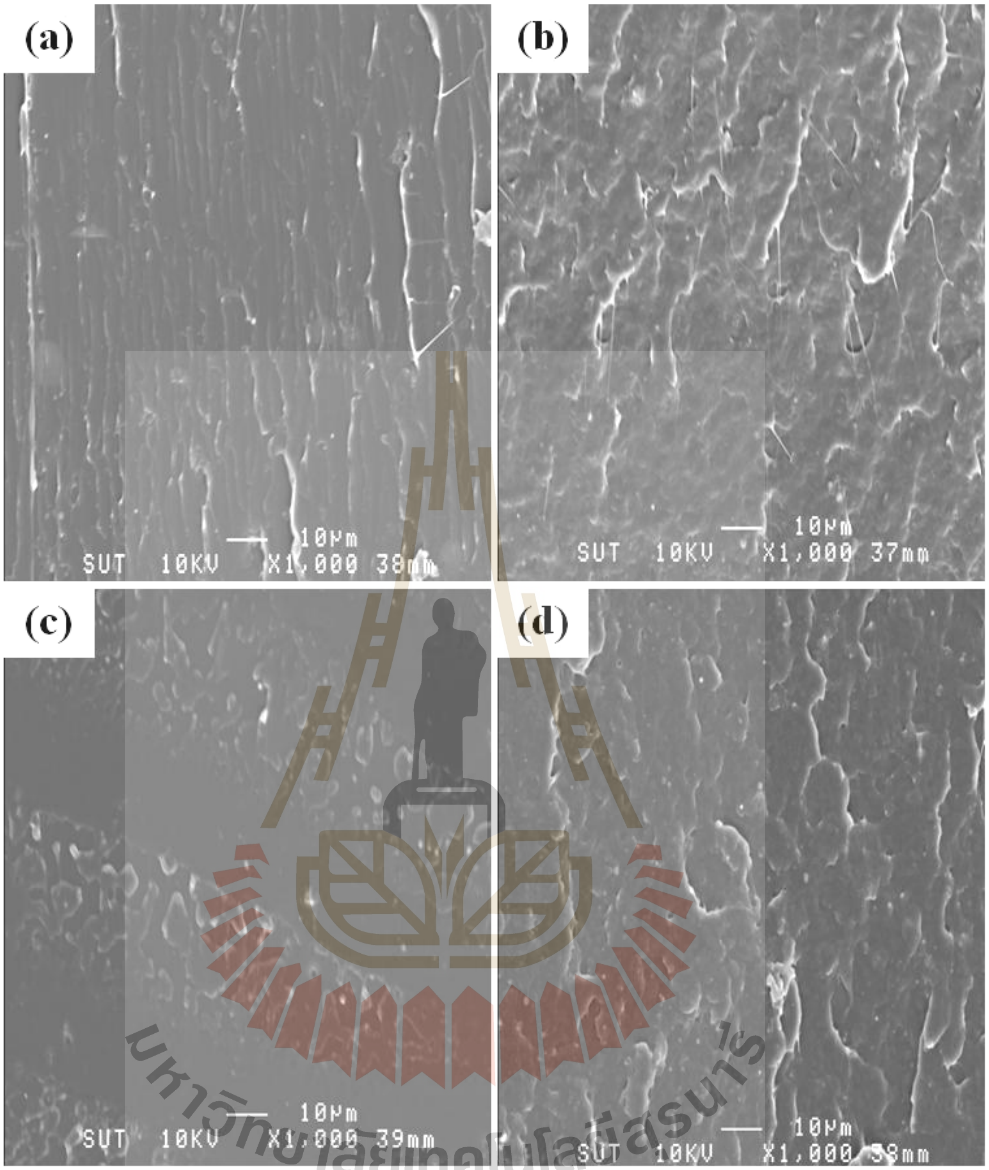


Figure 4.24 SEM micrographs of the fractured surfaces of PLA compound; (**a**) with 0.2 phr (original), (**b**) with 0.2 phr (cured), (**c**) with 0.3 phr (original) and (**d**) with 0.3 phr(cured) of isocyanate contents, respectively.

4.4 The Effect of Peroxide on PLA Compound

From the previous experiment, the addition of *gamma*-aminopropyltriethoxysilane (APS, A-1100) as epoxy crosslink agent into the PLA compound, the result indicated that HDT was improved but still lower than the target value at 100^{o}C. In this research exploration, the use of vinyltrimethoxysilane (VTMS, A-171), vinyl type silane, will be discussed. In order to achieve the grafting process of this silane on the polymer chain, the free radical is required for vinyl initiation. Vinyltrimethoxysilane (VTMS) is normally grafted onto the polymer backbone by reactive extrusion melt mixer. In this study, dicumyl peroxide (DCP) was employed as free radical initiator. The crosslinked PLA could be achieved by the silane grafted chain undergo addition/condensation reaction through the moisture molecule during the sauna treatment. The outcome crosslinked chain would led to the improvement in the mechanical and thermal properties of the PLA compound.

The compound formula in this study comprised of 1.0 phr of silane (VTMS), 2.0 phr of polyols, 0.3 phr of glycerol and 0.2 phr of isocyanate. The DCP addition was varied from 0 to 1.5 phr. Table 4.20 summarizes the compound ingredients investigated in this section. The PLA compounding was again performed in the twin screw extruder at the identical conditions given earlier. The injection molded samples were obtained and tested. The results obtained are summarized in Table 4.21.

Table 4.20 PLA compound ingredient and peroxide contents.

Runs	Composition (phr)					
	PLA	Silane	Polyols	Glycerol	Isocyanate	Peroxide
PLA	100	-	-	-	-	-
1	100	1.0	2.0	0.30	0.20	0.0
2	100	1.0	2.0	0.30	0.20	0.2
3	100	1.0	2.0	0.30	0.20	0.5
4	100	1.0	2.0	0.30	0.20	1.0
5	100	1.0	2.0	0.30	0.20	1.5

Table 4.21 Test results of PLA compound with difference in the peroxide contents.

Runs	Peroxide contents (phr)	MFI (g/10min)		HDT (°C)		Tensile strength (MPa)		Young's modulus (GPa)		Strain at break (%)		Notched impact (kJ/m^2)		Unnotched impact (kJ/m^2)		Gel fraction (%)	
		original	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**
PLA	PLA	20.35±0.79	32.70±1.94	53.1 ± 0.83	53.1 ± 1.51	24.17±0.87	26.28±0.79	1.21 ± 0.08	1.23 ± 0.02	4.49 ± 0.78	3.99 ± 0.48	3.36 ± 0.39	3.16 ± 0.21	23.56±1.21	21.34±4.86	0	0
1	0.0	26.17±0.74	30.84±0.88	52.0±0.47	54.2±0.35	52.93±5.66	59.86±3.13	2.43±0.09	2.48±0.13	4.03±1.44	3.74±0.42	3.22±0.27	3.40±0.20	32.61±5.46	27.31±6.44	1.44±0.09	4.18±0.32
2	0.2	25.48±0.80	28.49±0.37	51.1±0.31	56.6±1.15	49.23±4.18	54.83±3.00	2.50±0.09	2.38±0.06	5.09±1.37	3.98±0.35	3.11±0.11	3.47±0.15	32.12±4.94	30.35±4.55	2.12±0.18	4.96±0.87
3	0.5	18.22±0.68	27.90±0.55	50.5±0.35	60.1±1.77	47.11±2.05	59.40±3.46	2.22±0.06	2.47±0.08	5.67±1.48	4.16±0.33	3.05±0.61	3.83±0.39	33.55±7.69	31.43±2.64	12.05±0.93	15.86±1.02
4	1.0	9.78±0.73	18.30±0.89	49.7±0.40	63.1±1.70	54.23±6.42	62.97±6.63	2.44±0.16	2.69±0.22	4.65±0.99	4.14±0.88	3.54±0.49	3.38±0.10	38.15±9.79	38.87±5.07	28.38±1.23	34.10±1.14
5	1.5	0.26±0.19	0.47±0.20	49.6±0.40	60.0±1.41	55.29±4.31	62.50±3.61	2.49±0.14	2.53±0.21	4.71±0.80	4.08±0.02	3.46±0.45	3.34±0.66	39.08±7.26	39.14±3.39	32.17±1.12	45.12±1.05

4.4.1 The MFI of PLA compound

Table 4.21 and Figure 4.25 present the melt flow index at 230/2.16 of PLA compounds. General observation, it is seen that the MFI of the compound is decreased with increasing the peroxide contents for both original and sauna cured samples. It is also observed that the flow index is higher after undergoing sauna incubation. The decreasing in the polymer melt could be due to the increasing in the molar mass of chain either by grafting or crosslinking. This flow ability result indicates that the PLA chains are extended by the silane/DCP crosslink system. The confirmation by crosslink density determination will be discussed later on. However, the test figures indicate that the MFI of the sauna cured sample at the given DCP content is increased comparing with the original one. This phenomenon is might be due to the moisture residual during the prolong incubation in the moisture saturated oven. The traces would accelerate the chain hydrolysis during the melting in the test barrel. Shorter chain would higher the flow ability of the polymer melt. Taken only the MFI result, it is strongly suggested that either grafting or crosslinking of PLA chain to extend the molar mass of the polymer could be accomplished by introducing the vinyl silane/peroxide crosslinking system into the compound ingredient.

4.4.2 The HDT of PLA compound

The HDT result shown in Table 4.21 and also in Figure 4.25 was obtained at 445 kPa standard load. The test figures reveal that HDT is marginally decreased with increasing the DCP content for the test sample without sauna curing. However for the samples after performing the sauna incubation, the service temperature is noticeably increased with increasing the peroxide addition. The elevating in the HDT via the sauna treatment could be the positive effect from the molar mass increase resolved from the silane/moisture induced crosslink reaction. According to the test results, it could say that the improvement in the thermal property is due to the chain crosslinked process. It is also seen that further hurdle the DCP content beyond 1.0 phr, the HDT is lowered. Excess crosslink density would resist the flow during the injection of the compound. Consequently, homogeneity of the molded specimen would be incompetence. Therefore, the HDT figure resolved from the test would be lowered than usual.

According to the HDT investigation from this study section, the temperature was improved with increasing the DCP adding. Only approx. 63°C is the highest value. It is far below the expectation at 100°C.

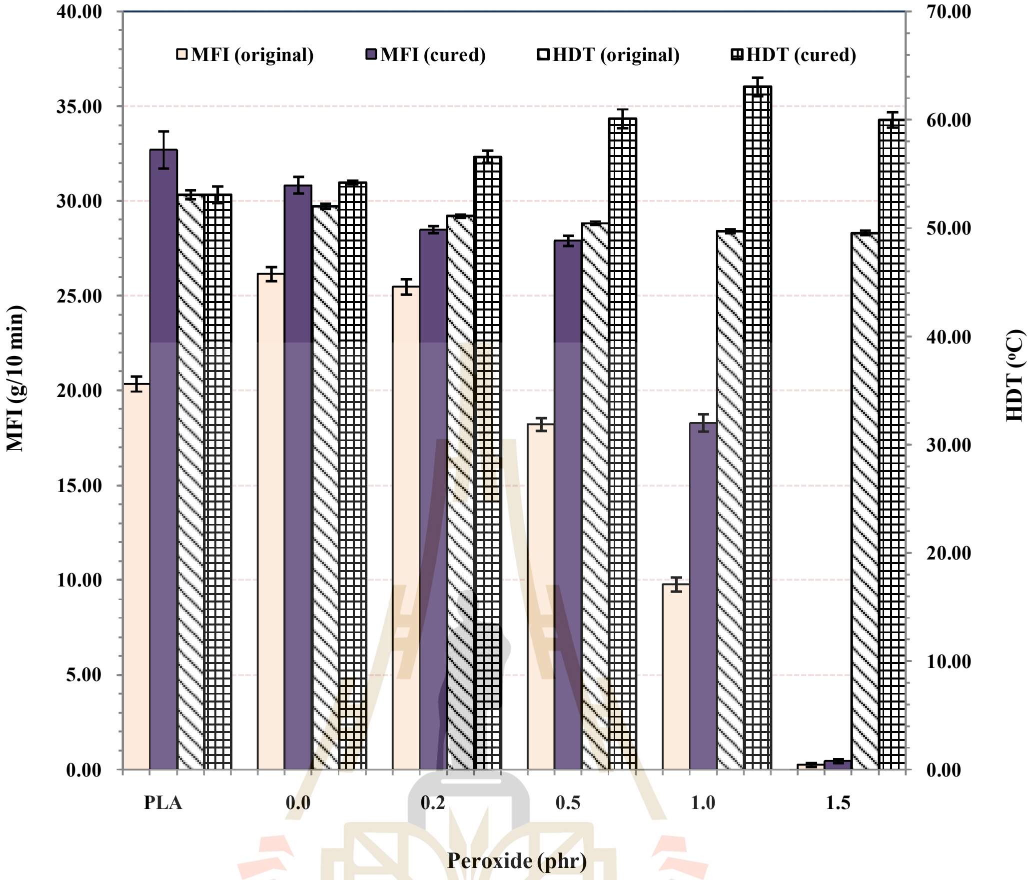


Figure 4.25 MFI and HDT of PLA compound with DCP contents.

4.4.3 The tensile properties of PLA compound

In Table 4.21, the tensile properties by mean of strength, Young's modulus and % strain at break of the PLA compounds before and after sauna incubation are reported. The plot of tensile strength and Young's modulus with the DCP concentration is given in Figure 4.26. The % strain at break and the DCP used is plotted and presented in Figure 4.27. According to the tensile strength, it is evidenced that the DCP initiated PLA compound has the tendency to be increased with increasing the peroxide content. It is obvious that the strength of the compound is higher than neat PLA. Further increasing in the tensile strength is found when the specimen was undergone sauna treatment. It is also noticed that the strength is likely to become constant at high peroxide loading, more than 1.0 phr. For the tensile modulus, the similar trend to the strength is observed. Also, the plot of % strain at break indicates that slightly increase from 4% to 6% when the peroxide was added at 0.0 to 0.5 phr into the compound ingredient. Further increase the DCP content more than 0.5 phr, it reduces the % strain at break. It is well known that low strength, low modulus but high % elongation before fail is the common characteristic of linear chain thermoplastics. Vice versa, high strength and high modulus but low % strain at break are the outstanding properties of crosslinked chain polymers or thermoset materials. Regarding to the tensile figures of the PLA compound derived from this experiment, it could be hypothesized, especially in the case of sauna cured samples, that increasing in the DCP in the compound ingredient would increase the chain length of the polymer. At above the critical DCP loading, the loosely crosslinked chains would be formed. Therefore, the thermoplastic in nature is reduced but domination of thermosetting is observed. Apparently, silane/moisture condensation reaction via the sauna incubation would have the great prompt to become the thermosets in nature.

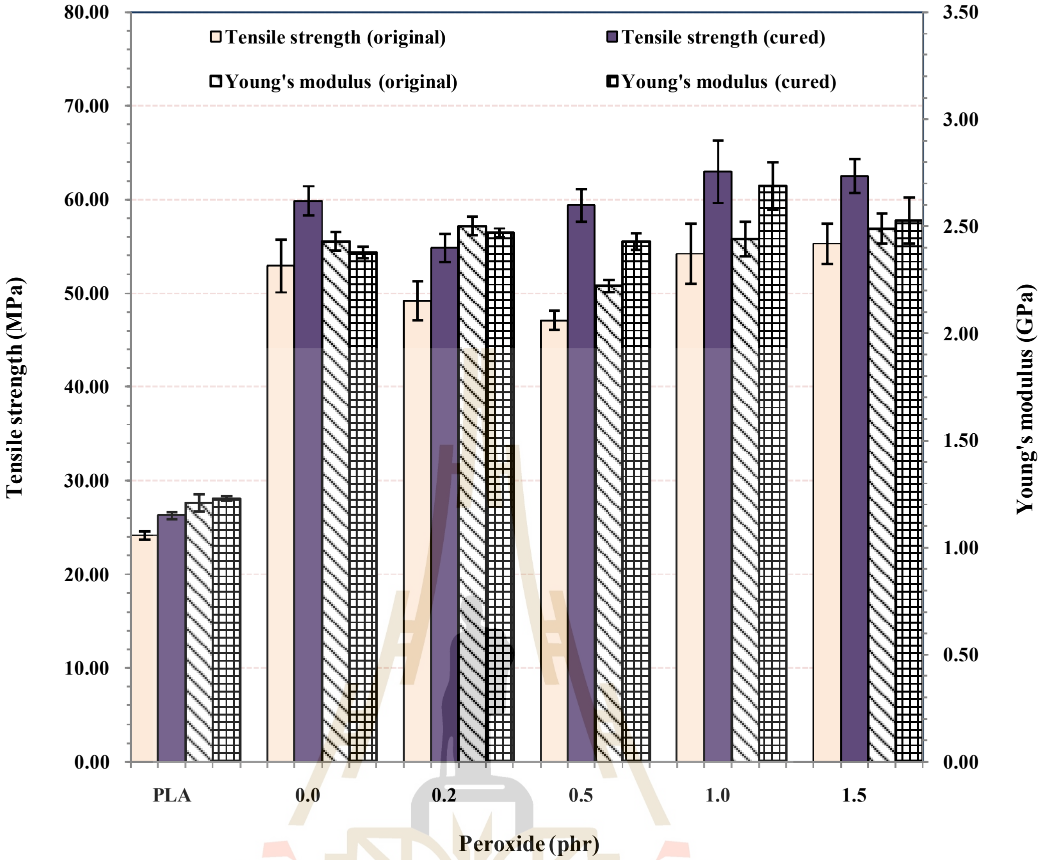


Figure 4.26 The strength and modulus of PLA compound with DCP contents.

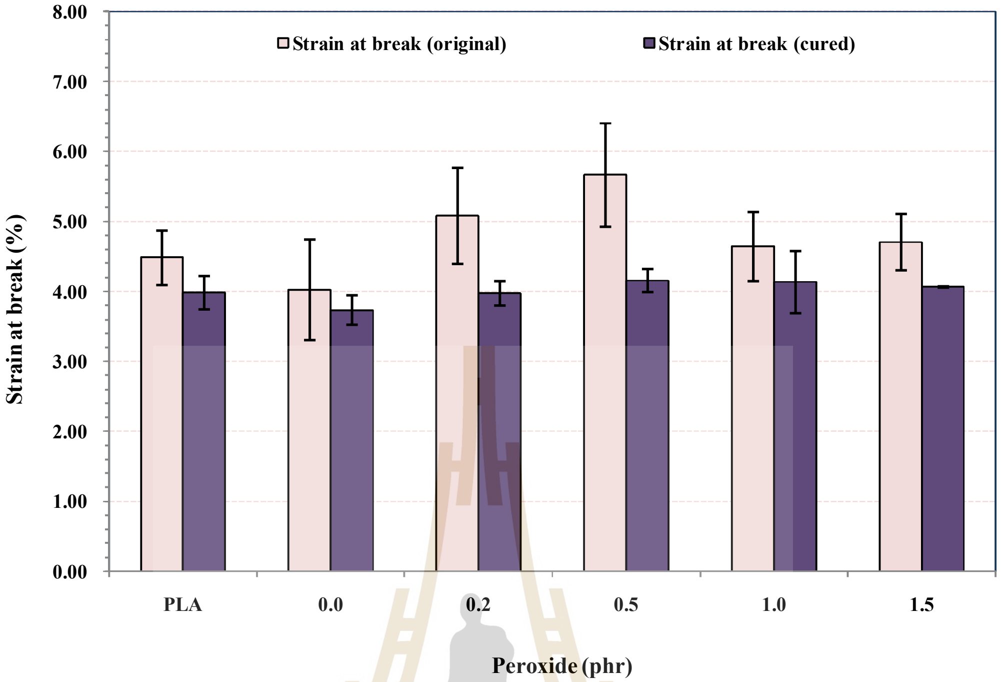


Figure 4.27 The strain at break of PLA compound with DCP contents.

4.4.4 The impact strengths of PLA compound

PLA base itself is commonly and incompetently known as the brittle polymeric material. The PLA compound with high heat resistance but absolutely low impact resistance would be useless in term of engineering design. Therefore, the investigation of the fracture toughness by mean of the impact strengths, both notched and unnotched, is essential. The impact testing result of the silane/DCP added PLA compound is illustrated in Table 4.21 and plotted against the DCP content in Figure 4.28 for notched and unnotched impact tests, respectively.

Undoubtedly, the notched impact strength of PLA compound before sauna treatment is almost constant when 0.0 to 0.5 phr of DCP was added. But further increase the peroxide initiator to 1.5 phr, the impact strength is marginally increased.

Almost completely opposite trend is seen for the sauna cured specimen. The increase in the crosslink density via the treatment would be used to explain this observation.

For the unnotched mode of impact testing, the unnotched impact strength of PLA compounds are improved with rising the peroxide concentration for both original and cured samples. Closer observations, the unnotched impact strength of the PLA compounds are lowered when the sauna incubation was performed. It is indicated that brittle material is obtained. The thermoset characteristic due to the increasing in the crosslink density is explained.

Base on this impact testing result in this study, it could postulate that added vinyl type silane and DCP, as crosslink system, into the PLA compound would result in the crosslink of PLA chain. Hence, the brittle like material or thermoset polymers, would be evidenced. Lower the concentration of DCP mixing, highly branched PLA would be consequently formed. Thus, tougher material, high impact strength, is resolved.

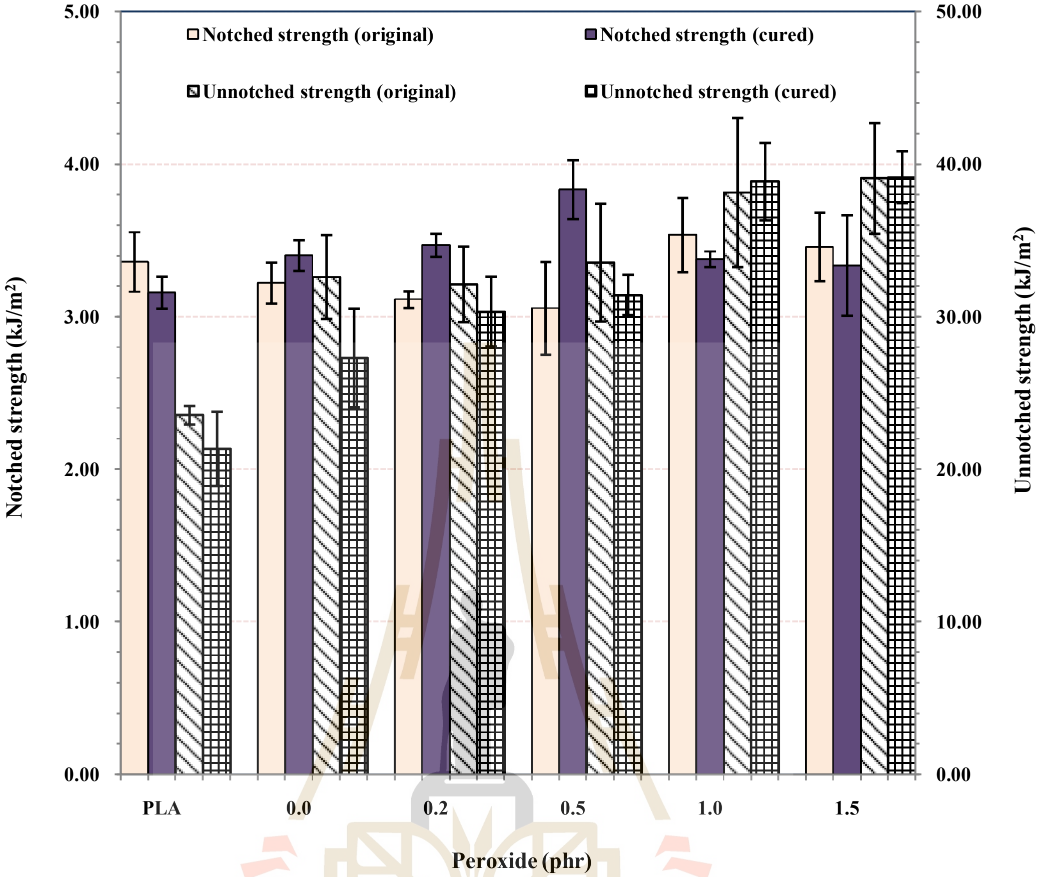


Figure 4.28 The impact strength of PLA compound with DCP contents.

