POLYLACTIC ACID COMPOUNDING FOR SUB ZERO TEMPERATURE APPLICATIONS

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตร์มหาบัณฑิต
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POLYLACTIC ACID COMPOUNDING FOR SUB ZERO TEMPERATURE APPLICATIONS

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

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อภิชาติ เขียนสระน้อย : การปรับปรุงคุณสมบัติของพอลิแลคติกแอซิดสำหรับการใช้งานที่อุณหภูมิต่ำ (POLYLACTIC ACID COMPOUNDING FOR SUB ZERO TEMPERATURE APPLICATIONS) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.อุทัย มีคำ, 169 หน้า.

การศึกษาการผสมระหว่างพอลิแลคติกแอซิด(polylactic acid, PLA) กับยางซิลิโคน (silicone rubber) ชนิด 2 และ 1 องค์ประกอบโดยใช้การศึกษาเชิงสถิติ ด้วยวิธีการออกแบบการทดลอง(Design of Experiment, DOE) ของการผสมในระบบของซิลิโคนชนิด 2 องค์ประกอบ พบว่าซิลิโคนส่งผลเชิงบวก และ มีผลอย่างมีนัยสำคัญต่อค่าความแข็งเหนียวของพอลิเมอร์ผสมที่เตรียมได้ ทั้งที่การทดสอบที่อุณหภูมิห้องและอุณหภูมิต่ำกว่าจุดเยือกแข็ง พอลิเมอร์ผสมระหว่างพอลิแลคติกแอซิดกับยางซิลิโคนชนิด 2 องค์ประกอบ ที่มีไซเลน(silane) ทำหน้าที่เป็นสารคู่ควบ และ พอลิออล ชนิด พอลิเอสเทอร์(polyester polyol) ทำหน้าที่เป็นพลาสติไซเซอร์ พบว่าการใช้ซิลิโคนที่ 8.0 ส่วนในร้อยส่วนโดยน้ำหนัก มีผลทำให้คุณสมบัติที่ดีในทุกๆ ค่าการทดสอบ การเติมสารเพื่อการคงรูปของซิลิโคนชนิด ไตรเอทธิลเตรทตระเอมีน(TETA) ที่ปริมาณต่ำกว่า 0.4 ส่วนในร้อยส่วนโดยน้ำหนักของซิลิโคน ช่วยเพิ่มคุณสมบัติการทนต่อแรงดึงยืดที่ดีขึ้น พอลิเมอร์ผสมระหว่างพอลิแลคติกแอซิด กับ ยางซิลิโคนชนิด 2 องค์ประกอบ สามารถย่อยสลายตัวเชิงชีวภาพได้ภายใน 4 สัปดาห์ การผสมระหว่างพอลิแลคติกแอซิด กับ ยางซิลิโคนชนิด 1 องค์ประกอบ ที่ปริมาณการใช้ซิลิโคนเท่ากับ 8.0 ส่วนในร้อยส่วนโดยน้ำหนัก ทำให้ได้พอลิเมอร์ผสมที่มีคุณสมบัติที่ดีเมื่อเปรียบเทียบกับแอลดีพีอี (LDPE) โดยเฉพาะคุณสมบัติการทนต่อแรงตกกระแทกที่อุณหภูมิต่ำกว่าจุดเยือกแข็ง การผสมระหว่างพอลิแลคติก แอซิด กับยางซิลิโคนชนิด 1 องค์ประกอบ ที่มีการเติมผงตัวเติมชนิดทาล์คัม(Talc) ลงไปในอัตราส่วน 40 ส่วนในร้อยส่วนโดยน้ำหนัก สามารถนำไปทดสอบการเป่าขึ้นรูปเป็นฟิล์มได้ ในระดับที่การควบคุมกระบวนการเป่าฟิล์มกระทำได้ยาก แต่สามารถเป่าขึ้นรูปได้

สาขาวิชา วิศวกรรมพอลิเมอร์ ลายมือชื่อนักศึกษา อภิชาติ
ปีการศึกษา 2554 ลายมือชื่ออาจารย์ที่ปรึกษา

APICHART KHIANSANOI : POLYLACTIC ACID COMPOUNDING FOR SUB ZERO TEMPERATURE APPLICATIONS. THESIS ADVISOR : ASST. PROF. UTAI MEEKUM, Ph.D., 169 PP.