4.4.5 Gel fraction of PLA compound

According to the early discussion, the network structure of the PLA chain through the silane/peroxide induced crosslink reaction, especially after undergoing sauna incubation, was one of, and most likely, the prime suspects for the changing of the compound properties. Therefore, the degree of crosslinking of the PLA compound was determined by gel fraction in chloroform. The result of the % insoluble fraction is presented in Figure 4.29. The plot shows that % gel fraction is exponentially increased with increasing the DCP content both for original and cured sample. The figure is also exhibited that higher in % gel fraction when the compound was underwent sauna treatment. It implies that PLA chain was somehow reconstructed into longer chains either by branching or macro crosslink through the VTMS/DCP addition. Moreover, prolong annealing the sample in the moisture saturated oven at 60°C was accelerated the silane/moisture condensation reaction into competition and hence increasing the chain crosslink density. From the test result, it is also observed that approx. 2-4% of the insoluble fraction is noticed for the compound without DCP addition. This evident suggests that other ingredients added, polyols, glycerol and isocyanate, could manipulate the chain structure of PLA to form the non dissolvable, in chloroform, polymer.

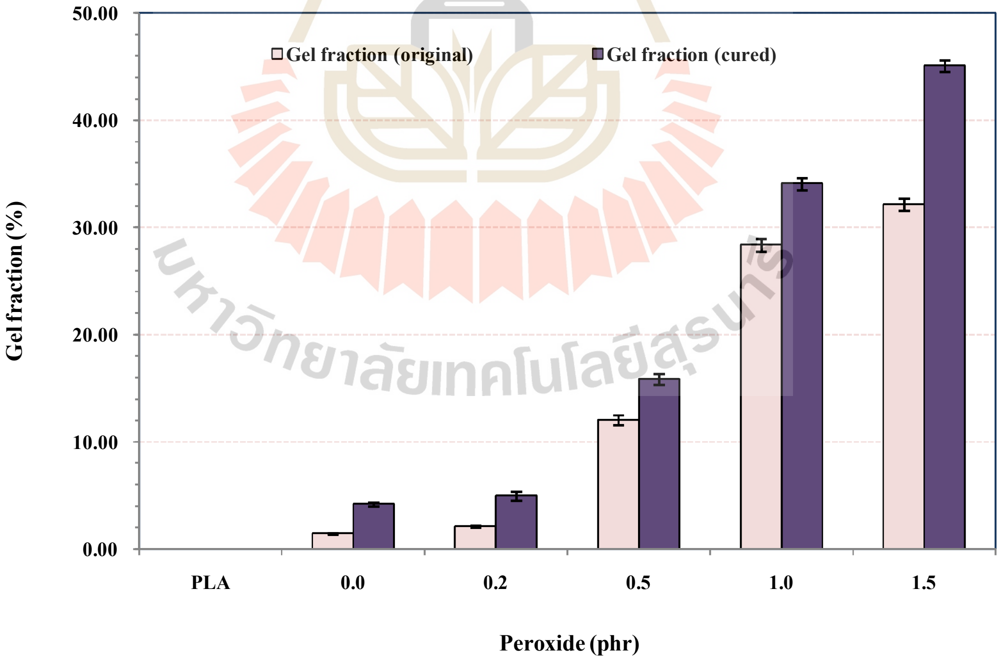


Figure 4.29 The % gel fraction of PLA compound with DCP contents.

4.4.6 The morphology of silane/DCP added PLA compound

The SEM photographs of the fractured surface of PLA compound samples with 0.2 and 1.0 phr of DCP added are shown in Figure 4.30 (**a**) - 4.30 (**d**), respectively. From the previous section, the notched impact strengths of these two materials were 3.11 and 3.47 kJ/m^2 and 3.54 and 3.38 kJ/m^2 for the original and sauna conditioned, respectively. They are relatively brittle material. Regarding to the SEM investigation, the fractured traces confirm that the compounds are fragile because quite smooth crake propagation phenomenon are seen. Apparently, the fibril like at the beginning of the crake tips is noticed, especially at high DCP concentration and after sauna incubation. This fibre trace would indicate the stronger bonding of the long chain or macro crosslink chain formed via the addition of silane/peroxide crosslink system.

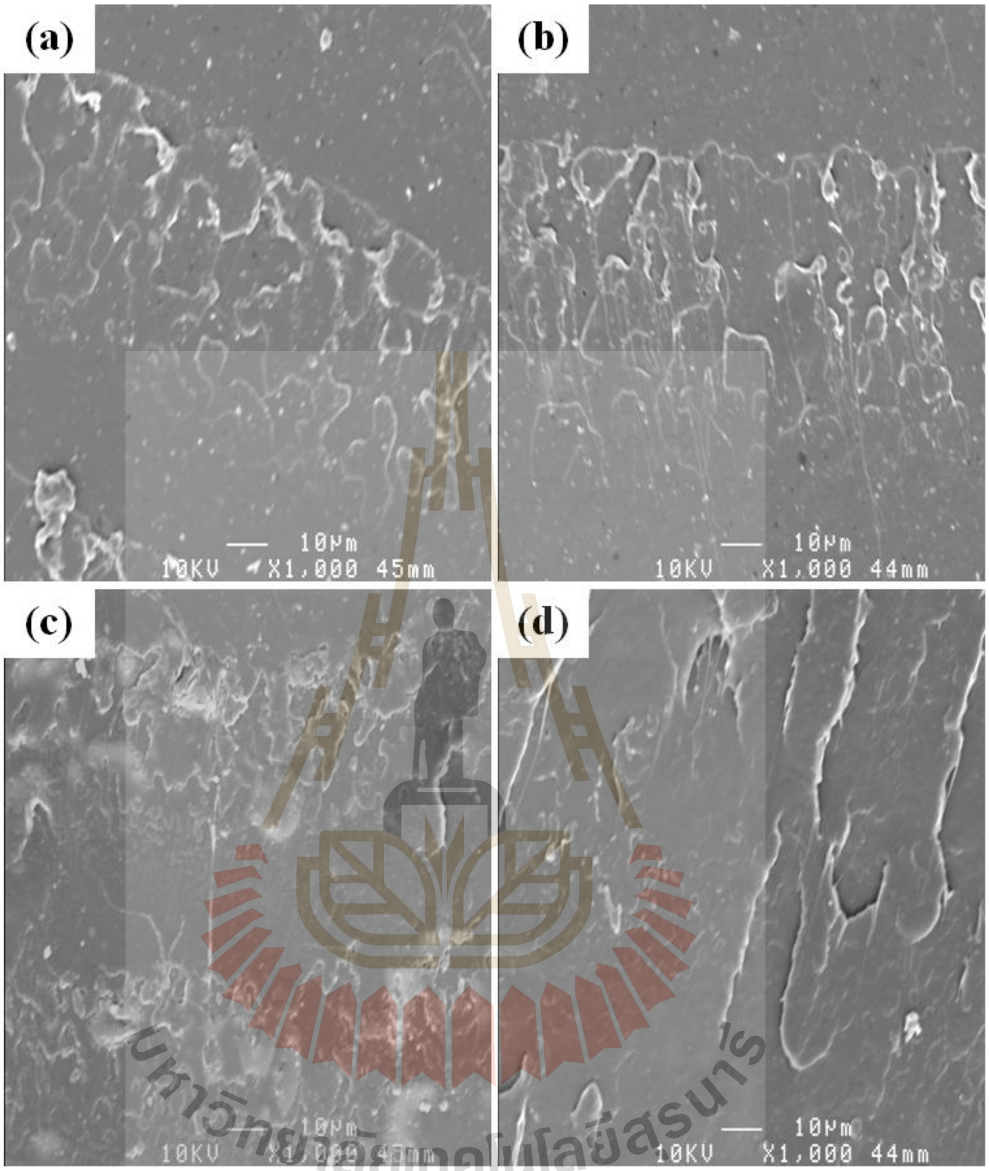


Figure 4.30 The morphology of the fractured surface PLA compound at the DCP content of; (**a**) 0.2 phr (original), (**b**) 0.2 phr (cured), (**c**) 1.0 phr (original) and (**d**) 1.0 phr (cured), respectively.

4.4.7 The biodegradability observation

One of the main purposes for this study is to obtain the biodegradable compound with good mechanical and thermal properties. Therefore, the biodegradability of the compound samples obtained is necessarily verified. They were preliminary conducted by using simulated landfill chamber as described in the experimental section at 60^{o}C under aerobic atmosphere. Figure 4.31 shows the plot the % retrained sample weigh with the weekly basis buried times for the neat PLA and PLA compound at 0 phr of DCP with having gel content between 2-4%. The result indicates that neat PLA sample is slightly degraded for the first four weeks buried time. After that the sample weight is noticeably decreased. More than eight weeks of the composting time, neat PLA sample were observed to be disintegrated into small pieces where weight loss measurement could not be performed. Similar trend is noticed for the original sample of PLA compound. But after ten weeks time, the measurement was unable to perform on the small pieces broken sample. In comparison between original and sauna cured PLA compound and also between virgin PLA and sauna incubated PLA compound, it is evidenced that the degradation rate of the cured sample is quicker than those two polymers. Because of within six weeks time approx. 65% of retrained weight is obtained comparing with approx. more than 95% for those two biodegradable materials. Taken this biogradability investigation, it could say that the PLA compound having 2-4% of the crosslinked chain able to be degraded under the biological test chamber as similar well defined manner found for the PLA.

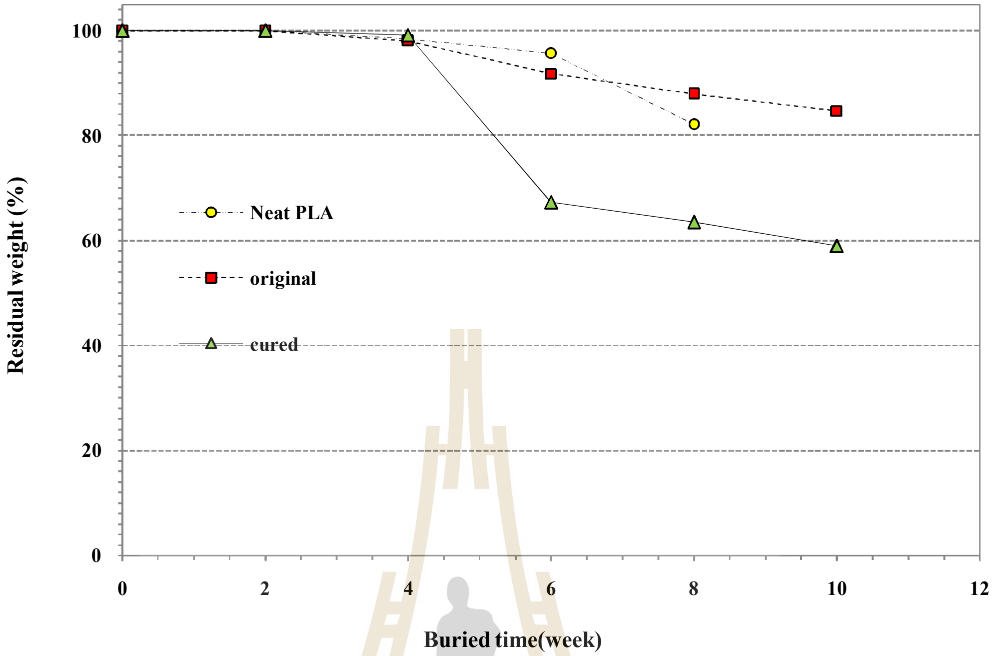


Figure 4.31 % weight retrained and the buried time of PLA compound having 0 phr of DCP.

Attempting to hurdle the service temperature of the PLA compound by introduction the vinyl silane/peroxide crosslink system into the compound ingredient found that the MFI was decreased and HDT, tensile and impact properties were increased with increasing the DCP concentration. On the other word, the thermoset characteristic was observed. The network chain formation, confirmed by the gel determination, was drawn to explain the outcome. However, the target service temperature for this research study, HDT more than 100^{o}C, has not yet been established. Further exploration will be taken into challenging.

4.5 The Effect of Talc on PLA Compound

From the previous experimental discussion, it was found that adding silane/peroxide crosslink system into the PLA compound was not able to elevate the HDT of the material but also found that the flow index was relative low. This melt property would retard the feasibility to produce the product by injection molding process. It is commonly known by polymer engineers that adding the particulate filler such as talc into the polymer compound not only lower the cost and thermal properties but also it act normally act as the solid lubricator. Hence, the compound could be easily injected into the mold. In this research section, study of talc added PLA compound to improve the process ability, especially injection based process, and perhaps to enhance the thermal property was explored and being discussed. The PLA compound having the DCP content at 1.0 phr was established with the talc loading varied from 1 to 50 phr.

Table 4.22 summarizes the compound formula of the talc filled PLA. The mixing was achieved in twin screw extruder. The standard tests were conducted on the injected specimen. The results are concluded in Table 4.23.

Table 4.22 The composition of PLA compound with various talc contents.

Runs	**Composition (phr)**						
	PLA	**Silane**	**Polyols**	**Glycerol**	**Isocyanate**	**DCP**	**Talc**
Neat PLA	100	-	-	-	-	-	-
1	100	1.0	2.0	0.30	0.20	1.0	-
2	100	1.0	2.0	0.30	0.20	1.0	1.0
3	100	1.0	2.0	0.30	0.20	1.0	20
4	100	1.0	2.0	0.30	0.20	1.0	30
5	100	1.0	2.0	0.30	0.20	1.0	40
6	100	1.0	2.0	0.30	0.20	1.0	50

Table 4.23 Test results of the talc filled PLA compounds.

Runs	Talc (phr)	MFI (g/10min)		HDT (^{o}C)		Tensile strength (MPa)		Young's modulus (GPa)		Strain at break (%)		Notched impact (kJ/m^2)		Unnotched impact (kJ/m^2)	
		original	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**	**original**	**cured**
Neat PLA	-	31.74 ± 1.07	36.53 ± 1.46	53.1 ± 0.83	53.1 ± 1.51	24.17 ± 0.87	26.28 ± 0.79	1.21 ± 0.08	1.23 ± 0.02	4.49 ± 0.78	3.99 ± 0.48	3.36 ± 0.39	3.16 ± 0.21	23.56 ± 1.21	21.34 ± 4.86
1	0	9.78±0.73	18.30±0.89	49.7±0.40	63.1±1.70	54.23±6.42	62.97±6.63	2.44±0.16	2.69±0.22	4.65±0.99	4.14±0.88	3.54±0.49	3.38±0.10	38.15±9.79	38.87±5.07
2	1.0	3.75 ± 0.96	5.95 ± 0.58	52.2 ± 0.20	76.2 ± 6.04	61.58 ± 2.61	70.98 ± 0.91	2.94 ± 0.08	2.99 ± 0.15	3.45 ± 0.33	3.38 ±0.13	3.35 ± 0.53	6.00 ± 0.13	30.75 ± 3.13	28.69± 3.85
3	20	1.44 ± 0.79	3.41 ± 0.96	51.9 ± 0.23	81.2 ± 5.84	58.03 ± 2.81	61.21 ± 2.80	3.50 ± 0.22	3.41 ± 0.10	2.36 ± 0.12	2.50 ± 0.19	3.78 ± 0.43	3.98 ± 1.00	21.31 ± 4.54	20.28 ± 4.59
4	30	0.23± 0.02	0.30 ± 0.05	52.4 ± 0.53	86.5 ± 0.64	52.66 ± 3.81	53.14 ± 3.03	3.87 ± 0.18	3.48 ± 0.23	1.84 ± 0.08	1.97 ± 0.14	4.98 ± 0.58	3.11 ± 0.65	17.40 ± 1.48	16.36 ± 4.85
5	40	0.68 ± 0.19	0.99 ± 0.19	52.5 ± 0.06	87.8 ± 4.78	50.99± 7.96	51.55 ± 2.06	4.00 ± 0.20	3.87 ± 0.22	1.67 ± 0.21	1.75 ± 0.14	4.50 ± 0.46	3.00 ± 0.32	16.06 ± 4.13	14.71 ± 0.38
6	50	0.65 ± 0.11	1.16 ± 0.49	53.4 ± 0.32	89.7 ± 5.93	50.53 ± 3.37	61.23 ± 3.43	4.29 ± 0.16	4.56 ± 0.17	1.66 ± 0.05	1.86 ± 0.12	4.46 ± 0.47	3.13 ± 0.73	16.20 ± 1.99	15.25 ± 0.70

4.5.1 The MFI of compound with talc contents

The plot of melt flow index, at 230/5.0, of talc filled PLA compound with the talc loading is illustrated in Figure 4.32. In this experimental section, the measurement of the flow index on the compound undergone sauna treatment were also observed and compared with the sample before the treatment. General observation, it is seen that MFI of the compound for both before and after the moisture incubation is dramatically decreased with increasing talc loading, especially in comparison with the index of neat PLA. It is also seen that the flow index is higher after undergoing moisture cured. The result is contradicted with the hypothesis that the chains crosslink via the silane/moisture condensation would be formed during the curing process. Consequently, the flow ability would be retarded. According to the result of increasing the MFI after the sauna incubation, the moisture absorption during the prolong annealing in the moisture saturated oven would be the suspect explanation. The moisture residual would induce the chain hydrolysis, degradation, during the melting in the tester barrel. As the result, the MFI of the compound would be increased. More verification on this observation will be discussed on the vacuum dried of the sauna cured sample later on in this study.

However, typically as expected, the flow ability of the talc filled PLA compound observed in this study is decreased with increasing the filler content.

4.5.2 The HDT of compound with talc contents

As the HDT is one of our prime interests in this research study, the service temperature test result of the talc filled PLA compounds with respect to the talc loaded are plotted and also illustrated in Figure 4.32. Within the statistical error, it is found that HDT of the original sample is almost constant with the talc loading. It is more or less similar to the HDT of neat PLA at approx. 53°C. However, when the talc filled compound was undergone the sauna curing the HDT of the sample is significant increased by the degree of roughly 35°C. It is also seen that the HDT of cured compound is hurdled with the talc addition. The maximum HDT of 89.7±5.93°C is evidenced at the talc content of 50 phr. The increasing in the HDT by the sauna incubation at a temperature slightly higher than the T_g of the PLA matrix could be due to the two folds effect; chain network formation and the surface adhesion improvement through the silane/moisture reaction. Accordingly, the higher in heat resistance characteristic would be improved. Based on this result, targeted HDT value at 100°C for high temperature resistance PLA compound is promising.

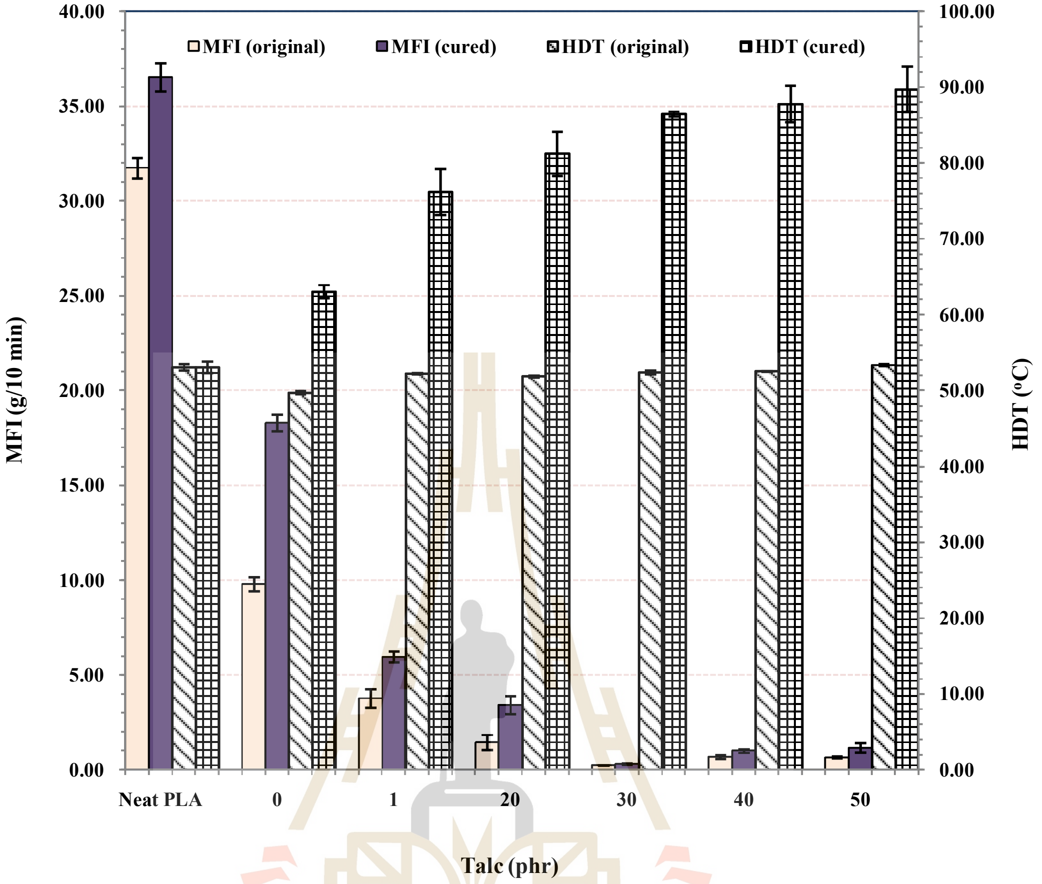


Figure 4.32 The MFI and HDT of the talc filled PLA compound.

4.5.3 The tensile properties

The biodegradable polymer compound with good service temperature but lack of the mechanical properties would be disaster for the industrial applications. The high heat resistance compound without sacrificing the mechanical performance is also importance. The tensile properties test by mean of strength, Young's modulus and strain at break of the talc filled PLA compound was conducted and they are graphically presented with respect to the filler contents in Figure 4.33 and 4.34, respectively. In Figure 4.32, it shows that the strength of the original compound samples is linearly decreased with increasing the filler consumption from 1 to 40 phr. Further increasing the loading to 50 phr, there is no obviously changed in the strength. The similar trend is also found for the sauna cured sample. But when compare between original and cured samples, it is noticed that the tensile strength of the compound is higher through the sauna treatment. Again, the chain crosslink together with the strong bonding between talc particle and PLA matrix would be responsible for the superiority. In contrast with the strength, the modulus of the talc filled PLA compound is slowly increased with increasing the talc loading. It is quite common observation the particulate filled polymers compound where the tensile modulus is normally increased with increasing the filler loading. Taken both strength and modulus together, it could suggest that the more talc added the more brittle material characteristic is found. Carefully observed on both tensile properties, it also noticed that adding only 1 phr of talc to the PLA compound the performance of the material is superior to neat PLA and the compound without adding talc. This observation could indicate that talc added not only act as reinforced filler but at ultra low content it could performed as nucleating agent to promote the crystallinity of the PLA matrix. In accordingly, the tensile properties of the material could be improved.

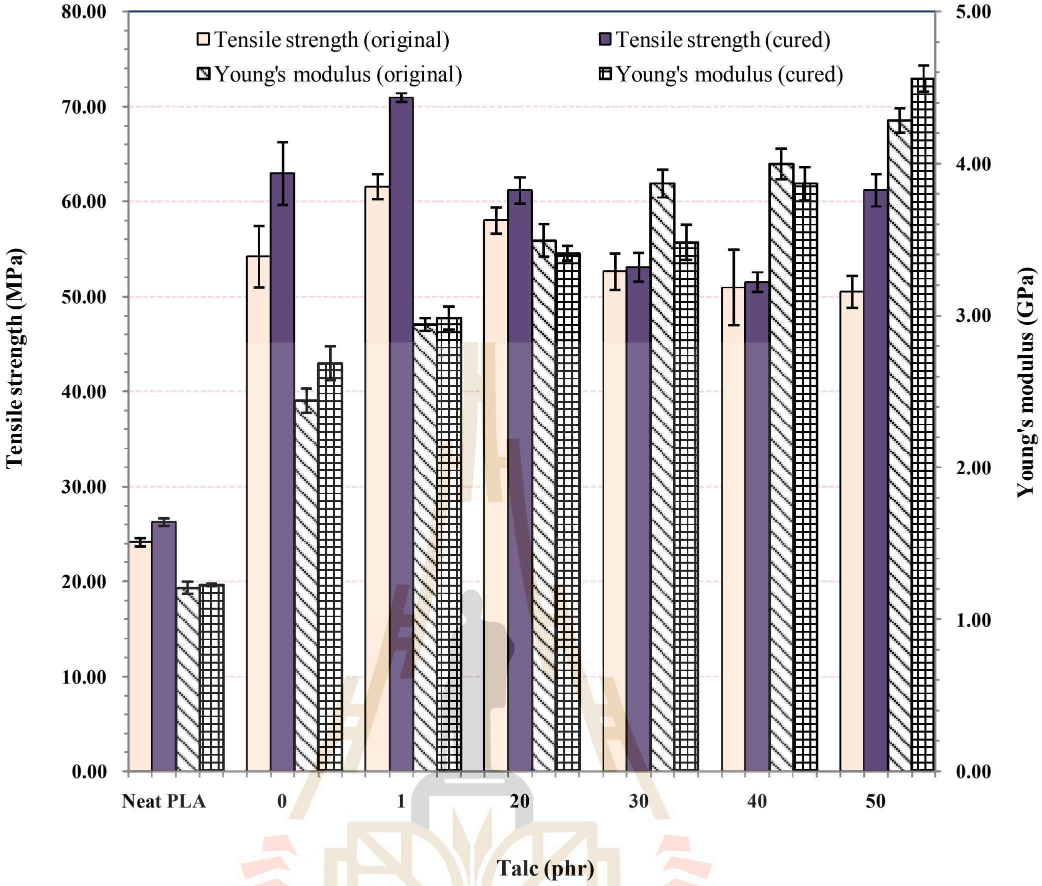


Figure 4.33 The strength and modulus of the talc filled PLA compound.

For the stain at break shown in Figure 4.34, the result strengthen the above postulation that brittle materials was detected by increasing the talc loading because the % strain at break of the talc filled PLA compound is lowered when the increasing the filler content. It is also noticed that crosslink formation after the moisture incubation has less effect to the brittleness characteristic of the material than the filler addition. Because there is only marginally changed in the % strain at break between the original and cured samples.

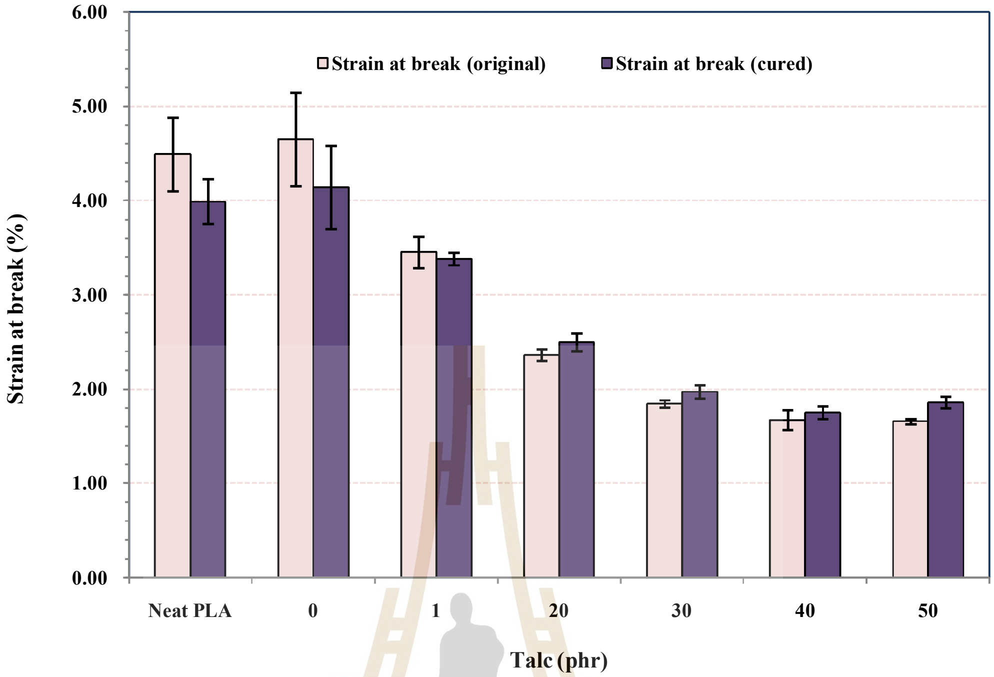


Figure 4.34 % strain at break of the talc filled PLA compound.

4.5.4 Impact strengths of talc filled PLA compound

From the tensile outcome it was seen that the more brittleness characteristic of the PLA compound with increased the talc content. Therefore, the fracture toughness of the compound monitored by notched and unnotched impact strengths are obtained. The results are summarized in Table 4.23 and graphically presented in Figure 4.35. There are agreed with the tensile examination. The test values show that both notched and unnocthed impact strengths of the filler filled PLA compound is decreased with increasing the talc used. It is also visualized that most of the sauna cured compound shows the lower impact strengths than the original samples. It enforces that increasing in the crosslinking and crystallinity of the compound are inferior the fracture toughness of the material.

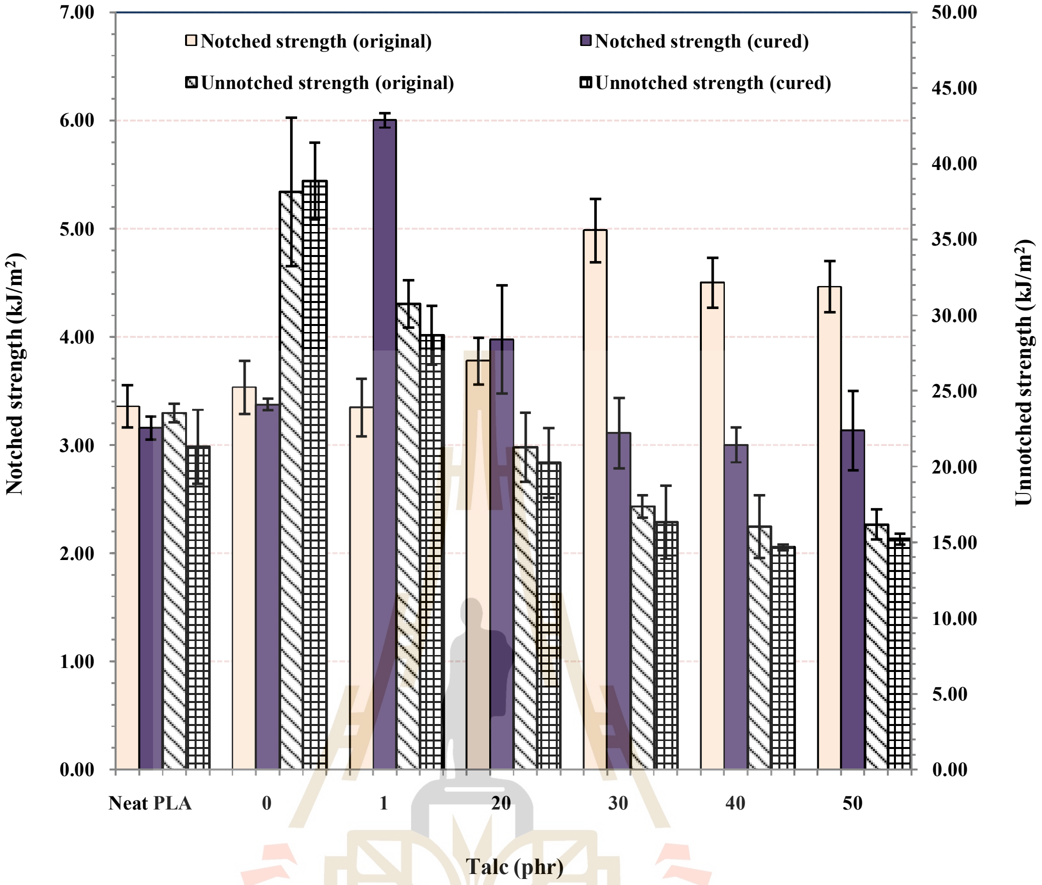


Figure 4.35 The impact strengths of the talc filled PLA compound.

4.5.5 SEM investigation of the talc filled PLA compound

Figure 4.36 (**a**) – 4.36 (**d**) are SEM photographs of the fractured surface obtained from notched specimens of the PLA compound having the talc contents at 1.0 and 50.0 for the original and sauna cured, respectively. It is obviously seen that the rougher fracture traces are evidenced when the filler contents increased from 1 to 50 phr. By the fracture phenomenon observed by the SEM method, the more uneven surface means the more brittleness in nature. Also at the given filler content, the SEM examination reveals that obvious irregular surface is seen when the sample was undergone sauna treatment.

From the visual evidences through the SEM pictures and also the previous properties, the conclusion with high confident can be made that the higher heat resistance PLA compound was achieved by the addition of talc filler. But carefully control of the filler content must be taken into consideration because the mechanical incompetency was observed at high talc content. According to this experimental section talc at above 40 phr is required.

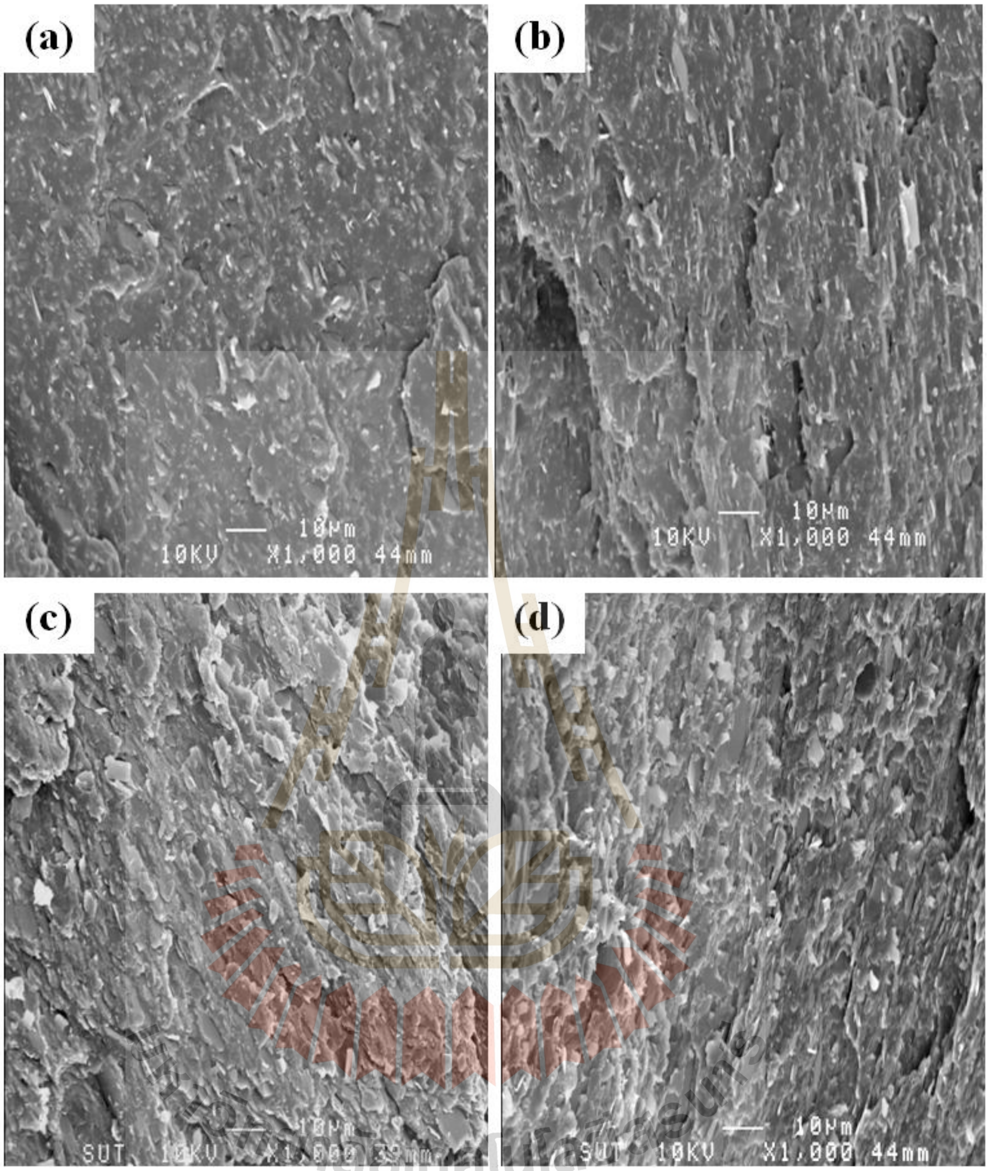


Figure 4.36 SEM photographs of the talc filled PLA compounds having the talc content of; (**a**) 1 phr (original), (**b**) 1 phr (cured), (**c**) 50 phr (original) and (**d**) 50 phr (cured), respectively.

4.6 Effect of Silane and Polyols by the Design of Experiment

The promising in the service temperature, HDT, of the PLA compound material was observed with high talc loading. However, the mechanical properties especially toughness of the polymer was abysmal. There are pro and con for the crosslinking of the PLA matrix via the vinyl silane/DCP system. Good chemical resistivity and high heat resistance are the common positive effect from the crosslinked PLA but the lost in the toughness is typically experience. In this research work, the polyester type polyols not only added as the processing aid but good elastomeric properties of the polymer would toughening the compound. Therefore, it is merit to make use of the polyols as the fracture toughener in the compound. One thing have to be taken into consideration that adding more of polyester polyols toughener would lower the heat distortion temperature of the material. In this experimental section, the balancing between the crosslink density by mean of silane content and the toughening of the material by blending with polyester polyols were explored by using the statistical approach namely 2^k design of experiment. Two parameters ($k = 2$); silane and polyols, were assigned. As the common practice, MFI, HDT, tensile and impacts properties were measured and used for the statistical responds analysis.

The amount of VTMS and polyols was statistically assigned as parameter A and B, respectively. The levels of the parameters are shown in Table 4.24; silane content more than 2.5 was given as high level and at below 2.0 was low level, accordingly. According to the rule of design, four combinations of the designed formula or design matrices ($2^2 = 4$) were constructed and summarized in Table 4.25. , Run#1 to Run#4. The test samples obtained from the designed compound. was prepared by melt mixing in the twin screw and measured by standard test methods. The test values are reported in Table 4.26. In the table, the values derived from the neat PLA and the PLA compound having the silane at 1.0 phr and polyols at 2.0 phr as shown in the previous experiment are included as the referees.

Table 4.24 The levels of silane and polyols in the DOE.

Parameters	**Low level (-1)**		**High level (+1)**	
Silane(phr)	1.5	2.0	2.5	3.0
Polyols(phr)	5.0	6.0	8.0	9.0

Table 4.25 The design matrix of the silane and polyols parameters.

Runs	**Compound Composition(phr)**					
	Silane (A)	**Polyols (B)**	**Glycerol**	**Isocyanate**	**Peroxide**	**Talc**
Neat PLA	-	-	-	-	-	-
PLA Com.	1.0	2.0	0.30	0.20	1.0	50
1	- 1.5	- 5.0	0.30	0.20	1.0	50
2	- 2.0	+ 8.0	0.30	0.20	1.0	50
3	+ 2.5	- 6.0	0.30	0.20	1.0	50
4	+ 3.0	+ 9.0	0.30	0.20	1.0	50

Table 4.26 Respond data of the original and cured samples.

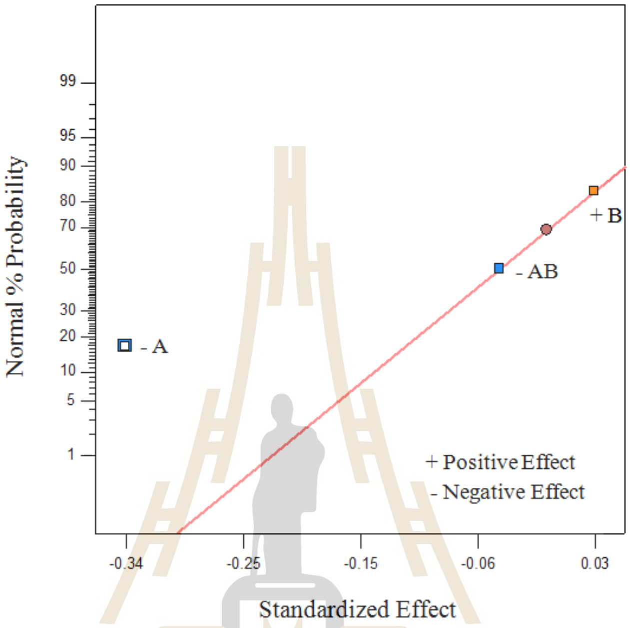
Runs	MFI (g/10min)		HDT (^{o}C)		Tensile strength (MPa)		Young's modulus (GPa)		Strain at break (%)		Notched impact (kJ/m^2)		Unnotched impact (kJ/m^2)	
	original	cured	original	cured	original	cured	original	cured	original	cured	original	cured	original	cured
Neat PLA	31.74 ± 1.07	36.53 ± 1.46	53.1 ± 0.83	53.1 ± 1.51	24.17 ± 0.87	26.28 ± 0.79	1.21 ± 0.08	1.23 ± 0.02	4.49 ± 0.78	3.99 ± 0.48	3.36 ± 0.39	3.16 ± 0.21	23.56 ± 1.21	21.34 ± 4.86
PLA com.	0.652 ± 0.106	1.160 ± 0.485	53.4 ± 0.32	89.7 ± 5.93	50.53 ± 3.37	61.23 ± 3.43	4.29 ± 0.16	4.56 ± 0.17	1.66 ± 0.05	1.86 ± 0.12	4.46 ± 0.47	3.13 ± 0.73	16.20 ± 1.99	15.25 ± 0.70
1	0.367 ± 0.044	0.948 ± 0.294	50.3 ± 0.46	81.1 ± 4.00	60.80 ± 2.15	55.34 ± 4.57	4.27 ± 0.37	4.01 ± 0.21	2.11 ± 0.20	1.77 ± 0.27	3.77 ± 0.83	2.96 ± 0.21	12.01 ± 1.36	12.19 ± 1.11
2	0.444 ± 0.048	0.853 ± 0.368	47.1 ± 0.23	83.2 ± 5.32	56.99 ± 1.19	53.19 ± 1.02	4.00 ± 0.23	3.83 ± 0.16	2.18 ± 0.10	2.14 ± 0.18	4.24 ± 0.63	3.16 ± 0.13	12.10 ± 1.74	12.22 ± 1.75
3	0.071± 0.008	0.061 ± 0.002	48.7 ± 0.42	78.6 ± 3.08	56.28 ± 2.71	52.31 ± 2.36	3.86 ± 0.27	3.85 ± 0.13	2.09 ± 0.13	1.82 ± 0.15	3.41 ± 0.54	3.27 ± 0.48	12.75 ± 1.82	12.30 ± 1.40
4	0.062± 0.035	0.030 ± 0.003	47.7 ± 0.29	79.2 ± 3.70	50.49 ± 0.57	46.43 ± 0.89	3.90 ± 0.20	3.27 ± 0.22	1.77 ± 0.06	1.84 ± 0.09	3.62 ± 0.65	2.46 ± 0.61	9.34 ± 1.05	11.09 ± 1.58

4.6.1 Effect of silane and polyols on the MFI

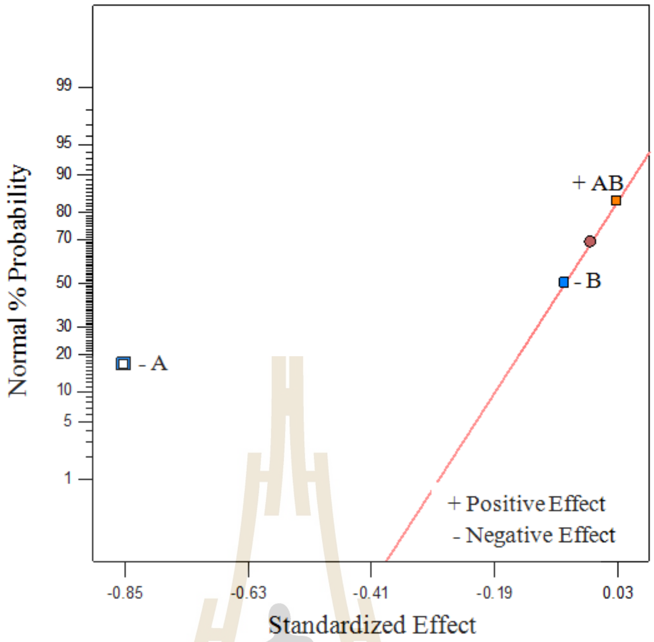
Rheological property, by mean of the MFI obtained at 230/5.0, of the designed compounds without and with sauna incubation is summarized in Table 4.26, respectively. Quickly observation, it is noticed that the MFI of the sauna cured is slightly higher than the original sample except at high silane contents, Run#3 and Run#4 where the index are lower. The moisture contamination on the compound via the prolong moisture incubation as described in the previous section is suspected for the increasing in the test value. The residual would induce the chain hydrolysis during the melting in the tester chamber. Hence, the index value would be increased. However at the high silane content, the residual would be diminished by reacting with the excess silane.

In term of the statistical analysis, the standardized normal probability plots of the MFI respond for the original and cured sample are presented in Figure 4.37 (**a**) and 4.37 (**b**), respectively. It is obviously seen that negative effect silane (-A) content is excluded from the linear trend line for both sample conditions. It would be the significant effect to the flow index of the designed PLA compound. Strengthen this statement by the pareto charts shown in Figure 4.38 (**a**) and 4.38 (**b**), it is evidenced that *t*-value of the silane content is far above the critical value. So, it is indicated that this parameter is the negative and significant effect to the MFI of the PLA compound. To have the solid conclusion, ANOVA analysis result given in Table 4.27 (**a**) and 4.27 (**b**), respectively, is reinforced that the designed experiment and also the silane content used in the compound are significant effect to the MFI of the material because the calculated *p*-values are lower than the boundary value at 0.05. Based on the statistical result it can say that MFI of the PLA compound will be decreased if the

PLA is compounded using high silane content. On the other word, the crosslink density would be increased with increasing the silane loading.