POLY(LACTIC ACID)/ LOW TEMPERATURE IMPACT STRENGTH/ SILICONE RUBBER/ TALC/ MECHANICAL PROPERTIES/ BIODEGRADABILITY

The blends between PLA with two and single component silicone rubbers were studied, respectively. Statistical, 2^K factorial DOE, results showed that the silicone was positively and significantly improved the fracture toughness, at room and sub zero temperature, of the PLA and two components silicone rubber blend having silane as coupling agent and polyester polyols as plasticizer. Further refinement indicated that the blend manifested better overall properties at 8.0 phr of the silicone rubber content. The tensile properties of the PLA/silicone rubber blend were enhanced by adding not more than 0.4 phr of TETA. The initial observation revealed that the PLA/silicone rubber blend can be biologically degraded within four weeks.

The blend between PLA and single component silicone rubber at 8.0 phr of the silicone rubber fraction showed adequate properties, especially impact strength at sub zero temperature, when compare with LDPE blow film grade. The PLA/silicone rubber blend having 40 phr of talc filler was chosen to perform the blown film process. It was observed that blown film process was feasible with great difficulty to control the stability of the film bubble.

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SYMBOLS AND ABBREVIATIONS

% = Percent

^{o}C = Degree Celsius

µm = Micrometer

T_g = Glass transition temperature

phr = Part per hundred of resin

rpm = Revolution per minute

hrs = Hours

min = Minute

wt/wt = Weight by weight

kg_f = Kilo gram force

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 background

Starch fermentation provides an abundant supply of lactic acid. Polymerization of lactic acid via ring opening of lactide resulting poly(lactic acid) (PLA) which is biodegradable thermoplastic polyester in nature. The polymer shows excellent functional properties comparable to many petroleum based plastics. PLA polymer is made into useful items using commercial fabrication processes, such as injection molding and extrusion. PLA is becoming increasingly popular. PLA has high mechanical strength, thermal plasticity, biodegradability, and biocompatibility. It has been proposed as a renewable, degradable plastic for uses in service ware, grocery, waste and composting bags, mulch films. However, the typical problems of PLA are the mechanical brittleness and difficult to processing.

1.1.1 Poly(lactic acid) (PLA)

PLA is eco-friendly, apart from being derived from renewable resources (e.g., corn, wheat, or rice). It is biodegradable, recyclable, and compostable. Its path way of production also consumes carbon dioxide. These sustainability and eco-friendly characteristics make PLA an attractive biopolymer. Biocompatibility is the most attractive aspect of PLA especially with respect to biomedical applications. A biocompatible material should not produce toxic or carcinogenic effects in local tissues. There has no report on those issues for PLA. In term of process ability, PLA has better thermal processibility compared to other biopolymers such as poly(hydroxyl alkanoates) (PHAs), poly(ethyele glycol) (PEG), poly(ε-caprolactone) (PCL), etc. It can be processed by injection molding, film extrusion, blow molding, thermoforming, fiber spinning, and film forming. Energy savings, PLA requires 25-55% less energy to produce than petroleum-based polymers. Lower energy use makes PLA production potentially advantageous with respect to cost as well. However, self lubrication behavior from molten PLA that causing the incomplete fusion via frictional induce melting in screw is one of the main hinders for polymer processor.

1.1.2 PLA incompetency

Poor toughness, PLA is a very brittle material with less than 10% elongation at break. Although, its tensile strength and elastic modulus are comparable to poly(ethylene terephthalate) (PET). The poor toughness limits it used in the applications that need plastic deformation at higher stress levels, e.g., screws and fracture fixation plates. Slow degradation rate, PLA degrades through the hydrolysis of backbone ester groups and the degradation rate depends on the PLA crystallinity, molecular weight, molecular weight distribution, morphology, water diffusion rate into the polymer, and the stereoisomeric content, *d*- and *L*-form. The degradation rate is often considered to be an important selection criterion for biomedical applications.

For improving properties, blending is probably the most extensively used methodology to enhance PLA mechanical properties. PLA has been blended with different plasticizers and polymers, both biodegradable and non-biodegradable, to achieve desired mechanical properties (Rasal, R. M., Janorkar, A. V., and Hirt, D. E., n.d.).

The improvement of mechanical brittleness can be done by adding rubber parts into polymer matrix. Good distribution and dispersion of the small rubber particles in polymer matrix is the basic of brittleness improvement. Based on theories of rubber toughened polymer, the blend morphology and characteristics such as average rubber particles size and content of rubber influence on the final mechanical properties. The phase morphology and mechanical properties of rubber toughened polymers depend on type and content of the rubber (Miles, I. S. and Rostami, S., 1992), the viscosity ratio and the mixing condition (Rauwendaal, C., 1998).