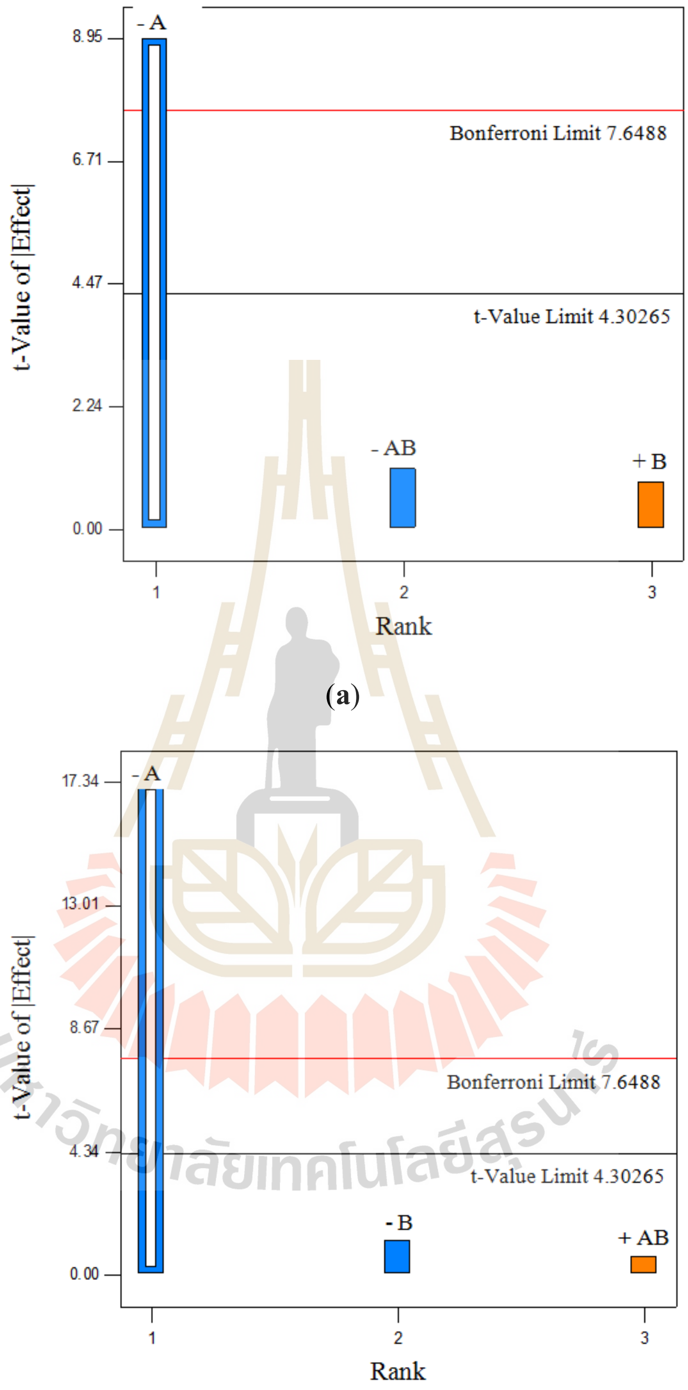


(a)



(b)

Figure 4.37 Normal plot of MFI for (**a**) original and (**b**) cured of the designed PLA compound.



(**a**)

(**b**)

Figure 4.38 Pareto charts of MFI for (**a**) original and (**b**) cured of the designed PLA compound.

Table 4.27 ANOVA conclusion of MFI for (**a**) original and (**b**) cured of the designed PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	***p*-value Prob > F**
Model	0.12	1	0.12	80.10	0.0123
A-Silane	0.12	1	0.12	80.10	0.0123
Residual	0.00	2	0.00		
Cor Total	0.12	3			

(a)

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	***p*-value Prob > F**
Model	0.73	1	0.73	300.70	0.0033
A-Silane	0.73	1	0.73	300.70	0.0033
Residual	0.00	2	0.00		
Cor Total	0.73	3			

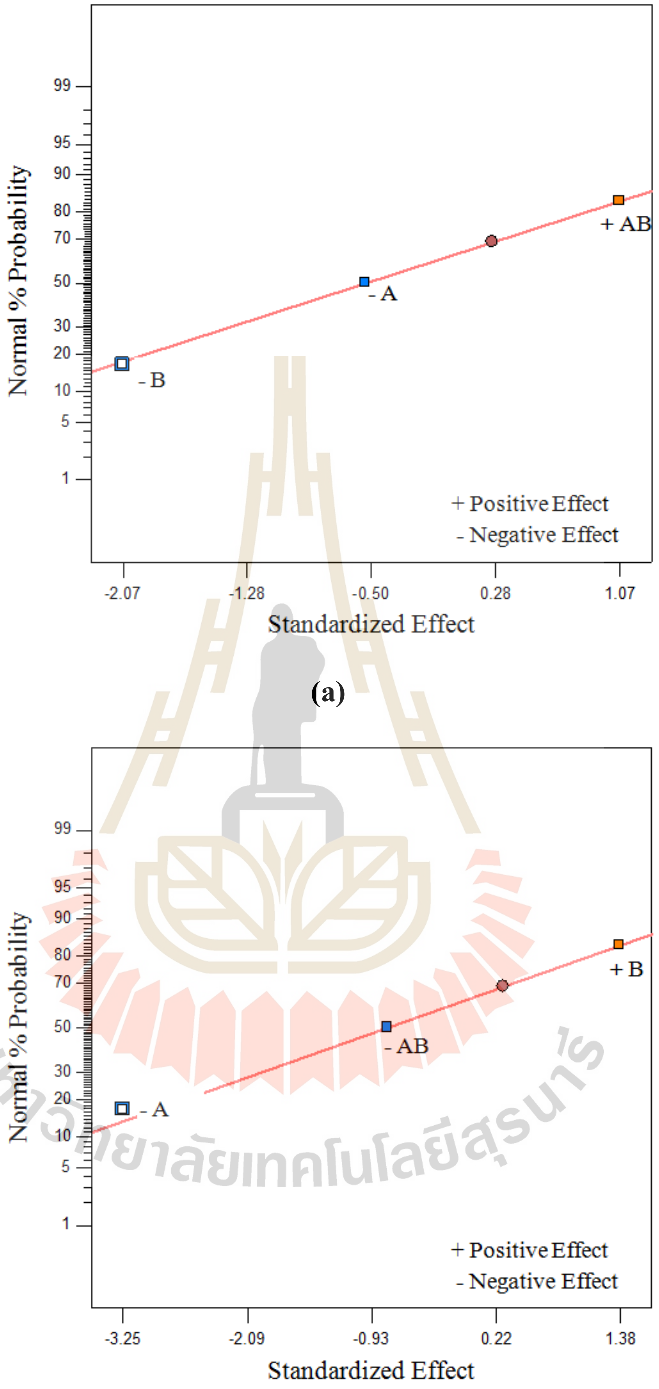
(b)

4.6.2 Effect of silane and polyols on the HDT

HDT is our prime interests in this research work. High HDT polymer with no scarifying the mechanical properties is the main goal. Consequently, investigation of increasing the crosslink density, hence improving the HDT, by adding silane and toughness enhancement by adding elastomeric polyester polyols was carefully designed and is being analyzed in this chapter. The service temperature of the designed compound is presented Table 4.26. It is quite apparent that the HDT of the PLA compounds are lowered with higher in the concentration of polyester polyols.

Nevertheless, the interaction effect between chain crosslink density through the silane/moisture condensation reaction and the soft segment of the polyols on the

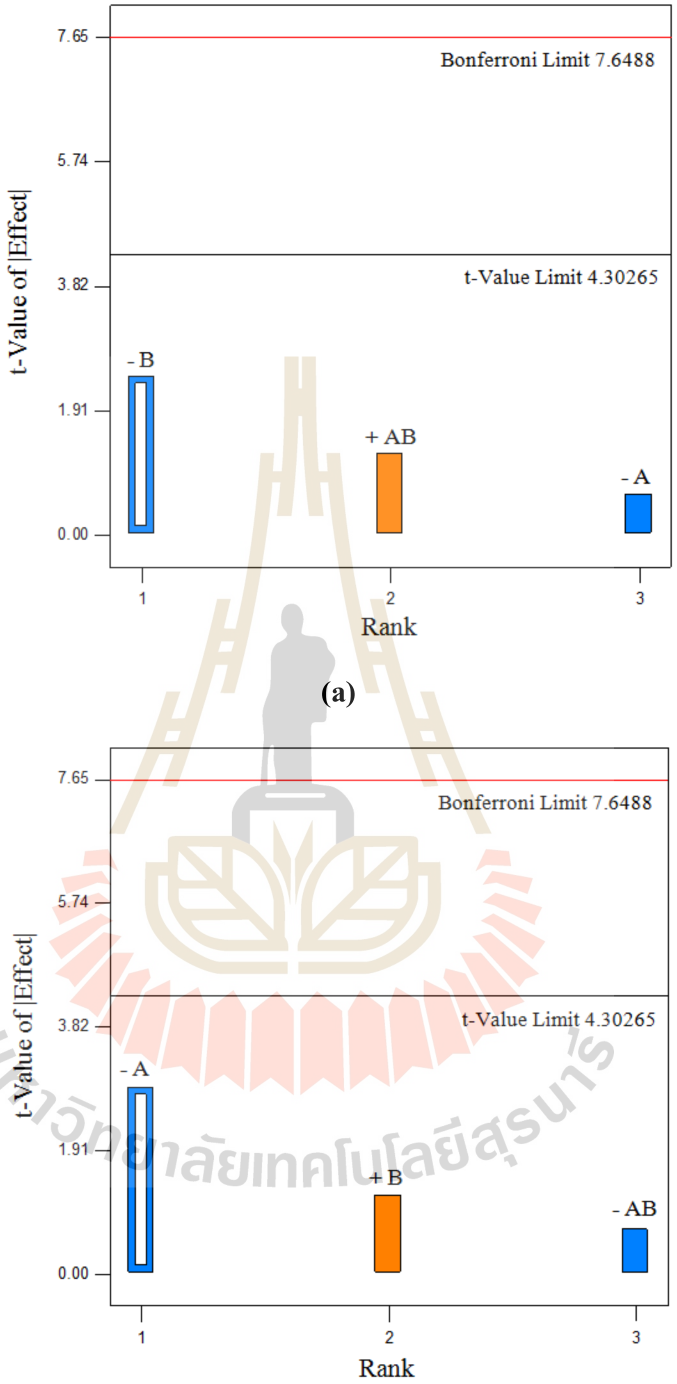
HDT must be statistically discussed. The plot of the standardized effect and normal probability of the HDT respond of the original and cured samples is Figure 4.39 (**a**) and 4.39 (**b**), respectively. It is seen that all the calculated effects are perfectly fitted onto the linear trend line for both conditioned samples. They indicate that both silane and polyols and also the interaction between those two parameters are like not be significant effect to the HDT of the PLA compound. Enhancing the statement by analyzing the pareto charts as shown Figure 3.40 (**a**) and 3.40 (**b**), they are confirmed that the given parameters do not have the significant effect to the service temperature of the polymer compound. Because of the calculated *t*-values are below the critical ones. To finalize the statistical conclusion by considering the ANOVA results, it is seen in the Table 4.28 (**a**) and 4.28 (**b**) that the computed *p*-values of either the designed model or the designed parameters are above the assigned critical value at 0.05. Therefore, it can conclude with 95% of confidence that the amount of silane and polyols used in this experiment do not have the significant effect on the HDT of the compound sample before and sauna treatment.



(a)

(b)

Figure 4.39 Normal plot of HDT for (**a**) original and (**b**) cured of the designed PLA compound.



(a)

(b)

Figure 4.40 Pareto chart of the HDT respond for (**a**) original and (**b**) cured of the designed PLA compound.

Table 4.28 ANOVA conclusion of HDT for (**a**) original and (**b**) cured of the designed PLA compound.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	4.271	1	4.271	6.006	0.1339
B-Polyols	4.271	1	4.271	6.006	0.1339
Residual	1.422	2	0.711		
Cor Total	5.693	3			

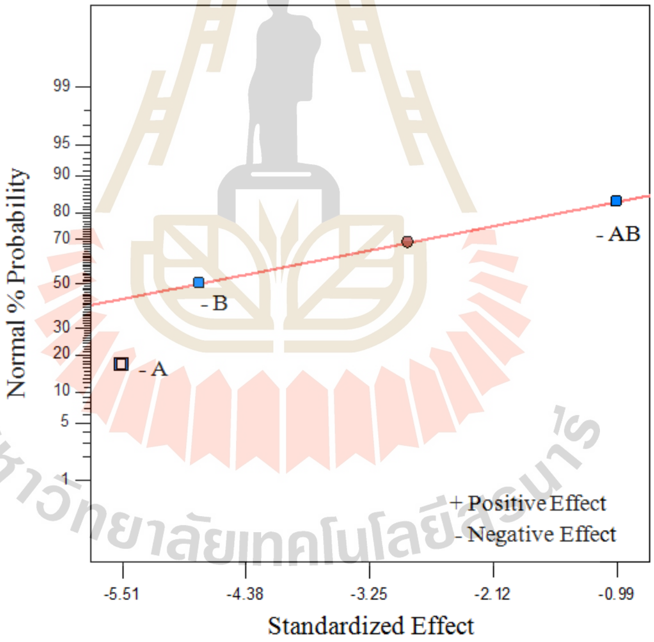
(a)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	10.563	1	10.563	8.359	0.1017
A-Silane	10.563	1	10.563	8.359	0.1017
Residual	2.527	2	1.264		
Cor Total	13.090	3			

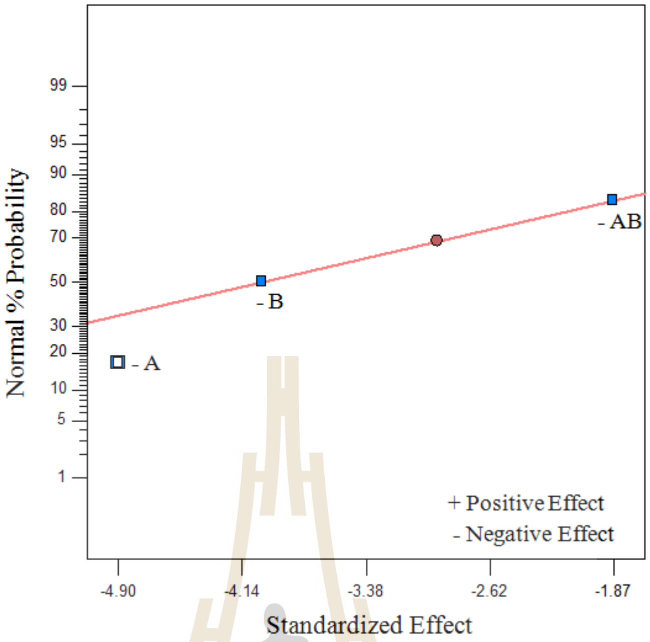
(b)

4.6.3 Effect of silane and polyols on tensile properties

Tensile properties measured as the strength, modulus and % strain at break of the designed compound with the difference levels of silane and polyols contents are given in Table 4.26. The statistical discussion on the effect of the parameters on the strength by using the normal plots of both original and sauna cured are given in Figure 4.41 (**a**) and 4.41 (**b**), respectively. The exact indicator, where the parameter **A**, silane content, is the highest negative effect value and excluded from the others, is observed. It triggers that this designed variable likely to be the significant effect to the tensile strength of the PLA compound specimens. However, when consider the pareto chart obtained, it is obviously seen that the silane content, **-A**, show the calculated *t*-values below the limit line for both type of samples. Therefore, it could say that the tensile strength is not affected by the levels of the silane content employed for the compounding the PLA in this study. Strengthen the conclusion by the ANOVA analysis, the test results shown in Table 4.29 (**a**) and 4.29 (**b**) are given that the computed *p*-values of the designed model for both type of samples are equal to 0.2530 and 0.2584, respectively. Exactly the same in *p*-values of the selected parameter are obtained. Taken the above statistical outcomes, it can manifest that the levels of the concentration of either silane or polyester polyols does not have the real effect to the tensile strength of the PLA compound obtained in this study.

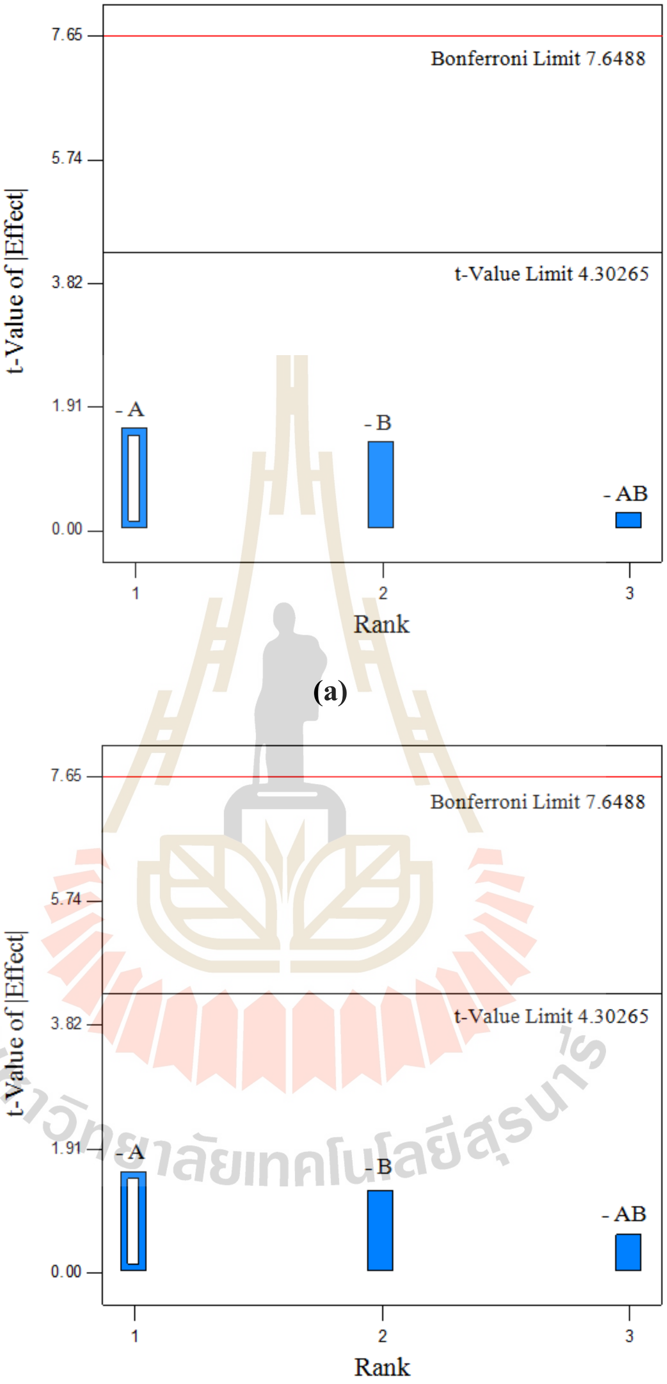


(a)



(b)

Figure 4.41 Normal plot of tensile strength of PLA compound (**a**) original and (**b**) cured of the designed PLA compound.



(a)

(b)

Figure 4.42 Pareto chart of the tensile strength for the (**a**) original and (**b**) cured of the designed PLA compound.

Table 4.29 ANOVA results of the tensile strength for the (**a**) original and (**b**) cured of the designed PLA compound

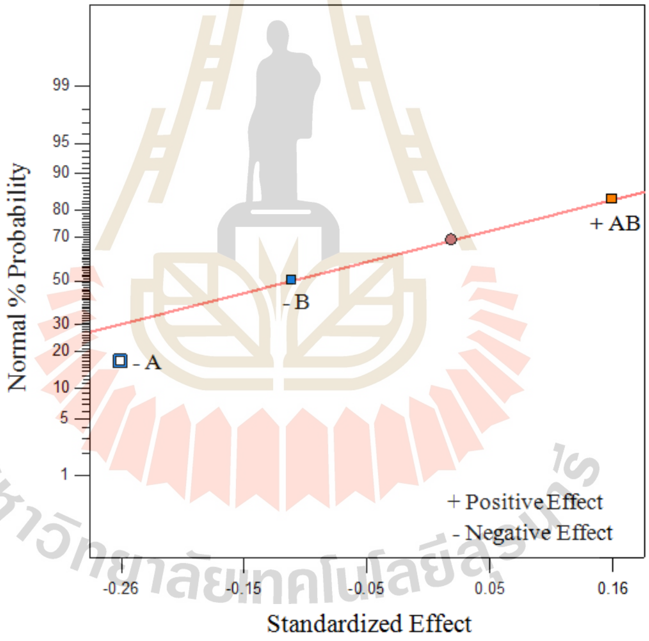
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	30.360	1	30.360	2.525	0.2530
A-Silane	30.360	1	30.360	2.525	0.2530
Residual	24.043	2	12.022		
Cor Total	54.403	3			

(a)

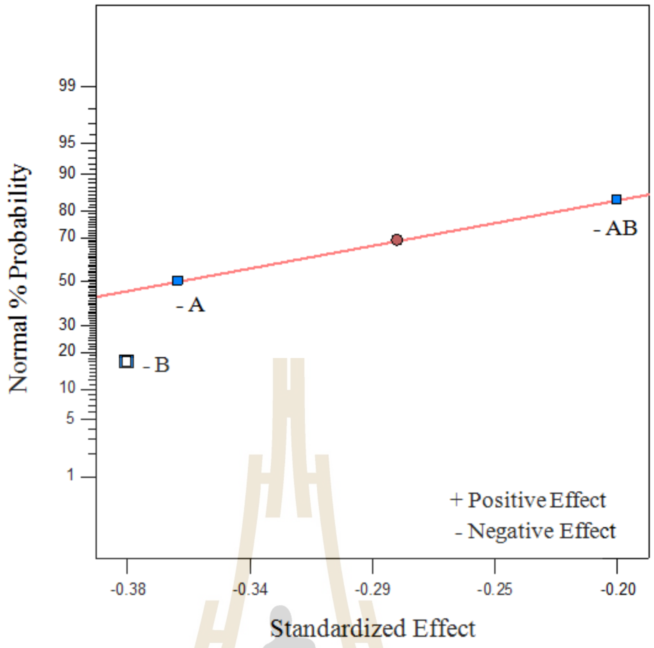
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	23.971	1	23.971	2.445	0.2584
A-Silane	23.971	1	23.971	2.445	0.2584
Residual	19.610	2	9.805		
Cor Total	43.581	3			

(b)

For the tensile modulus analysis, Figure 4.43 (**a**) and 4.43 (**b**) are the normal plot of the standardized effect of the modulus and the designed parameters. For the sample without the moisture incubation, it is noticed that the calculated effects are well fitted with the linear trend line. Except, the negative effect derived from the silane content, -**A**, is slightly lined beyond the regression trend. In case of the modulus measured on the sauna cured samples, it is observed that the negative effect of polyols, -**B**, is shown the highest effect value and cannot be included with the others. For the sake of the statistical analysis, the parameter **A** for the original sample and the *B* for the cured are taken into the significant effect verification. Consequently, the pareto indicators illustrated in Figure 4.44 (**a**) and 4.44 (**b**) reveal that the parameter either **A** or **B** would not be the significant effect to the tensile modulus of the PLA compound sample before and after undergoing moisture incubation, respectively. It is because the designed *t*-values are much below the limit lines. This statement is again sealed off with the ANOVA testing conclusion. It is seen that the obtained *p*-values of both models and also the suspected parameters are over the critical limit at 0.05. So, it can say that the levels of both silane and polyols used for compounding the PLA in this research experiment do not have the significant effect to the tensile modulus of the injected compound samples.

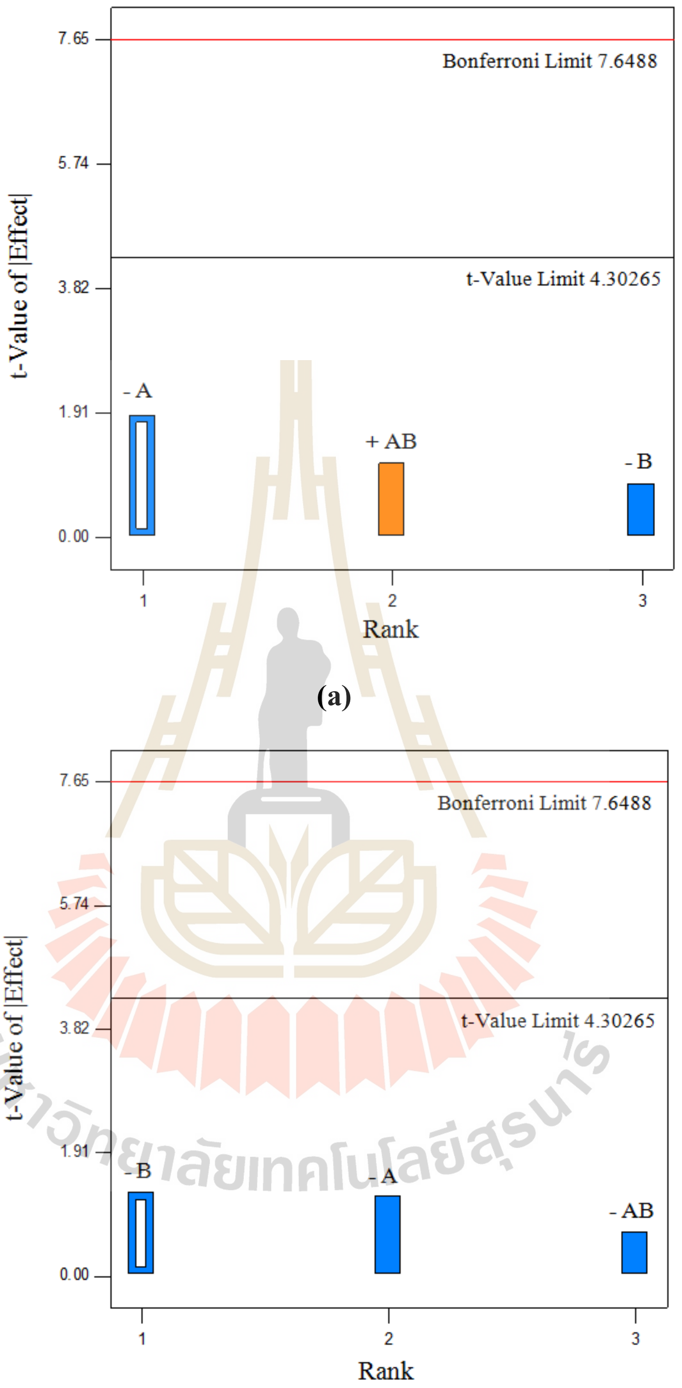


(a)



(b)

Figure 4.43 Normal plots of Young's modulus for the (**a**) original and (**b**) cured of the designed PLA compound.



(a)

(b)

Figure 4.44 Pareto chart of the Young's modulus for the (**a**) original and (**b**) cured of the designed PLA compound.

Table 4.30 ANOVA results of the Young's modulus for the (**a**) original and (**b**) cured of the designed PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	0.066	1	0.066	3.541	0.2006
A-Silane	0.066	1	0.066	3.541	0.2006
Residual	0.037	2	0.019		
Cor Total	0.103	3			

(a)

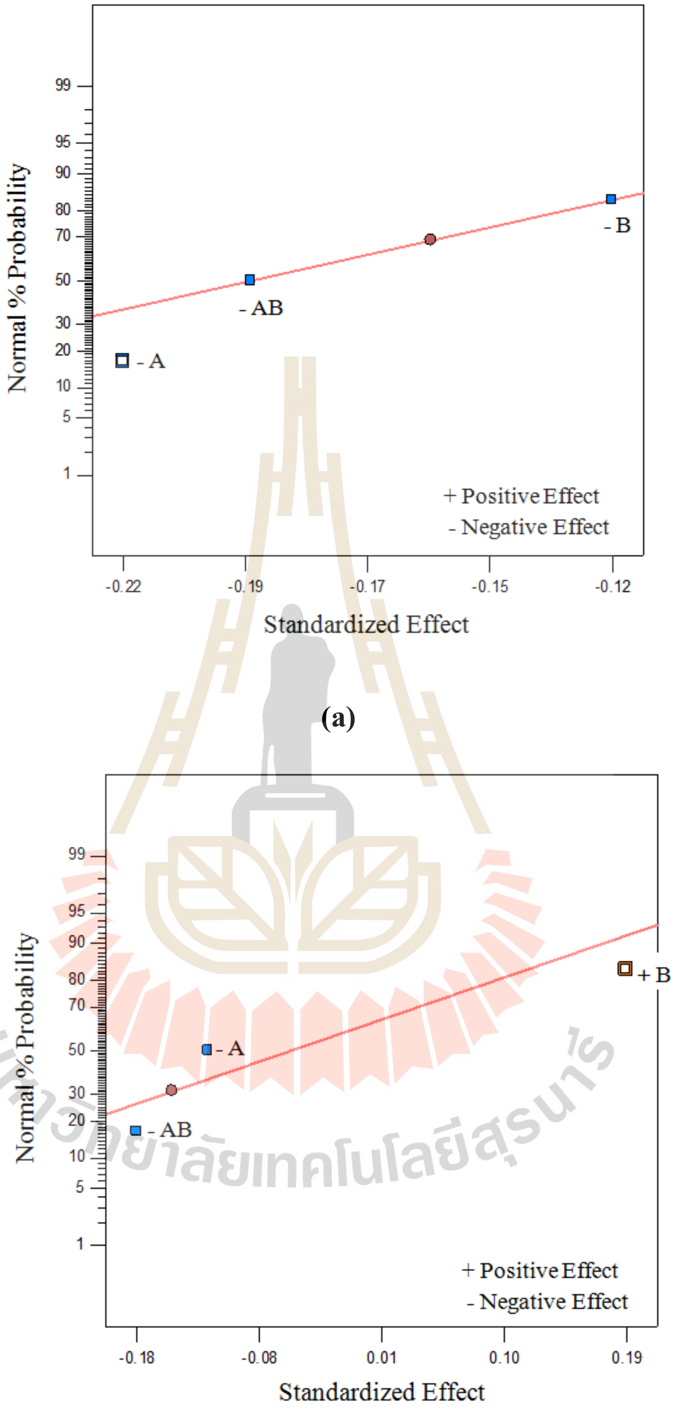
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	0.144	1	0.144	1.683	0.3240
B-Polyols	0.144	1	0.144	1.683	0.3240
Residual	0.171	2	0.086		
Cor Total	0.316	3			

(b)

It is worth to see the effect of the silane and polyols levels used as one the PLA compound ingredient on the % strain at break of the samples. Because these two chemical recipes do have the opposite affects. High silane dosage mean high crosslink density and hence less flexible, lower in the % strain at break. Vice versa, compounding with greater amount of polyester polyols, reactive plasticizer, would result in the more flexible, higher in % yield point, of the compound sample. By considering the standardized normal plots of the % strain at break of the designed experimental specimen in Figure 4.45 (**a**) and 4.45 (**b**) for the original and cured samples, respectively, it is evidenced that all the parameters are well fitted as the linear line for the type of samples. It is indicated that the parameters and their levels would not have the significant effect to the % strain of the PLA compound obtained.

Confirmation of the above hypothesis with the pareto charts shown in Figure 4.46 (**a**) and 4.46 (**b**), it is manifested that the assigned parameters do not have the significant effect to the % strain at break of the injected PLA compound samples. The calculated *t*-values of the parameters are below the critical limit value. Identical conclusion is obtained by the ANOVA testing. Table 4.31 (**a**) and 4.31 (**b**) summarize the calculated *p*-values derived from the original and sauna cured analysis. It is seen that the *p*-values for the designed model and also for the designed parameters are above the critical value, $\alpha = 0.05$. It means that % strain at break of the PLA compound samples are not affected by the parameter and their levels of the content used in the compounding process.

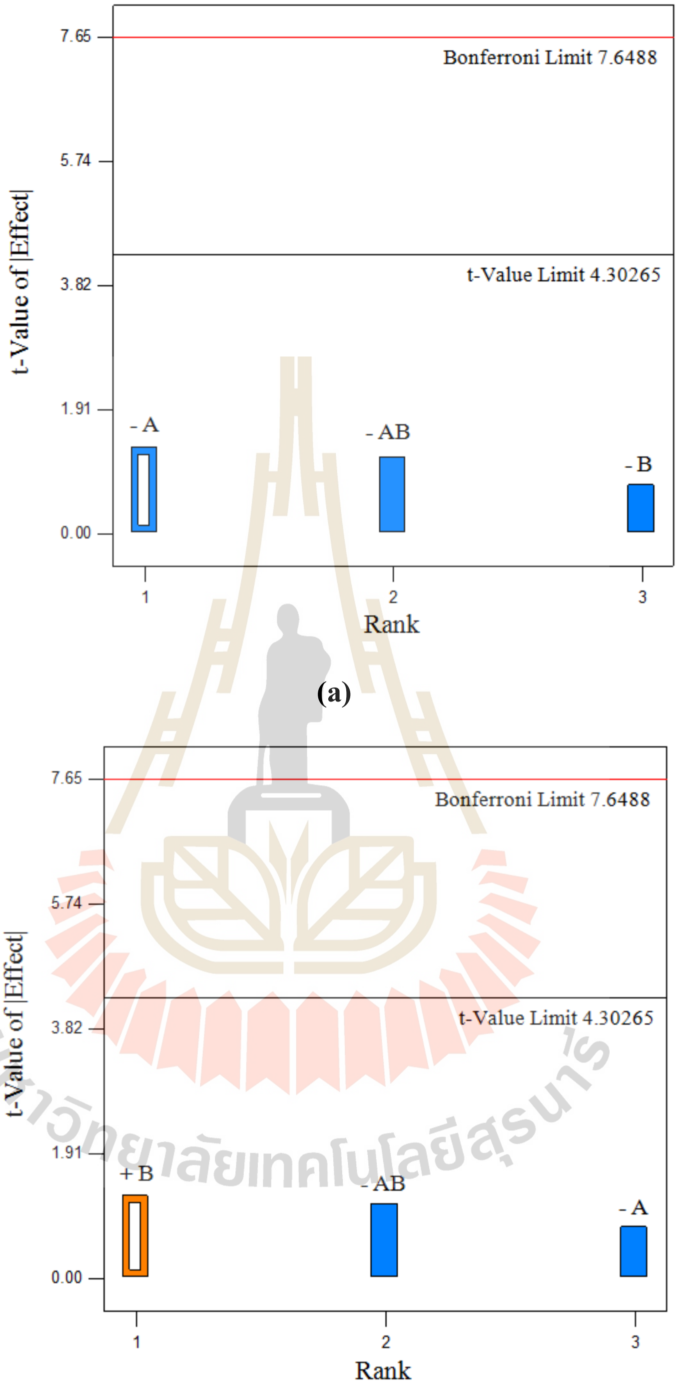
From this discussion section, the conclusion can be made that the silane and polyols, at the given levels used in this experimental study, do not statistically effect on the tensile properties; strength, modulus and % strain at break, of the PLA compound filled with 50 phr of talc.



(a)

(b)

Figure 4.45 Normal plot of % strain at break for the (**a**) original and (**b**) cured the designed PLA compound.



(a)

(b)

Figure 4.46 Pareto chart of the strain at break for the (**a**) original and (**b**) cured of the designed PLA compound**.**

Table 4.31 ANOVA results of the strain at break for the (**a**) original and (**b**) cured of the designed PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	0.047	1	0.047	1.786	0.3131
A-Silane	0.047	1	0.047	1.786	0.3131
Residual	0.052	2	0.026		
Cor Total	0.099	3			

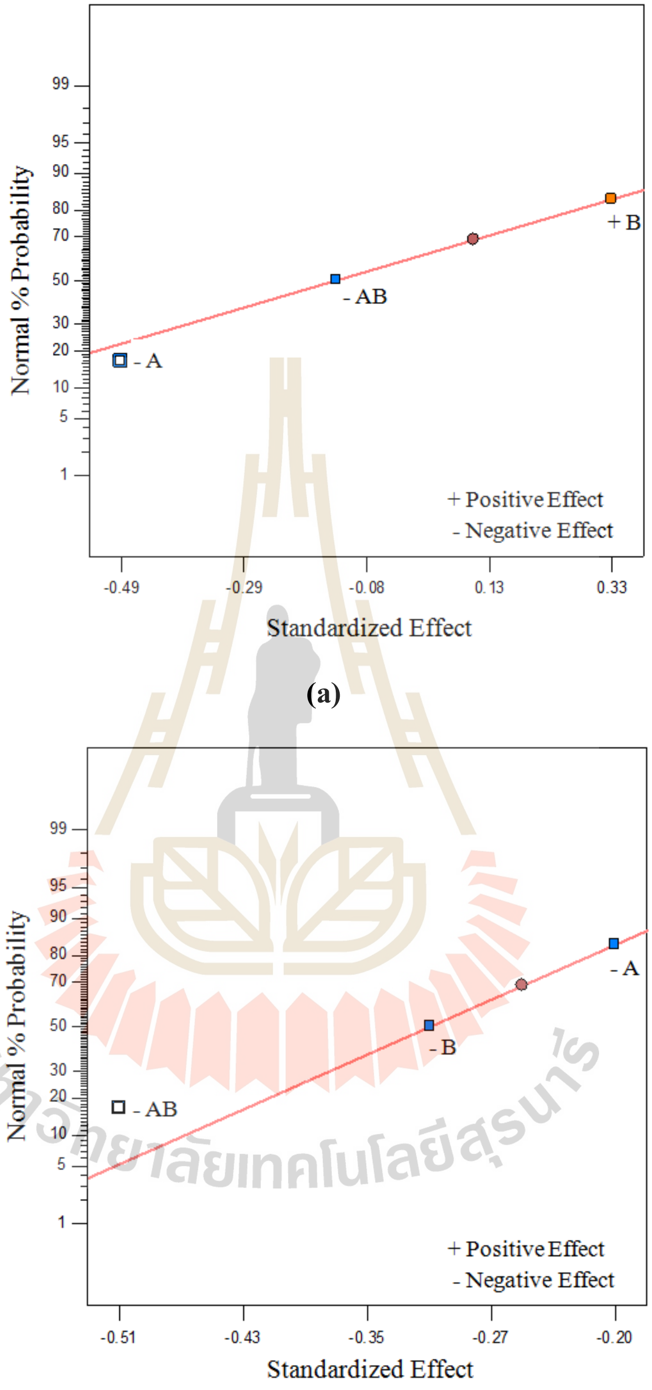
(a)

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	0.038	1	0.038	1.641	0.3286
B-Polyols	0.038	1	0.038	1.641	0.3286
Residual	0.046	2	0.023		
Cor Total	0.083	3			

(b)

4.6.4 Effect of silane and polyols on impact strengths

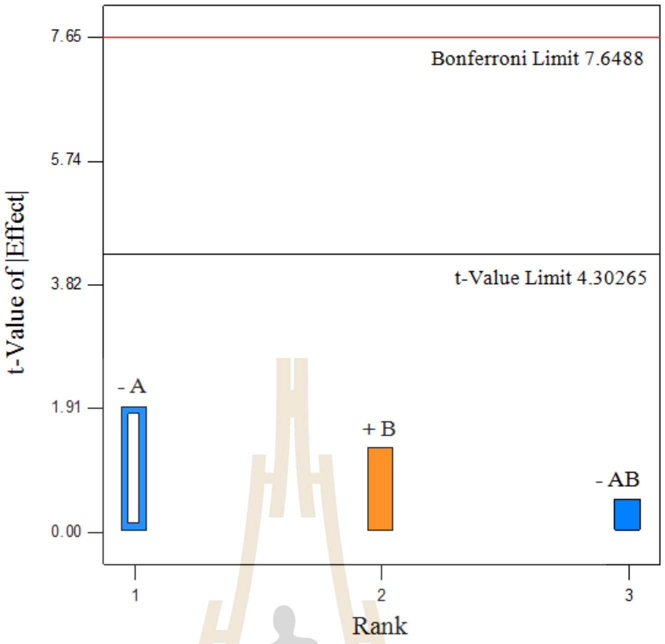
The impact strengths were measure by both notched and unnotched samples. The test values obtained from the designed compound, shown in Table 4.25, with the difference levels of silane and polyols contents is given in Table 4.26. For the statistical analysis of the notched impact, the normal plot of the standardized effect for the original and cured are presented in Figure 4.47 (**a**) and 4.47 (**b**), respectively. It is seen that all of the parameter and interacted parameters are well on the linear line. It indicates that the given designed parameters do not have the tendency to become the significant effect on the notched impact strength. For the sake of the computation, the parameter **A** for the original case and **AB** for the cured sample case; showing the highest calculated effect values, are selected as suspected parameters for further analysis, respectively. Consequently, the pareto indicators illustrated in Figure 4.48 (**a**) and 4.48 (**b**) shown that the both parameters; either **A** or **AB,** are not the significant effect to the notched impact strength of the PLA compound sample before and after undergoing moisture incubation. Because of the calculated *t*-values of both variables are much below the limit lines. This is again reinforced that the parameter **A** for the original and **AB** for the sauna cured ones do not have the significant effect on the notched impact strength. To verify the conclusion, the ANOVA testing result is taken into account. From the result shown in Table 4.32 (**a**) and 4.32 (**b**), it is seen that the obtained model *p*-value for both type of samples and also for the suspected parameters are above the critical set value at 0.05. Therefore, it can manifest that the level of contents, both silane and polyols, used for compounding the PLA in this research experiment do not have the significant effect on the notched impact strength of the PLA compound samples.



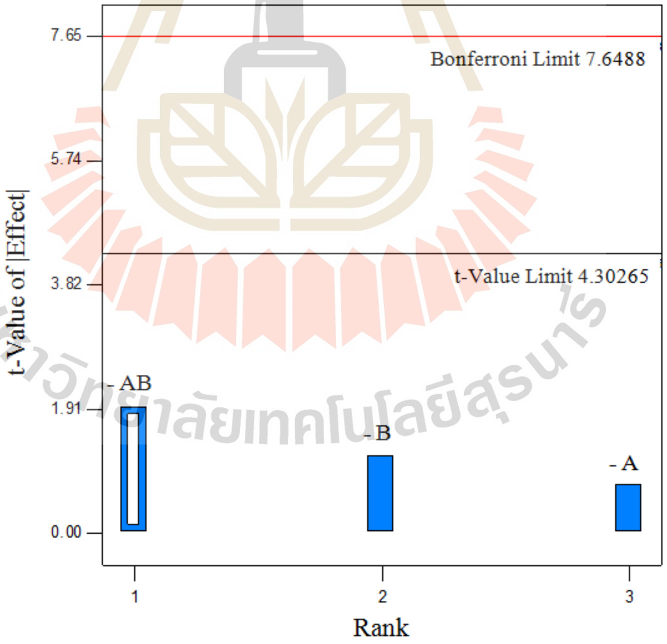
(a)

(b)

Figure 4.47 Normal plot of notched impact strength for the (**a**) original and (**b**) cured of the designed PLA compound.



(a)



(b)

Figure 4.48 Pareto chart of the notched impact strength for the (**a**) original and (**b**) cured of the designed PLA compound.

Table 4.32 ANOVA results of the notched impact strength for the (**a**) original and (**b**) cured of the designed PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	0.243	1	0.243	3.772	0.1916
A-Silane	0.243	1	0.243	3.772	0.1916
Residual	0.129	2	0.064		
Cor Total	0.372	3			

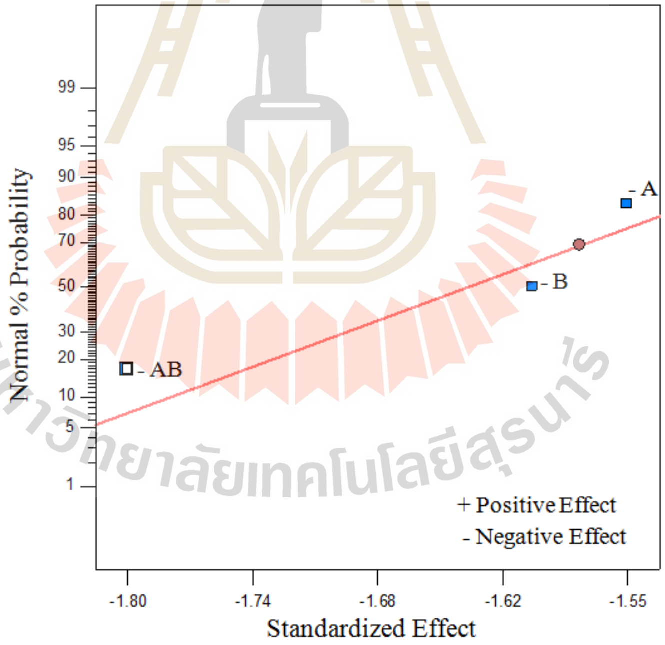
(a)

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	0.257	1	0.257	3.798	0.1906
AB	0.257	1	0.257	3.798	0.1906
Residual	0.135	2	0.068		
Cor Total	0.392	3			

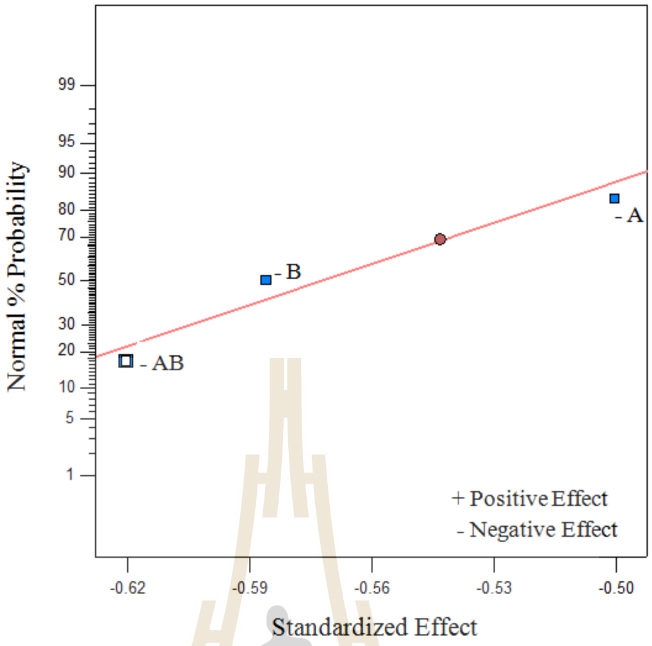
(b)

The statistical discussion on the effect of the parameters on the unnotched impact strength by using the normal plots of both original and sauna cured are given in Figure 4.49 (**a**) and 4.49 (**b**), respectively. The similar trend to the notched impact is observed for both samples conditioned. All the parameters and the interaction one can, more or less, be fitted to form the linear trend line. The plots demonstrate that the designed parameters, silane and polyols content, are not likely to be the significant effect to the unnotched impact value. Similar manner to the above analysis is applied. The highest calculated effect values derived from the AB is selected for the statistical analysis. The result from the pareto charts are presented in Figure 4.50 (**a**) and 4.50 (**b**) for the original and cured, respectively. It is obviously seen that the calculated *t*-values are below the designed critical values for both cases.