Polymer blends or alloys have been the subject of intense study for a long time. Blending is an attractive method of creating new materials with improvement and flexibility in performance, and better properties than existing polymers. Impact modifiers are key additives for increasing flexibility and impact strength to meet physical property requirements of rigid parts. Some unmodified polymers such as rigid polyvinyl chloride (PVC), polystyrene (PS) or styrene acrylonitrile (SAN) are brittle at ambient temperatures. But their toughness are increased when blending with rubber and/or toughener polymer(s). Others such as polyamides or polyolefins are ductile at ambient temperature but become brittle at low temperatures. Some, such as polycarbonate (PC), may have good dart impact but poor notch impact resistance. An impact modifier is needed whenever the polymer system does not meet the impact requirements for a particular application. A variety of impact modifiers are available depending on the host polymer and the required properties.

1.2 Polymer in packaging industries

For a long time polymers have supplied most of common packaging materials because they present several desired features like softness, lightness and transparency.

However, increased use of synthetic packaging films has led to serious ecological problems due to their totally non-biodegradability. Although their complete replacement with eco-friendly packaging films is just impossible to achieve, at least for specific applications like food packaging the use of bio-plastics should be the future (Siracusa, V., Rocculi, P., Romani, S., and Rosa, M. D., 2008).

The materials most used for food packaging are the petrochemical-based polymers, due to their availability in large quantities at low cost and favourable functionality characteristics, such as, good tensile and tear strength, good barrier properties to oxygen and heat sealability. However, these materials are totally non-biodegradable, leading to serious ecological problems. As a consequence, the consumer demand has shifted to eco-friendly biodegradable materials, especially from renewable agriculture by-products, food processing industry wastes and low cost natural resources (Alvesa, V., Costa, N., Hilliou, L., Larotonda, F., Gonalves, M., Sereno, A., et al., 2006).

Polymeric materials derived from renewable resources can be biodegradable or compostable under specific environmental conditions. They are classified according to the method of production or their source, first, polymers directly extracted or removed from biomass such as polysaccharides and proteins. Second, polymers produced by classical chemical synthesis starting from renewable bio-based monomers such as PLA. The last, polymers produced by micro-organisms or genetically modified bacteria such as polyhydroxyalkanoates, bacterial cellulose. In order to tailor physico-chemical properties of plastics obtained from renewable resources to meet specific processing requirements, functional and structural demands, several types of chemicals and additives, such as stabilizers, antioxidant, plasticizers, fillers and processing aids, are added to the polymeric macromolecules. Moreover, with the aim to expand the range of applications of these products, blends, composites and laminates have been developed by combining polymers obtained from renewable sources with other synthetic polymers (Mensitieri, G., Di Maio, E., Buonocore, G. G., Nedi, I., Oliviero, M., Sansone, L., et al., n.d.).

1.3 Research objectives

The main research directions of this present work include;

(1) To study the blend of PLA and silicone rubbers especially at low temperature properties.

(2) To investigate the possibility of applying the PLA/Silicones blends for low temperature food packaging.

1.4 Scope and limitation of the study

The main study of this research was to produce PLA/silicone blends for low temperature food packaging applications especially in film aspect. Statistical approach by mean of design of experiment (DOE) was pursued. The 2^k factorial method was applied. The effect of silicone, silane, and polyester polyol quantity are the main interest parameters for PLA/silicone blends. The mechanical properties include tensile and impact tests were conducted. Heat deflection temperature (HDT), rheological, morphological investigation were also resolved. The results of those tests were used as both DOE respond and experimental evaluation.

CHAPTER II

LITERATURE REVIEW

2.1 General background

A polymer blend is compounding at least two polymers together and resulting difference material. It is normally and quickly used to design new polymeric material. It creates material with different physical properties. Polymer blends can be classified into miscible or immiscible blend by mean of phase morphology. On the other hand, compatible and incompatible blends are classified by their performance in engineering sense. Blending polymers and innovating better material, normally mechanical ones, it is called compatible blend. Vice versa, it is incompatible blends. Not only polymers are needed for blending but also other ingredients such as compatibilizers or processing aids are normally added during melt mixing process.

In this chapter, the reviewed of previous works that related to the polymer blends, especially on PLA matrix, are briefly discussed.