Therefore, it could say that the unnotched impact strength is not affected by the levels of the silane and polyols content employed for the compounding the PLA in this study. Confirmation of the conclusion statement by the ANOVA analysis, the test results shown in Table 4.33 (**a**) and 4.33(**b**) indicate that the computed *p*-values of the designed model for both types of samples are equal to 0.3717 and 0.3740, respectively. They are higher than confidential value at 0.05. Accordingly, it manifests that the levels of the concentration of either silane or polyester polyols does not have the real effect to the unnotched impact strength of the PLA compound obtained in this study.

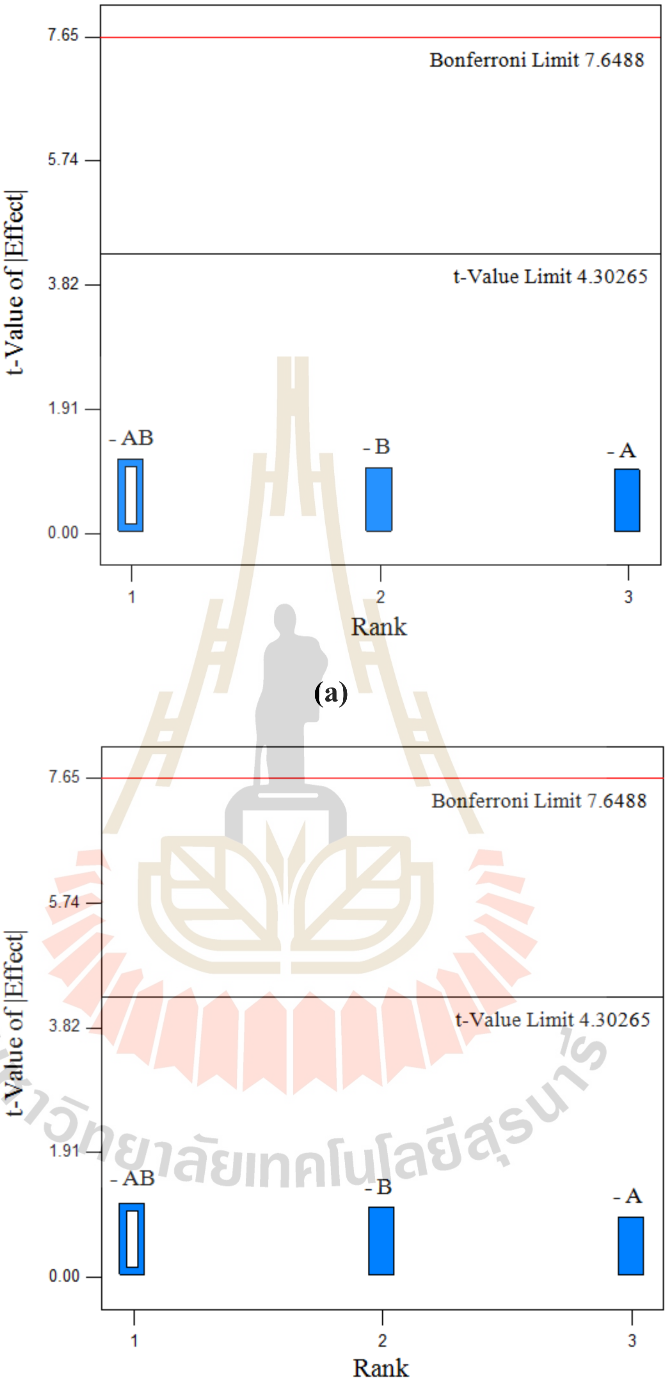


(a)



(b)

Figure 4.49 Normal plot of unnotched impact strength for the (**a**) original and (**b**) cured of the designed PLA compound.



(b)

Figure 4.50 Pareto chart of the unnotched impact strength for the (**a**) original and (**b**) cured of the designed PLA compound.

Table 4.33 ANOVA results of the unnotched impact strength for the (**a**) original and (**b**) cured of the designed PLA compound.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	3.249	1	3.249	1.305	0.3717
AB	3.249	1	3.249	1.305	0.3717
Residual	4.980	2	2.490		
Cor Total	8.229	3			

(a)

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	0.388	1	0.388	1.289	0.3740
AB	0.388	1	0.388	1.289	0.3740
Residual	0.601	2	0.301		
Cor Total	0.989	3			

(b)

Throughout the DOE analysis, Table 4.34 shows the conclusion of the effect of silane and polyols at the given level of contents used in the present design of experiment. Only silane content does have the negative and significant effect to the melt flow index of the compound. It means that compounding the PLA with high silane content would give raise the low melt flow of the material. This statement is agree with the previous discussion that for the compound system using the DCP/silane as the crosslink system the increasing in the DCP/silane ratio would increase the crosslink density of the PLA chain, hence lower the flow ability of the polymer compound. Unexpectedly, adding the polyester polyols at the given concentration to assist the flow ability of the designed material did not have significant influence to the properties of the compound, especially the MFI. It could be the fact that the level of the polyols used was too low to overcome the resistance of the flow from the chain crosslinking. However, further increasing the polyols content must be carefully considered. Improving the flow ability by increasing the polyols addition would significantly decrease the HDT. Therefore, these effects must be traded off.

Table 4.34 Statistical conclusions derived from the DOE study.

Response		Effect			Significant factor(s)
		A (Silane)	B (Polyols)	AB	
Original	MFI	-	+	-	A
	HDT	-	-	+	None
	Tensile strength	-	-	-	None
	Young's modulus	-	-	+	None
	Strain at break	-	-	-	None
	Notched impact strength	-	+	-	None
	Unnotched impact strength	-	-	-	None
Cured	MFI	-	-	+	A
	HDT	-	+	-	None
	Tensile strength	-	-	-	None
	Young's modulus	-	-	-	None
	Strain at break	-	+	-	None
	Notched impact strength	-	-	-	None
	Unnotched impact strength	-	-	-	None

4.7 The Effect of Polyols and Removing of Moisture Residual by Vacuum Drying on PLA/PU Blends

Polyurethane is formed by reacting an isocyanate with a polyols. In this study, both isocyanate and polyols at 0.2 and 8.0 phr were used in the compounding ingredient. It has been classified as the reactive compatibilizer and also the processing aids. In the mixing process, the added isocyanate could react with either hydroxyl end-group of the PLA chain or the –OH groups of the literately added polyols to form the urethane linkage. According to the previous pre blending method, the isocyanate, MDI, and polyols were separately added into the compound ingredient. Therefore by ignoring the size and shape of the molecule, the probability of the reaction between MDI and the PLA end group and MDI with polyols would be equal. In this study section, the MDI and polyols were priory and vigorously premixed before adding into the compound ingredient. By doing so, the possibility of the polyurethane reaction between MDI and polyols would be greater than the reaction between the PLA end groups. Theoretically, the polyurethane chain(PU) would be more likely to form in the final polymer blend than the separate addition method. Consequently, the PLA/PU blends would be the matrix for the compound materials. If the hypothesis is succeed, it means that the properties especially HDT and toughness of the compound would be enhanced compare with the previous mixing method. Miscible blend with higher molecular weight polymer chains would increase the thermal and mechanical properties of the blend. In this section, the term of PLA/PU will be applied for the blending of PLA and the premixed MDI and polyols.

Another point of discussion in this report section is the effect of moisture residual in the specimen on the tested properties. The contaminated moisture is literately penetrated into the sample during the sauna incubation process. The infusion of the foreign molecule into the polymer phase, especially the hydrophilic ones, would have the great influence to the properties of the polymer. Normally, it would lower the HDT and ductility of the material. Therefore, in this research topic the extra set of sauna cured specimen were vacuum dried at 80°C for 2 hours to remove the moisture residual raised from the sauna curing process. It will be called "**dried**" sample in this discussion. Therefore, in this discussion, there are three types of specimen; (*i*) original, (*ii*) cured and (*iii*) dried samples, were tested and compared.

Table 4.35 illustrates the composition of PLA/PU compound used in the study. The constant PU ingredient was prepared at the MDI and polyols mixing ratio of 0.2 to 8.0 phr with respect to the PLA. Extra polyols as the processing aids and also compatibilizer was varied from 0.0 to 8.0 phr, respectively. The last sample, No. 6, is the sample without PU, by definition of this study section, and having the polyols content is 8.0 phr. In fact, it is the compound ingredient obtained from the previous DOE experiment at the low level of silane and high level of polyols contents, respectively. The mixing procedure was performed in the twin screw in the same manner as described in the previous sections. The injection molded specimen of the three categorized samples and were tested and the results are summarized in Table 4.36.

Table 4.35 The composition of PLA/PU compound and the polyols contents.

Sample No.	Composition(phr)							
	PLA	Silane	Polyurethane		Glycerol	DCP	Talc	Polyols
			Polyols	Isocyanate				
1	100	2.0	8.0	0.2	0.3	1.0	50	0.0
2	100	2.0	8.0	0.2	0.3	1.0	50	2.0
3	100	2.0	8.0	0.2	0.3	1.0	50	4.0
4	100	2.0	8.0	0.2	0.3	1.0	50	6.0
5	100	2.0	8.0	0.2	0.3	1.0	50	8.0
6	100	2.0	-	0.2	0.3	1.0	50	8.0

Table 4.36 Summary of the test results for the PLA/PU compounds.

Polyols content	MFI (g/10min)			HDT (^oC)			Tensile strength (MPa)			Young's modulus (GPa)		
	original	cured	dried*	original	cured	dried*	original	cured	dried*	original	cured	dried*
0.0	0.158 ± 0.018	No flow	No flow	47.5 ± 0.30	83.1±1.27	97.1±1.55	52.11 ± 0.99	47.77 ± 2.56	47.30 ± 4.09	3.66 ± 0.14	3.36 ± 0.11	2.97 ± 0.16
2.0	0.071 ± 0.014	No flow	No flow	45.6 ± 0.69	81.7±0.42	96.1±1.12	46.19 ± 2.18	44.12 ± 0.46	43.84 ± 1.82	3.28 ± 0.15	2.87 ± 0.05	2.79 ± 0.21
4.0	0.049 ± 0.007	No flow	No flow	45.3 ± 0.58	81.5±2.83	94.7±2.72	43.36 ± 0.75	41.75 ± 0.41	41.12 ± 0.57	3.09 ± 0.05	2.71 ± 0.09	2.55 ± 0.10
6.0	0.042 ± 0.011	No flow	No flow	44.0 ± 0.00	79.7±2.31	94.7±2.42	41.97 ± 0.67	40.30 ± 0.36	39.57 ± 0.97	2.82 ± 0.10	2.46 ± 0.06	2.34 ± 0.17
8.0	0.030 ± 0.002	No flow	No flow	42.7 ± 0.58	78.0±1.00	94.0±1.10	36.04 ± 2.00	35.41 ± 1.94	35.72 ± 0.98	2.59 ± 0.08	2.10 ± 0.12	2.16 ± 0.14
8.0**	0.444 ± 0.142	0.853 ± 0.368	No flow	47.1 ± 0.23	83.2 ± 5.32	106.3±2.52	56.99 ± 1.19	53.19 ± 1.02	52.18±1.83	4.00 ± 0.23	3.83 ± 0.16	3.77±0.20

Polyols content	Strain at break (%)			Notched impact (kJ/m^2)			Unnotched impact (kJ/m^2)		
	original	cured	dried*	original	cured	dried*	original	cured	dried*
0.0	2.15 ± 0.13	2.04 ±0.24	2.12 ± 0.15	3.93 ± 1.09	3.46 ± 0.22	4.13 ± 0.17	13.78 ± 0.11	15.32 ± 2.73	15.27 ±0.96
2.0	2.21 ± 0.20	2.28 ± 0.12	2.25 ± 0.11	3.98 ± 0.93	3.39 ± 0.19	4.22 ± 0.15	15.68 ± 1.34	17.66 ± 2.40	17.16± 1.38
4.0	2.22 ± 0.05	2.41 ± 0.10	2.34± 0.14	4.02 ± 0.63	3.95 ± 0.97	5.34 ± 0.75	16.42 ± 1.50	15.61 ± 2.68	15.57 ± 1.93
6.0	2.50 ± 0.16	2.95 ± 0.06	2.87 ± 0.42	4.38 ± 0.25	4.09 ± 0.44	5.38 ± 0.14	17.27 ± 1.72	16.89 ± 2.58	15.26 ± 1.33
8.0	2.64 ± 0.24	2.78 ± 0.37	2.67 ± 0.12	6.27 ± 1.09	4.18 ± 0.24	5.44 ± 0.37	17.40 ± 2.08	14.34 ± 1.54	12.95 ± 1.69
8.0**	2.18 ± 0.10	2.14 ± 0.18	2.50±0.13	4.24 ± 0.63	3.16 ± 0.13	2.86±0.35	12.10 ± 1.74	12.22 ± 1.75	14.44±0.31

* Dried in vacuum oven at 80^{o}C for 2 hours,

** The PLA compound without PU contents

4.7.1 MFI of PLA compound

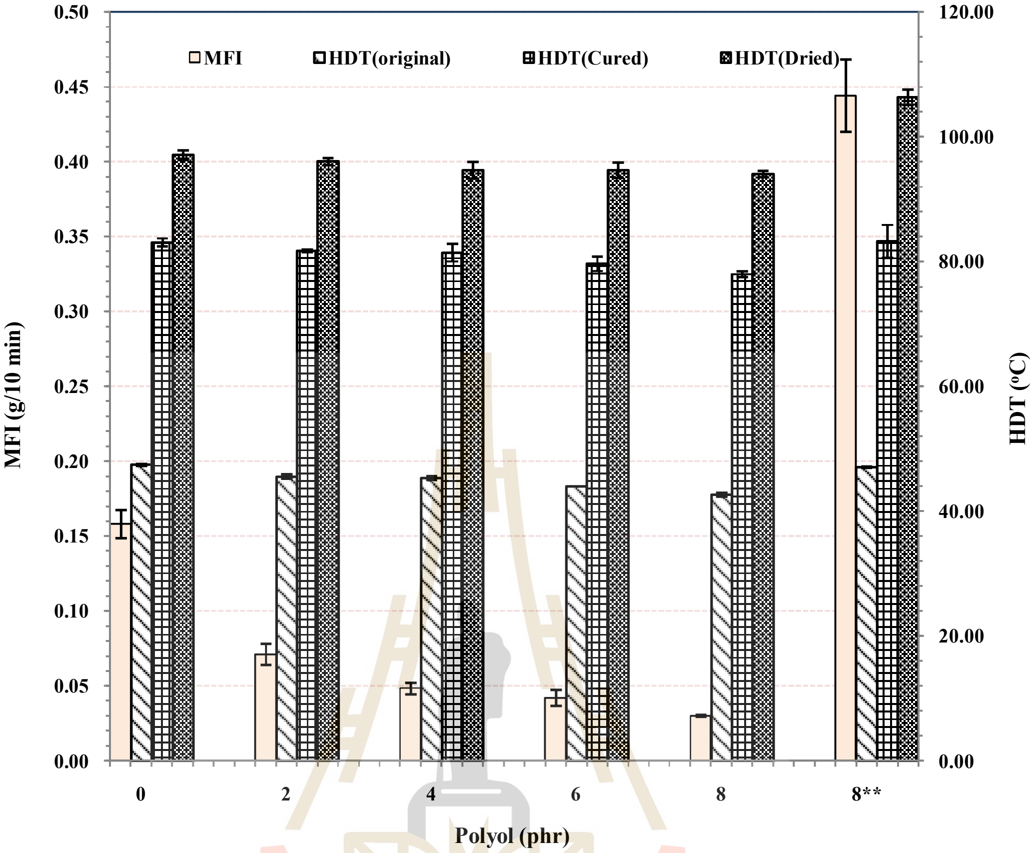
The flow ability of the PLA/PU compound measured at 230/5 is reported in Table 4.36 and they are plotted with respect to the polyols content as illustrated in Figure 4.51. From the result, MFI of the original sample, before undergoing sauna incubation, was decreased with increasing the polyols content. After the sample was treated in the sauna oven for at least 12 hours, it is seen that, within the standard testing condition conducted in this study, MFI of the sauna cured PLA/PU compounds was unable to obtain. The melt was unable to flow through the capillary die. The similar observation was found for the "**dried**" sample, undergone moisture incubation and then vacuum dried to remove the moisture residual, where the compound was no flow at the given test condition. Comparing with the compound system using only polyols and isocyanate, sample#6, the MFI of the original and cured samples were higher than the PLA/PU systems. However, the restriction of flow was observed on the "**dried**" sample. From the MFI result experienced, it could say that compounding the PLA with the PU system give rise to the lower MFI, higher melt viscosity, than the method using separate addition of polyols and isocyanate. It could be due to the mentioned hypothesis that the high molecular weight PU chain was formed during the prior mixed polyols/isocyanate and the longer chain was further achieved during the melt mixing in the screw barrel. As the result, the final compound obtained was most likely to be the blending between PLA and PU polymers rather than PLA blended with polyester polyols as might be found for the previous mixing method. Compatible blending the PLA with high molecular weight PU would have the higher viscosity than the blending PLA with low molecular weight polymer.

From the MFI investigation, it can also conclude that sauna incubation, of both the PLA/PU and PLA/Polyols compounds having the silane/DCP crosslink system, resulted in the macro crosslinked chains through the siloxane/moisture condensation reaction. The loosely network formed increase the melt viscosity, lower the flow ability, of the blends. Further removing of the residual moisture derived from the incubation process and hence preventing the chain hydrolysis during the high temperature melting, the flow ability of the vacuum dried compound is even restricted. The high viscosity of flow would limit the choice of polymer processing, especially for the injection molding.

4.7.2 Heat distortion temperature of PLA/PU compound

In this study, biodegradable polymer having the outstanding HDT, above 100°C, aiming for the high temperature packaging is one of the prime objectives. From the previous discussion, the PLA compound having the HDT close to 100°C was found. In this final experimental section, the blending of PLA with longer chain PU and the removing of moisture contamination during the prolong sauna incubation by post vacuum drying, was performed to obtain the higher HDT PLA compound. The HDT of PLA/PU compound prepared is reported in Table 4.36 and graphically presented with respect to the polyols concentration added in Figure 4.51 for the original, cured and dried samples, respectively. According to the test figures, it is found that the HDT of the original PLA/PU sample are almost constant. Within the standard deviation, it is marginally decreased with increasing the polyols addition. Interestingly at the given polyols content, the HDT of the PLA/PU compound is dramatically increased via the sauna treatment, cured sample. The further increasing in the HDT is observed when the moisture residual of the sample was got rid-off. The HDT above 90^{o}C is evidenced for the "**dried**" samples. Again HDT of both cured and dried samples are fractionally decreased with increasing the polyols concentration. The crosslinking of polymer chains via the silane/moisture condensation reaction can be used to explain the significant improvement of thermal properties of the PLA/PU compounds. Adding the soft segment of the polyester polyols chain into the compound ingredient has the minor effect to the HDT. Also, the removing of the moisture contamination has the great positive effect, increase HDT, to the thermal characteristic of the polymer compounds. It is indicated that the dissolution effect between hydrophilic PLA compound and contaminated water molecules lower the thermal stress of the compound.

In comparison between the PLA/PU system, sample#1, and PLA/polyols system, sample#6, the result show that, for the "**dried**" sample, HDT of PLA/polyols is higher than the PLA/PU system. HDT at approx. 106^{o}C is observed for the "**dried**" PLA/polyols compound. This number has reached the target goal for the research objective. The outcome indicates that higher in the density crosslink found for the PLA/polyols case has the greater effect to the HDT than the system by blending with high PU chain. However, the lower in the toughness for the high crosslink density system would be experienced as will be discussed later on this section.



*8** is referred to non PU system*

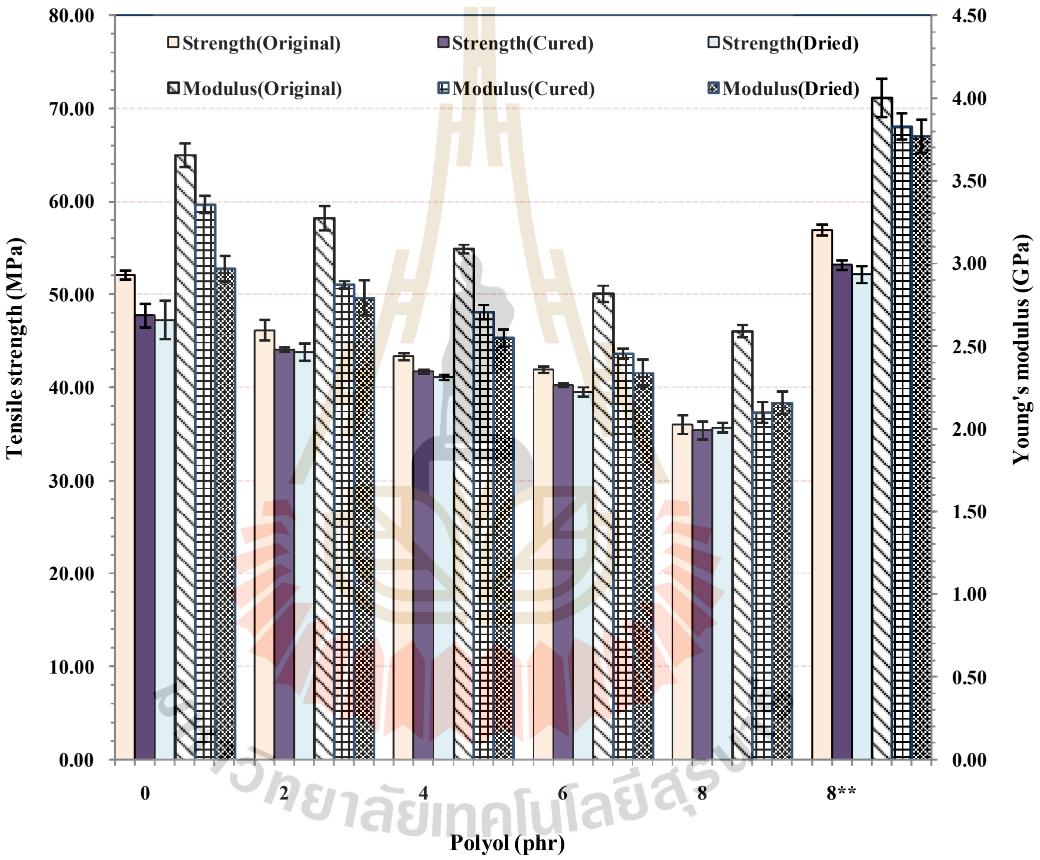
Figure 4.51 The MFI and HDT of PLA/PU compound.

4.7.3 Tensile properties of PLA/PU compound

The tensile strength, modulus and % strain at break of the PLA/PU compound with respect to the polyols loading are summarized and graphically presented in Table 4.36 and Figure 4.52 and 4.53, respectively. As expected, the tensile strength of PLA/PU compounds for all sample conditions is lowered when the amount of polyols added is increased. Typically, at the given polyols content, the strength is slightly decreased after the sauna treatment. Roughly speaking, there is no change in the strength when the moisture was completely removed, by the vacuum drying, from the specimen. The exact trend is observed for the Young's modulus.

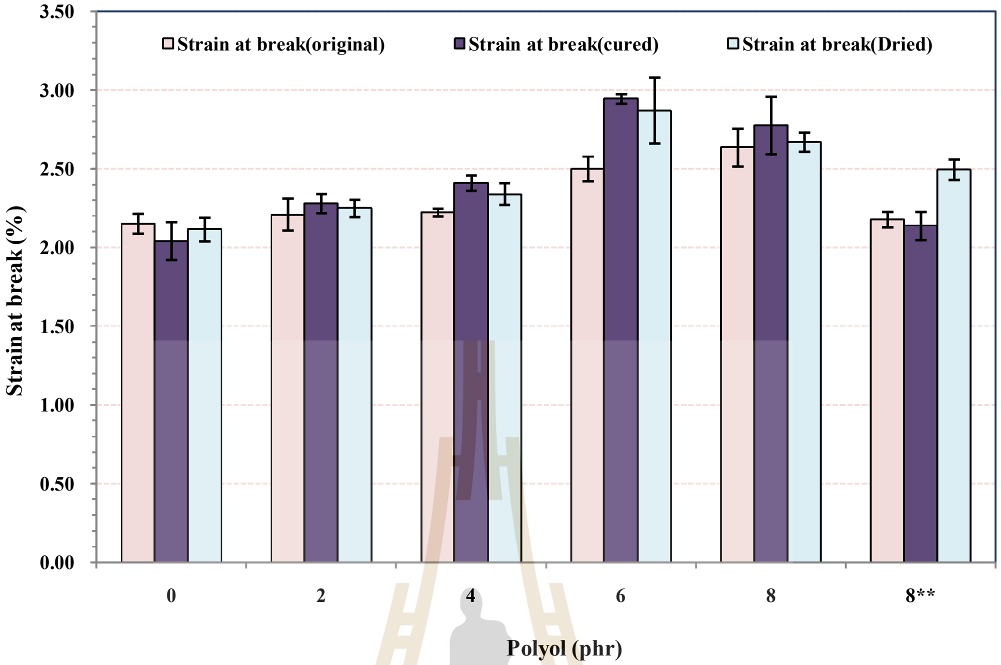
Vice versa, % strain at break of the PLA/PU compound, shown in Figure 4.53, there is slightly increased in the elongation at break with increasing the polyols content used for all conditioned samples. Closer investigation at the given polyols concentration, it is noticed that the % strain at break is marginally increased from original to cured and then fractionally decreased from cured to "**dried**" sample. Commonly, high flexible material, high % strain at break, would be resolved when adding more of flexible fraction. In this study, polyester polyols is higher flexible chain comparing with PLA and it is acted both as reactive compatibilizer and processing aids. Therefore, the % strain at break will be increased with increasing the polyols content. However, the degree of increasing is not as high as that expected because the reactive polyols would be part of the macro crosslink structure. Hence, the flexibility of the chain would be inhibited. For the slightly increasing in the strain at break of the cured sample, the dissolution effect by the contaminated moisture molecules, as mentioned earlier, would be taken into the explanation. Normally, the residual of high solubility solvent in the polymer matrix would dissolved the chain and thus behave as soft segment in the matrix phase. Consequently, the material would be softened, high in elasticity, and lowed in the thermal properties. After the moisture residual removing, "**dried**" sample, the dilution effect would be diminished. Then, the flexibility of material would be back to normal state.

In comparison between PLA/PU and PLA/polyols systems, sample#1 and sample#6, the tensile properties result indicates that the value of the strength and modulus of PLA/polyols system is higher than PLA/PU system but the % strain at break is more or less identical, for all conditioned samples. It reviews that the PLA/polyols system has better ductility than the PLA/PU blend. The better compatibility between polyester polyols with PLA than the long chain PU and PLA would be the suspect for the difference in the tensile properties.



*8** is referred to non PU system*

Figure 4.52 The tensile strength and modulus of PLA/PU compound.



*8** is referred to non PU system*

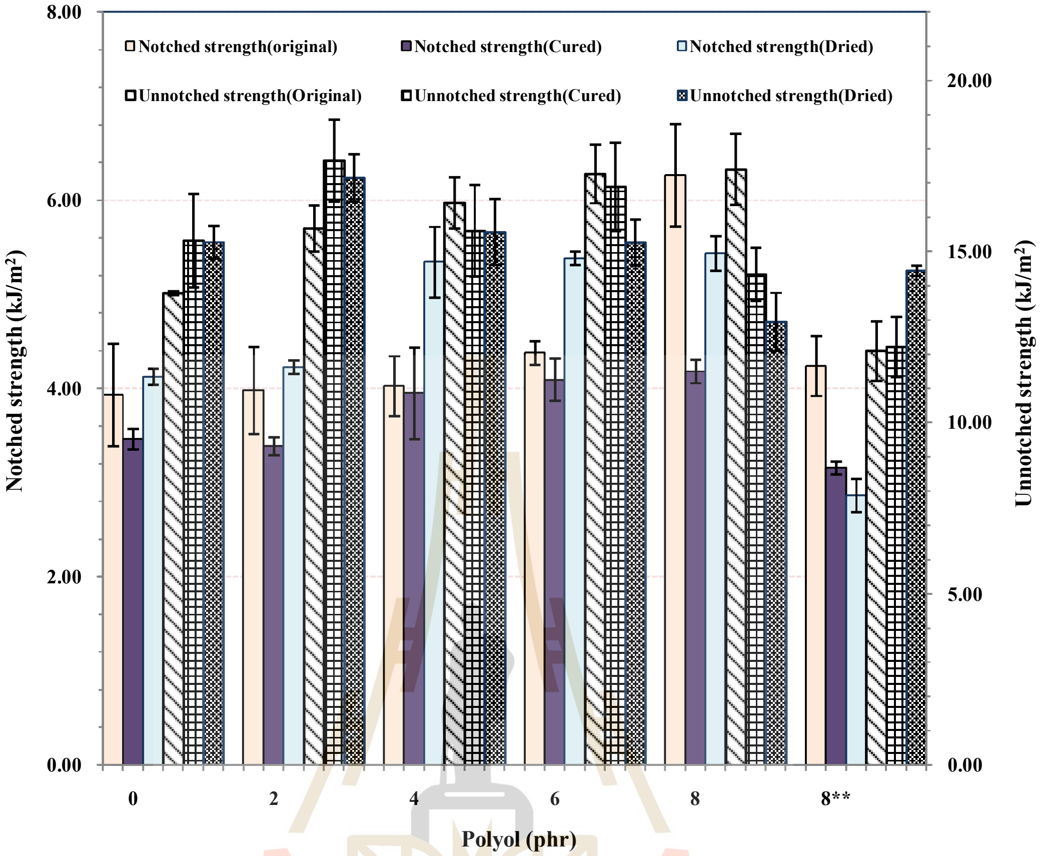
Figure 4.53 The % strain at break of PLA/PU compound.

4.7.4 Impact strengths of PLA/PU compound

In Table 4.36 and the plotted graph illustrated in Figure 4.54 shows the impact results of the PLA/PU compound at various polyols contents. The PLA/polyols blend is used for the sake of comparison. For the notched testing mode, it is seen that the impact strength of the PLA/PU compound is increased with increasing the polyols content for all conditioned specimens. Noticeable, at the given polyols content, that the notched impact strength is decreased when it was undergone sauna treatment. The impact is obviously increased again when the residual moisture due to the sauna process was completely removed by vacuum drying. The impact of the dried sample is even higher than the original one. This confirmed the previous statement that the dissolution effect of the moisture has the significant effect on the impact strength of the PLA/PU compound. Removing of the moisture molecule from the polymer phase not only get rid of the contamination but condensing the polymer matrix. Consequently, the superior impact value is obtained.

For the unnotched impact strength outcome, Figure 4.54 also indicates that the impact of original PLA/PU compound is increased when increasing polyols content. For the values tested on cured and vacuum dried specimen, the unnotched impact strength is decreased when the polyols content is above 2 phr. In fact, the polyester polyols added is not only the reactive compatilizer but it is also acted as the toughener. Therefore, when the content of the compatilizer is increased the impact strength of the original sample is increased. On the other hand, the polyester polyols is one of hydrophilic type polymers. Therefore, the moisture absorption during the sauna incubation would be higher when adding more of the polymer. Consequently, the unnotched impact strength would be decreased, due to the dissolution effect, when increasing the polyols content. Quickly removing the moisture contamination by vacuum drying would create micro void in the sample. Hence, crake propagation would be accelerated. The lower in the notched impact strength would be resolved.

When compare the strengths of PLA/PU and PLA/polyols compound, it is evidenced that the toughness strengths of PLA/PU are higher than PLA/polyols system. Commonly, polymer with higher chain length in the blend would result the better impact properties than blending with short chain molecule.



*8** is referred to non PU system*

Figure 4.54 The impact strengths of PLA/PU compound.

4.7.5 The morphology of PLA/PU compound

The SEM photographs of the fractured surface of PLA/PU compound samples#5; blending with PU system 8.0 phr and additional polyols at 8.0 phr, and PLA/polyols sample#6; compounding with 2 phr of isocyanate and 8 phr of polyols, are shown in Figure 4.55 (**a**) to Figure 4.55 (**f**) for the original, cured and dried samples, respectively. From the above discussion, these two samples showed the highest and lowest impact strengths. Obviously, the tougher fracture traces is seen on the PLA/PU system. From the SEM pictures, it is difficult to notice the difference between the original, cured and vacuum dried fractured traces for both compound systems. According to the impact; especially notched impact strength, outcome the values indicated that the toughness was inferior when the samples was treated and then dried. The dissolution of the moisture contaminant was taken into explain. But from the fractured traces reviewed by the SEM examination, the given hypothesis could not be clarified.

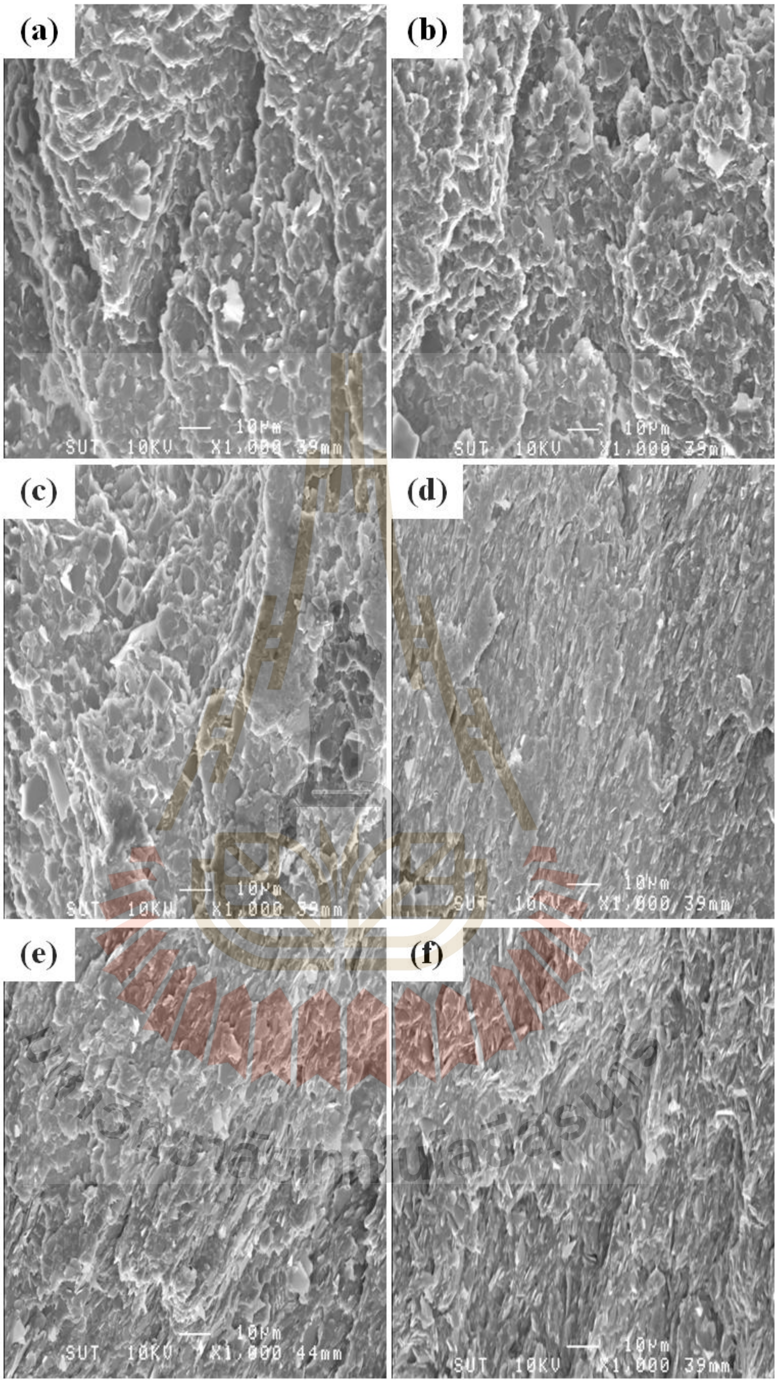


Figure 4.55 The SEM photograph of PLA/PU compounds for sample#5; (**a**) original, (**b**) cured, (**c**) vacuum dried, and PLA/polyols for sample#6; (**d**) original (**e**) cured and (**f**) vacuum dried, respectively.

From the above discussion in the properties of the PLA/PU compound system, the results review that lower in MFI, HDT and tensile properties but fractionally higher in impact strengths when increasing the amount of polyols in PLA/PU system. Vacuum drying to remove the moisture residual derived from the sauna incubation process has the positive effect to MFI and HDT of the compound at the given PU content. It was likely to have the negative effect to the mechanical properties. Dissolution effect by the moisture contamination and micro void after performing quick vacuum drying was used to rationalize the mentioned phenomena.

For the main objective of this research study, HDT above 100°C for the high temperature application of biopolymer, it was found that the vacuum dried of the silane/DCP crosslinked PLA/polyester polyols compound having the polyols and MDI ratio at 8 phr to 0.2 phr with respect to the PLA showed the HDT of 106°C. With the great obstruction of the flow ability, it could say that this compound can be used where service temperature above 100°C is required.

CHAPTER V

CONCLUSIONS

By employing the statistical approach namely 2^k factorial design of experiment (DOE) to study the effect of silane, polyols and glycerol content on the properties of the PLA compound, it was found that silane content (A) was negative and significantly effect on the tensile strength without sauna curing and notched impact strengths of the sample both original and sauna curing. It was also found that the interaction between polyols and glycerol (BC) was positive and significant effect on the Young's modulus after sauna cured process. With confidently conclusion, good ductility of PLA compound could be obtained if the silane addition was kept at low level, less than 1 phr.

For investigation of PLA compound by varying the amount of glycerol in the compound, it was found that adding glycerol as supplement plasticizer into the PLA compounding process, it was generally enhanced the flow ability and tensile properties of the compound when compare with pure PLA and the compound without glycerol. However, adding this plasticizer at high content, for example more than 0.2 phr, the fracture toughness properties of the PLA obtained was inferior.

In study of adding highly reactive isocyanate in conjunction with polyester polyols and glycerol to form the reactive poly(urethane) polymerization in the PLA compound process, the outcome showed that the thermal properties was slightly increased but not much as high as 100°C for the required figure. Also, the mechanical properties were inferior when compare with the compound without the isocyanate. The compounds also become thermosetting in nature because the reaction between isocynate group and hydroxyl group to form the dispersed hard segment.

Attempting to hurdle the service temperature, HDT, of the PLA compound by introduction the vinyl silane/peroxide crosslink system into the compound ingredient, it was found that the MFI was decreased and HDT, tensile and impact properties were increased with increasing the DCP concentration. On the other word, the thermoset characteristic was observed. The network chain formation, confirmed by the gel determination, was drawn to explain the outcome. However, the target service temperature, HDT more than 100°C, was not established.

From investigation by adding talc into PLA compound, the result indicated that higher heat resistance PLA compound was achieved by the addition of talc filler. But carefully control of the filler content must be taken into consideration because the mechanical incompetency was observed at high talc content. According to experimental indicator, talc at above 40 phr was required for high HDT PLA compound.

Through the 2^2 DOE set up, the conclusion of the effect of silane and polyols at the given level of contents used was established. Only silane content did have the negative and significant effect on the melt flow index of the PLA compound. It menifested that compounding the PLA with high silane content gave rise the low melt flow of the polymeric material. Unexpectedly, adding the polyester polyols at the given concentration to assist the flow ability of the designed material did not have significant influence to the properties of the PLA compound, especially the MFI. It was due to the fact that the level of the polyols used was too low to overcome the resistance of the flow from the chain crosslinked.

In the research study on the properties of the PLA compound using the PU system, the results reviewed that lower in MFI, HDT and tensile properties but fractionally higher in impact strengths when the amount of polyols in PLA/PU system was increased. Vacuum drying to remove the moisture residual derived from the sauna incubation process had the positive effect to MFI and HDT of the compound at the given PU content. It was likely, with some doubt, to have the negative effect to the mechanical properties. Dissolution effect by the moisture contamination and micro void after performing quick vacuum drying was used to rationalize the mentioned phenomena.

As the prime objective of this research study, the requirement of HDT above 100°C for the high temperature application of the PLA biopolymer, the study result found that the vacuum dried of the silane/DCP induced crosslinked PLA blended with polyester polyols having the polyols and MDI ratio at 8 phr to 0.2 phr with respect to the amount of PLA showed the HDT of 106°C. There was no scarify with other properties such as mechanical one. With the great obstruction of the flow ability, it could say that this compound can be used where service temperature above 100°C is required.

In conclusion, the PLA compound formula summarized in Table 5.1 was derived from this research study. This PLA compound ingredient offered the desired properties both thermal, HDT above 100°C, and decent mechanical properties in comparison with neat PLA.

Table 5.1 The composition of PLA compound.

Formula ingredient	**(phr)**
PLA	100
Silane(VTMS, A-171)	2.0
Polyester Polyols	8.0
Glycerol	0.3
Methylene Diphenyl Diisocyanate(MDI)	0.2
Dicumyl Peroxide(DCP)	1.0
Talc	50
Processing/Thermal Stabilizer	2.0

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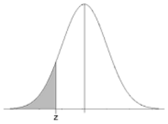
APPENDIX A

CUMULATIVE PROPABILITIES TABLES

Table A.1 Cumulative probabilities for negative Z-values table.

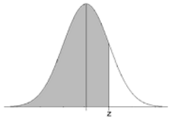


Z	0.09	0.08	0.07	0.06	0.05	0.04	0.03	0.02	0.01	0
-3.0	0.0010	0.0010	0.0011	0.0011	0.0011	0.0012	0.0012	0.0013	0.0013	0.0013
-2.9	0.0014	0.0014	0.0015	0.0015	0.0016	0.0016	0.0017	0.0018	0.0018	0.0019
-2.8	0.0019	0.002	0.0021	0.0021	0.0022	0.0023	0.0023	0.0024	0.0025	0.0026
-2.7	0.0026	0.0027	0.0028	0.0029	0.0030	0.0031	0.0032	0.0033	0.0034	0.0035
-2.6	0.0036	0.0037	0.0038	0.0039	0.004	0.0041	0.0043	0.0044	0.0045	0.0047
-2.5	0.0048	0.0049	0.0051	0.0052	0.0054	0.0055	0.0057	0.0059	0.0060	0.0062
-2.4	0.0064	0.0066	0.0068	0.0069	0.0071	0.0073	0.0075	0.0078	0.008	0.0082
-2.3	0.0084	0.0087	0.0089	0.0091	0.0094	0.0096	0.0099	0.0102	0.0104	0.0107
-2.2	0.0110	0.0113	0.0116	0.0119	0.0122	0.0125	0.0129	0.0132	0.0136	0.0139
-2.1	0.0143	0.0146	0.0150	0.0154	0.0158	0.0162	0.0166	0.017	0.0174	0.0179
-2.0	0.0183	0.0188	0.0192	0.0197	0.0202	0.0207	0.0212	0.0217	0.0222	0.0228
-1.9	0.0233	0.0239	0.0244	0.0250	0.0256	0.0262	0.0268	0.0274	0.0281	0.0287
-1.8	0.0294	0.0301	0.0307	0.0314	0.0322	0.0329	0.0336	0.0344	0.0351	0.0359
-1.7	0.0367	0.0375	0.0384	0.0392	0.0401	0.0409	0.0418	0.0427	0.0436	0.0446
-1.6	0.0455	0.0465	0.0475	0.0485	0.0495	0.0505	0.0516	0.0526	0.0537	0.0548
-1.5	0.0559	0.0571	0.0582	0.0594	0.0606	0.0618	0.063	0.0643	0.0655	0.0668

Table A.1 Cumulative probabilities for negative Z-values table (continued).

Z	**0.09**	**0.08**	**0.07**	**0.06**	**0.05**	**0.04**	**0.03**	**0.02**	**0.01**	**0**
-1.4	0.0681	0.0694	0.0708	0.0721	0.0735	0.0749	0.0764	0.0778	0.0793	0.0808
-1.3	0.0823	0.0838	0.0853	0.0869	0.0885	0.0901	0.0918	0.0934	0.0951	0.0968
-1.2	0.0985	0.1003	0.1020	0.1038	0.1056	0.1075	0.1093	0.1112	0.1131	0.1151
-1.1	0.1170	0.1190	0.1210	0.1230	0.1251	0.1271	0.1292	0.1314	0.1335	0.1357
-1.0	0.1379	0.1401	0.1423	0.1446	0.1469	0.1492	0.1515	0.1539	0.1562	0.1587
-0.9	0.1611	0.1635	0.1660	0.1685	0.1711	0.1736	0.1762	0.1788	0.1814	0.1841
-0.8	0.1867	0.1894	0.1922	0.1949	0.1977	0.2005	0.2033	0.2061	0.2090	0.2119
-0.7	0.2148	0.2177	0.2206	0.2236	0.2266	0.2296	0.2327	0.2358	0.2389	0.2420
-0.6	0.2451	0.2483	0.2514	0.2546	0.2578	0.2611	0.2643	0.2676	0.2709	0.2743
-0.5	0.2776	0.281	0.2843	0.2877	0.2912	0.2946	0.2981	0.3015	0.305	0.3085
-0.4	0.3121	0.3156	0.3192	0.3228	0.3264	0.3300	0.3336	0.3372	0.3409	0.3446
-0.3	0.3483	0.352	0.3557	0.3594	0.3632	0.3669	0.3707	0.3745	0.3783	0.3821
-0.2	0.3859	0.3897	0.3936	0.3974	0.4013	0.4052	0.4090	0.4129	0.4168	0.4207
-0.1	0.4247	0.4286	0.4325	0.4364	0.4404	0.4443	0.4483	0.4522	0.4562	0.4602
-0.0	0.4641	0.4681	0.4721	0.4761	0.4801	0.4840	0.4880	0.4920	0.4960	0.5000

Table A.2 Cumulative probabilities for positive Z-values table.



Z	0	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	0.5000	0.5040	0.5080	0.5120	0.5160	0.5199	0.5239	0.5279	0.5319	0.5359
0.1	0.5398	0.5438	0.5478	0.5517	0.5557	0.5596	0.5636	0.5675	0.5714	0.5753
0.2	0.5793	0.5832	0.5871	0.5910	0.5948	0.5987	0.6026	0.6064	0.6103	0.6141
0.3	0.6179	0.6217	0.6255	0.6293	0.6331	0.6368	0.6406	0.6443	0.6480	0.6517
0.4	0.6554	0.6591	0.6628	0.6664	0.6700	0.6736	0.6772	0.6808	0.6844	0.6879
0.5	0.6915	0.6950	0.6985	0.7019	0.7054	0.7088	0.7123	0.7157	0.7190	0.7224
0.6	0.7257	0.7291	0.7324	0.7357	0.7389	0.7422	0.7454	0.7486	0.7517	0.7549
0.7	0.7580	0.7611	0.7642	0.7673	0.7704	0.7734	0.7764	0.7794	0.7823	0.7852
0.8	0.7881	0.7910	0.7939	0.7967	0.7995	0.8023	0.8051	0.8078	0.8106	0.8133
0.9	0.8159	0.8186	0.8212	0.8238	0.8264	0.8289	0.8315	0.8340	0.8365	0.8389
1.0	0.8413	0.8438	0.8461	0.8485	0.8508	0.8531	0.8554	0.8577	0.8599	0.8621
1.1	0.8643	0.8665	0.8686	0.8708	0.8729	0.8749	0.8770	0.8790	0.8810	0.8830
1.2	0.8849	0.8869	0.8888	0.8907	0.8925	0.8944	0.8962	0.898	0.8997	0.9015
1.3	0.9032	0.9049	0.9066	0.9082	0.9099	0.9115	0.9131	0.9147	0.9162	0.9177
1.4	0.9192	0.9207	0.9222	0.9236	0.9251	0.9265	0.9279	0.9292	0.9306	0.9319
1.5	0.9332	0.9345	0.9357	0.9370	0.9382	0.9394	0.9406	0.9418	0.9429	0.9441

Table A.2 Cumulative probabilities for positive Z-values table (continued).

Z	**0**	**0.01**	**0.02**	**0.03**	**0.04**	**0.05**	**0.06**	**0.07**	**0.08**	**0.09**
1.6	0.9452	0.9463	0.9474	0.9484	0.9495	0.9505	0.9515	0.9525	0.9535	0.9545
1.7	0.9554	0.9564	0.9573	0.9582	0.9591	0.9599	0.9608	0.9616	0.9625	0.9633
1.8	0.9641	0.9649	0.9656	0.9664	0.9671	0.9678	0.9686	0.9693	0.9699	0.9706
1.9	0.9713	0.9719	0.9726	0.9732	0.9738	0.9744	0.9750	0.9756	0.9761	0.9767
2.0	0.9772	0.9778	0.9783	0.9788	0.9793	0.9798	0.9803	0.9808	0.9812	0.9817
2.1	0.9821	0.9826	0.9830	0.9834	0.9838	0.9842	0.9846	0.985	0.9854	0.9857
2.2	0.9861	0.9864	0.9868	0.9871	0.9875	0.9878	0.9881	0.9884	0.9887	0.989
2.3	0.9893	0.9896	0.9898	0.9901	0.9904	0.9906	0.9909	0.9911	0.9913	0.9916
2.4	0.9918	0.9920	0.9922	0.9925	0.9927	0.9929	0.9931	0.9932	0.9934	0.9936
2.5	0.9938	0.9940	0.9941	0.9943	0.9945	0.9946	0.9948	0.9949	0.9951	0.9952
2.6	0.9953	0.9955	0.9956	0.9957	0.9959	0.9960	0.9961	0.9962	0.9963	0.9964
2.7	0.9965	0.9966	0.9967	0.9968	0.9969	0.9970	0.9971	0.9972	0.9973	0.9974
2.8	0.9974	0.9975	0.9976	0.9977	0.9977	0.9978	0.9979	0.9979	0.998	0.9981
2.9	0.9981	0.9982	0.9982	0.9983	0.9984	0.9984	0.9985	0.9985	0.9986	0.9986
3.0	0.9987	0.9987	0.9987	0.9988	0.9988	0.9989	0.9989	0.9989	0.9990	0.9990

APPENDIX B

PUBLICATION

Publication

Katesa, P., Meekum, U. (2011). Design of Experiment: Micro Crosslinked Poly(Lactic Acid) via Silane Reaction. **The 2nd Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and The 17th PPC Symposium on Petroleum, Petrochemicals, and Polymers.** Bangkok, Thailand.

Certificate of Participation

This is to certify that

Ms. Phawitphon Katesa

has participated in *The 2nd Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and The 17th PPC Symposium on Petroleum, Petrochemicals, and Polymers* at Queen Sirikit National Convention Center, Bangkok, Thailand April 26, 2011.

She has given a poster presentation and the proceedings were published in the book of abstracts.

(Assistant Professor Pomthong Malakul Na Ayudhaya)

Dean

DESIGN OF EXPERIMENT: MICRO CROSSLINKED POLY(LACTIC ACID) VIA SILANE REACTION

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ABSTRACT

Polylactic acid was modified via silane moisture crosslinking reaction to improve the thermal properties. The PLA compound ingredient consisted of *gamma*-aminopropyltriethoxysilane (APS) as crosslinking agent, polyols and glycerol as plasticizers. The design of experiment was employed to optimize and quantify the amount of the mixing compositions. The 2^k factorial design was conducted to evaluating the statistical effects of material ingredient on the responds properties. Three parameters, k = 3, explicitly as silane(A), polyester polyols(B) and glycerol(C) contents were assigned. All eight designed compositions were compounded by co-rotating twin screw extruder and the specimens were prepared by injection molding. The sauna cured specimens were achieved by storage at 60°C for 12 hr in moisture saturated oven to accelerate the silane/moisture crosslink reaction. The morphology were visaulised by scanning electron microscope(SEM). Heat distortion temperature(HDT), notched impact and tensile were investigated as used as design responds. Without suana treatment, most properties of PLA compound were decreased with silane content. The properties of the compound were improved by introduction of crosslink structure via the silane/moisture crosslink reaction. Statistical analysis approach using ANOVA testing showed that silane had generally negative effect on the thermal and impact properties. The regressed models, obtained from the statistical processes, as the function of desired reponds against the significant parameter was constructed.

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INTRODUCTION

The starting material for the polylactic acid , lactic acid, is made by a fermentation process from 100% annually renewable resources, such as corn starch (in the United States), tapioca products (roots, chips or starch mostly in Asia) or sugarcanes (in the rest of world). The PLA also biodegrade in a compost environment and the byproducts are of very low toxicity, eventually being converted to carbon dioxide and water. It can be processed in most polymer processing equipments. However, its poor heat stability and mechanical properties have limited its range of applications[1]. Many studies have been undertaken on the physical and chemical modification of PLA in an effort to deal with these disadvantages. Crosslinking is a widely used method for the modification of polymer properties[2]. This process involves the formation of three dimensional structures – gels – causing substantial changes in material properties. By introducing crosslinks into PLA structures, physical properties such as the crystallinity and melting point and certain mechanical and thermal properties such as the modulus, tensile strength and elongation at break and HDT will be affected. Furthermore, the creep resistance and high temperature dimensional stability are in general improved by crosslinking. The characteristics of biodegradation and hydrolytic degradation will also be influenced[3]. The crosslinking of PLA can be initiated either in the melt (by thermal decomposition of peroxides) or in the solid state(by high energy irradiation). Silane grafting and subsequent moisture crosslinking of polymers have received much attention in recent years, not only for industrial applications, but also in fundamental research, because of various advantages, such as easy processing, low capital investment and favorable properties of the processed materials. Silane moisture-crosslinking is considered as a good candidate for crosslinking of PLA to give improved thermo mechanical properties and hydrolysis resistance without sacrificing its valuable biodegradation properties. In this paper PLA was compounded and crosslinked using silane moisture crosslinking technique. The prime objective was to raise the thermal stability of the PLA compound for high temperature packaging application. The statistical approach by mean of design of experimental(DOE) were used to verify and optimize the parameter(s) that given rise to better thermal properties of crosslinked PLA compound.

EXPERIMENTAL

A. Material

The polylactic acid(PLA), 2002D was purchased from Nature Works®. The silanes, *gamma*-aminopropyltriethoxysilane(APS), Silquest A-1100, was avialable from Crompton Corporation and used as crosslink agent. Aliphatic polyester polyols, Rayelast A 8770, from IRPC Polyols Co., Ltd was employed as processing aids. The commercial glycerol as plasticizer was added. Blend of Irganox 1076 and Irgafos 168, supplied from Ciba specialty chemicals, at weight ratio of 1:1 were added as thermal/processing stabilizer.

B. Design of experiment

The 2^k factorial design of experiment(DOE) was employed to optimize and quantify the amount of the compound compositions. Three parameters, k = 3, explicitly as silane(A), polyols(B) and glycerol(C) contents were assigned. Each parameter was divided into high(+) and low(-) levels, respectively. In each level, it was also split into two sub levels as shown in table 1. For example, silane content at 0.5 and 1 phr were assigned as low level, vice versa 1.5 and 2 phr, based on 100g of PLA, were assigned as high level, respectively. All eight compositions matrix for the test run were shown in table 2. The statistical analysis was assisted and performed by using commercial software, Design Expert™.

Table 1. The parameters for DOE analysis

Parameters	Low level (phr)		High level (phr)	
Silane	- 0.5	- 1.0	+ 1.5	+ 2.0
Polyols	- 0.5	- 1.0	+ 1.5	+ 2.0
Glycerol	- 0.1	- 0.2	+ 0.3	+ 0.4

Table 2. Factorial design matrix

Runs	Silane(A)	Polyols(B)	Glycerol(C)
1	- 0.5	- 0.5	- 0.1
2	- 0.5	- 1.0	+ 0.3
3	- 1.0	+ 1.5	- 0.2
4	- 1.0	+ 2.0	+ 0.4
5	+ 1.5	- 1.0	- 0.2
6	+ 1.5	- 0.5	+ 0.3
7	+ 2.0	+ 2.0	- 0.1
8	+ 2.0	+ 1.5	+ 0.4

C. Sample preparation

PLA pellets was underwent dehumidification in vacuum oven at 80°C for 2 hrs. The assigned amounts of silane, viscous polyester polyols and glycerol were manually and vigorously premixed. The dried PLA pellet was then coated with the liquids mixture. Finally, thermal/processing stabilizer solid powder was added and again vigorously stirred. The well premixed ingredient was melt compounded by self-wiping co-rotating intermeshing twin screw extruders, Brabender Model PL2100, having the screws diameter of 25 mm with L/D ratio of 20. The screw consisted of three kneader zones. The mixing was achieved at 10 rpm screw speed and barrel temperature profile at 140, 150, 170, 180, 190°C from feed to die zones, respectively. The extruded strand was allowed to anneal under atmospheric condition and granulated. The dehumidified pellet was molded into test specimen by using Tederic, model TRX60c, injection machine. The molded specimens were equally divided into two sets of sample; (*i*) allowed to annealing at room temperature for overnight and (*ii*) incubated at 60°C in sealed and moisture saturated oven for 12 hrs. The former was called original and the later called sauna cured sample, respectively.

D. Properties measurement and testing

MFI of PLA compound was obtained at 2.16/190 according to ASTM D1238. For the tensile properties, was performed according to ASTM D638 using Instron universal testing machine, model 5565, at cross head speed at 50 mm/min. Notched and unnotched impact strength of the sample was tested in accordance with ASTM D256. Both tensile and impact properties were conducted at room temperature. Following ASTM D648 testing method with the standard load of 0.455 MPa and heating rate of 2 ±0.2°C/min, the HDT of the compound was obtained. Morphology of the impact fractured surface was examined by scanning electron microscope(SEM). The samples were ionized coating with gold before investigation. Those test properties were used as responds and analysed for the DOE.

RESULTS AND DISCUSSION

A. DOE Analysis

The results of MFI, HDT, tensile and impacts tests are summarized in table 3. General observation, it is noticed that there are slightly increasing in test values after sauna cured process. This could be evidenced from silane/water condensation reaction. The reaction probably gives rise to the branch or network structure. Fortunately, the HDT of the compound does not reach to the desired level, 100°C. Using the Design Expert^{TM}, statistical analysis of the responds data were performed. Taking the HDT, as it is prime interest, into the analysis, the normal probability against the standardized effects is plotted and shown in figure 1(**a**) and 1(**b**), for original and sauna cured, respectively. In the former sample, the plot shows that silane(A), glycerol(C) and interaction between silane and glycerol(AC) contents are the greatest effect on HDT as they are out of the linear trend line. They are -A, -C and +AC effects, respectively. Applying the ANOVA testing at 95% of confidential, the result confirms that the designed model is significant and those three effects are also significant effects on the HDT for the annealed PLA compound sample. Analysing on the sauna cured specimen as presented in figure 1(**b**), the C-parameter and interaction between silane and polyols (AB) are the positive effect(+) but coupled between silane and glycerol (AC) is negative(-). Accordingly, the ANOVA results confirm that the design formula are significant and those mentioned parameters are also significant effects to HDT of cured sample. Applying the notched impact as respond for analysis, the plots shown in figure 2(**a**) and 2(**b**), for original and sauna cured, respectively. For the original case, it shows that silane(A) content is the greatest negative effect(-) on notched impact strength. Similarly, it exhibit effect to the sample undergo sauna curing. The ANOVA testing strongly confirms that silane(A) content is the significant negative effect on the notched impact strength for both original and sauna cured sample. It means that adding more silane into the compound ingredient will cause the polymer to become brittle. The regressed equations, the function of the desired respond against the significant parameters, can be statistically resolved from this testing. They are summarized in table 4. Repeat the analysis in the exact manner on the rest of the responds, both original and sauna cured conditions, the outcome results are added up into table 4. These model equations could be used to formulate the PLA compound to the desired properties.

Table 3. Result data of original and cured samples

Runs	MFI (g/10min)	HDT(°C)		Tensile strength(MPa)		Young's Modulus (MPa)		Strain at break (%)		Notched impact(kJ/m²)		Unnotched impact(kJ/m²)	
		original	cured	original	cured	original	cured	original	cured	original	cured	original	cured
PLA	5.81	53	53	24.17	26.28	1212	1231	4.49	3.99	3.36	3.16	23.56	21.34
1	5.34	52	51	24.85	25.65	1237	1209	3.55	3.77	3.16	3.28	19.41	21.45
2	8.21	49	57	23.75	29.63	1235	1190	3.73	3.75	3.56	3.60	17.67	19.98
3	7.54	50	50	23.04	25.44	1185	1147	3.78	3.62	2.94	2.95	19.77	21.15
4	8.99	48	58	23.36	29.13	1185	1165	3.68	3.51	2.75	3.91	25.73	16.76
5	9.16	49	53	23.02	25.92	1210	1030	4.49	3.64	2.63	2.70	23.86	20.57
6	11.63	49	50	23.11	22.88	1198	1117	4.13	4.48	2.96	2.75	20.07	23.16
7	9.78	48	56	22.04	24.86	1188	946	4.14	4.00	2.47	2.41	21.40	21.59
8	9.57	48	58	22.29	27.62	1163	1156	4.01	3.65	2.20	2.28	18.22	16.07

Table 4. The predicted regression model for the properties of PLA compound derived from ANOVA testing

Properties	Regressed models
Original:	
Melt flow index	No significant model
HDT(origin)	49.01-0.30(A)+0.029(B)-0.25(C)+0.12(AC)
Tensile strength(origin)	23.18-0.33(A)
Young's modulus(origin)	1197.92-6.01(A)-7.04(B)+1.80(AB)-1.79(AC)
Strain at break(origin)	3.94+0.094(A)
Notched impact(origin)	2.83-0.16(A)
Unnotched impact(origin)	20.47+0.65(A)-0.47(AC)+0.53(BC)
Sauna Cured:	
HDT(cured)	53.12+1.75(C)+0.67(AB)-0.31(AC)
Tensile strength(cured)	26.50+0.48(AB)-0.42(AC)+0.47(BC)+0.20(ABC)
Young's modulus(cured)	1117.14-25.14(A)+15.51(C)+6.91(AC)
Strain at break(cured)	No significant model
Notched impact(cured)	3.00-0.22(A)+0.089(C)-0.031(AC)
Unnotched impact(cured)	No significant model

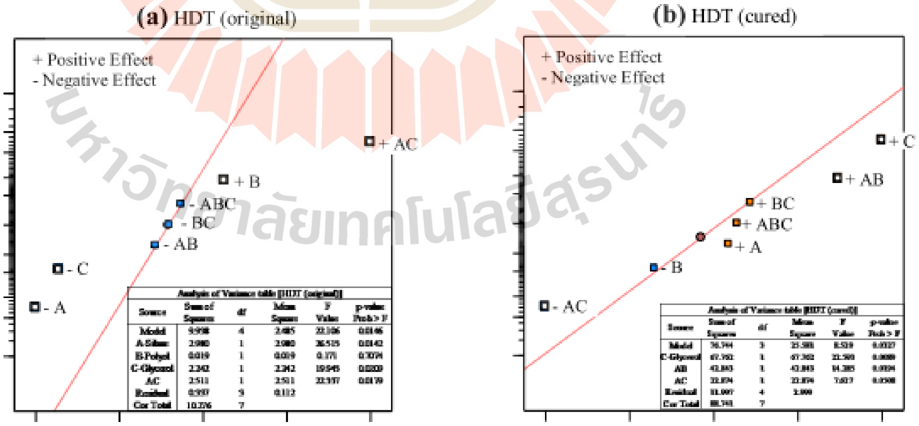
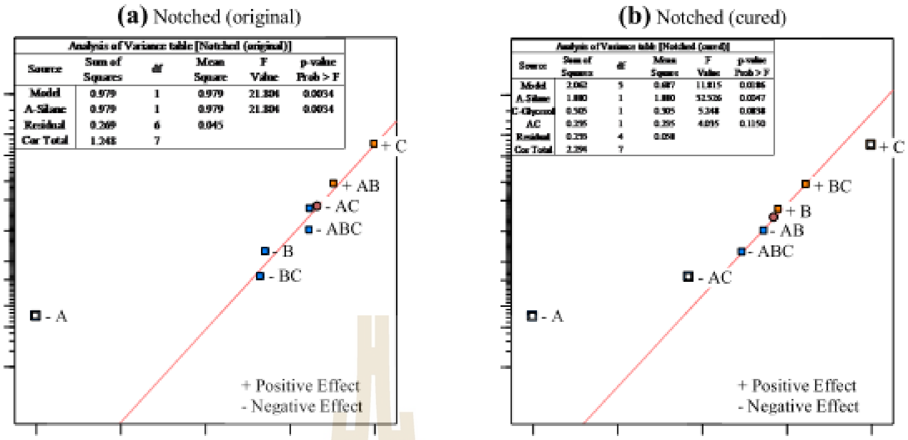


Figure 1. Normal probability and standardized effect plots of HDT;(**a**) original and (**b**) cured



Analysis of Variance table [Notched (original)]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	0.979	1	0.979	21.804	0.0034
A-Silane	0.979	1	0.979	21.804	0.0034
Residual	0.269	6	0.045		
Cor Total	1.248	7			

Analysis of Variance table [Notched (cured)]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	2.062	3	0.687	11.815	0.0186
A-Silane	1.880	1	1.880	32.326	0.0047
C-Glycerol	0.305	1	0.305	5.248	0.0838
AC	0.295	1	0.295	4.095	0.1150
Residual	0.233	4	0.058		
Cor Total	2.294	7			

Figure 2. Normal probability and standardized effect plots of notched impact strength; (**a**) original and (**b**) cured.

B. Scanning electron microscopy(SEM)

SEM photographs of the fractured surface of the sample obtained from neat PLA, Run#2 and Run#8 are shown in figure 3(**a**) -3(**d**), respectively. Figure 3(**a**) illustrates the fractured surface of neat PLA. It shows the fracture traces as found in common brittle polymers. Figure 3(**b**) illustrates the fractured surface of original sample of Run#2 in which low silane and polyester polyols but high glycerol contents was employed. The formula exhibits the highest notched impact properties. The surface is also smooth with some fibril like traces. The fractured surfaces of Run# 8, as shown in figure 3(**c**) and 3(**d**), whereas all ingredient parameters used were assigned at high levels and their notched impact test values are the lowest. The rougher fractured traces were obviously seen. It indicates the origin area of crack propagation and small droplet of immiscible phase. The separated tiny article may act as craze initiator and hence speed up the growing of crack through the matrix phase. As the result, the toughness of sample becomes inferior. Competition of crosslink bonding via silane/water condensation reaction has no pronounce enhancement of the toughness. On the other hand, it introduce the thermosetting characteristic into PLA compound.

CONCLUSIONS

Macro crosslinking PLA via silane/water condensation in the presence of only polyester polyols and glycerol as plasticizer was found to be an effective method for improving the thermal properties, by mean of HDT, of PLA. However, the sauna induced crosslink does evidently improve the mechanical performance of the polymer. The statistical method via design of experiment(DOE) can be used as the beginning guideline for optimizing the constituent ingredient that will give rise to the desired properties. Further exploring on crosslink method such as free radical induce via peroxide addition couple with filler addition selection are needed for achieving the PLA compound having the desired thermal properties threshold.

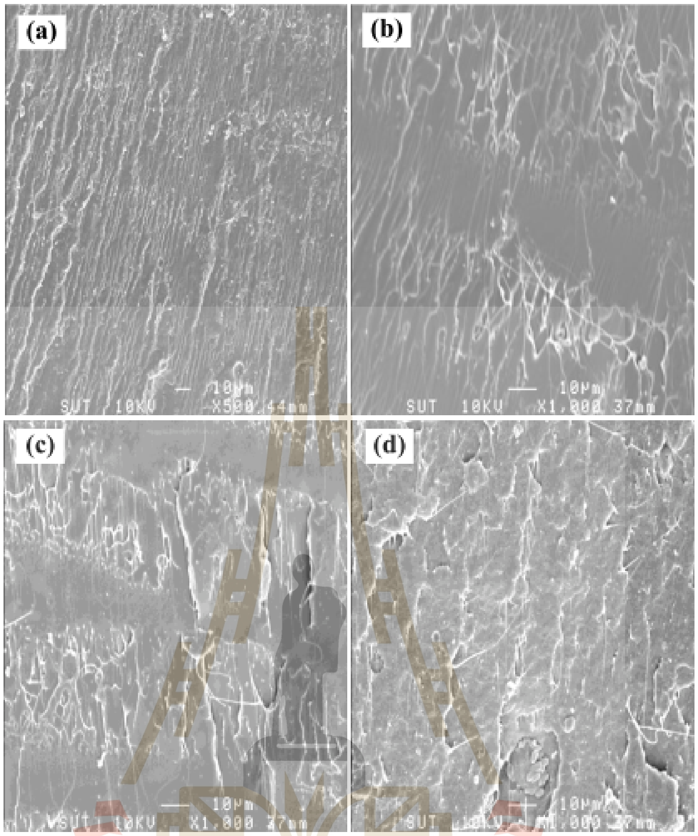


Figure 3. SEM micrograph of (**a**) neat PLA(500), (**b**) Run#2(original), (**c**) Run#8(original), (**d**) Run#8(cured), respectively.

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BIOGRAPHY

Miss. Phawitphon Katesa was born on May 31, 1983 in Mahasarakham, Thailand. She finished high school from Sri Kosum Wittaya Mitrapap 209 School in 2001. She earned her undergraduate degree in Mechanical Engineering at Suranaree University of Technology (SUT) in 2007, before attended her Master's degree in Polymer Engineering at School of Polymer Engineering, Suranaree University of Technology (SUT). During her graduate study, she got a research assistant scholarship from Center of Excellence for Petroleum, Petrochemical, and Advanced Materials. Her research was about improved heat distortion temperature of poly(lactic acid) compound via silane crosslinked. In the period of her study, she presented one poster presentation entitle: "Design of Experiment: Micro Crosslinked Poly(lactic acid) via Silane Reaction" at 2nd Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and The 17th PPC Symposium on Petroleum, Petrochemicals, and Polymers in Bangkok, Thailand.