2.2 Impact modifiers

Improving the impact strength of compounds by thoughener or impact modifier is one of the important groups of additives. They compensate for inherent brittleness, or embrittlement occurring at sub zero temperatures, notch sensitivity and crack propagation. The mechanism normally involves introducing a component that is elastomeric or rubbery in nature, which can absorb the energy of an impact or dissipate it. The dispersed rubber phase acts to absorb or dissipate the energy of impact in order to stop craze or crack propagation. In order to stop craze propagation and achieve good impact modification, the rubbery phase must be very well dispersed and the impact modifier must be compatible with the host polymer. Good adhesion was necessary to prevent the cracks from propagating around the elastomeric particle. The rubber particle should also have enough cohesive strength to prevent the crack from propagating easily through the rubber particle. To maintain impact at low temperature, the glass transition temperature (T_g) of the impact modifier should be very low. Impact modifiers are sometimes incorporated through polymerization in the reactor, such as grafting of styrene and acrylonitrile on polybutadiene rubber in the bulk ABS process. Impact modifiers may also be incorporated as additives in the compounding step. In some cases, the impact modifier and host polymer are naturally compatible such as ethylene propylene diene terpolymer (EPDM) impact modifiers in polypropylene (PP) blends. Often, chemical modification is required to compatibilizer the two polymers and allow good dispersion and cohesion with the continuous phase. Table 2.1 shows some of the common impact modifiers that was reported by Markarian, J. (2004).

Table 2.1 Some of the common impact modifiers

Impact modifier	**Host polymer**
ABS	PVC
ASA	PVC

Abreu, F. O. M. S., Forte, M. M. C., and Liberman, S. A. (2005) studied the blends of PP and thermoplastic elastomers (TPE), namely styrene-butadiene-styrene

(SBS) and styrene-ethylene/1-butene-styrene block copolymers (SEBS), to evaluate the effectiveness of the TPE as an impact modifier for PP and influence of the TPE concentration on the blends properties. Homo-PP and ethylene-propylene random copolymer were evaluated as the matrix. They found that TPEs had a nucleating effect that caused the PP crystallization temperature to increase, with SBS being more effective than SEBS. Microstructure characterization tests showed that in most cases PP/SEBS blends showed the smallest rubber droplets regardless of the matrix used. A similar behavior on tensile properties and flexural modulus were observed in both PP/TPE blends. Yield stress and tensile strength decreased and elongation at break increased by expanding the dispersed elastomeric phase in the PP matrix.

Tang, J., Tang, W., Yuan, H., and Jin, R. (n.d.) reported that blends of random copolymer PP with a novel impact modifier, namely ethylene/styrene inter polymer (ESI), They evaluated the effectiveness of ESI in toughening of random PP and the influence of ESI content on the mechanical, thermal, and rheological properties of the blends. They found that super-toughened PP/ESI blends were readily achieved with only 5% wt of ESI. The blends exhibited significant improvement in both impact strength and elongation, while small loss in tensile strength and elastic modulus when increasing ESI content. Rheology study indicated that both PP matrix and PP/ESI blends presented shear thinning behaviors during melt processing.

Lazzeri, A., Zebarjad, S. M., Pracella, M., Cavalier, K., and Rosa, R. (2005) published the compounding of the precipitated $CaCO_3$ (PCC) with High Density Polyethylene (HDPE) in twin screw mixer. The influenced of surface treatment of the particles, with and without stearic acid (SA) as processing aids, also studied. They found that addition of calcium carbonate at 10% by volume to HDPE, Young's modulus and yield stress of the composites was increased and it accompanied by a sharp drop in impact strength. The addition of SA, both Young's modulus and yield stress of the composites compared to the PCC composites without SA was slightly decreased, while the impact strength progressively increased.

Jang, J., and Lee, D. K. (2003) investigated the melting and crystallization behavior of polyvinyl alcohol (PVA) as a function of glycerin plasticizer contents. They found the melting temperature (T_m) of PVA decreased with increasing the amount of glycerine. The effect of a plasticizer rapidly diminished when the phase separation of glycerin in PVA occurred. In addition, the crystallization peak temperature (T_c) of a fully hydrolysed PVA was reduced. The thermal history did not affect the crystallization behavior of a fully hydrolysed PVA, but largely affected that of a partially hydrolysed PVA. In fully hydrolysed PVA and partially hydrolysed PVA blend systems, two T_m peaks appeared, and the concurrent crystallization occurred.

2.3 Toughness improvement of polymers

2.3.1 Commodity polymers

Ahn, Y. C., and Paul, D. R. (2006) investigated the rubber toughening of nylon 6 nanocomposites prepared from an organoclay. They found that rubber particles appropriately dispersed within neat nylon 6 matrix and increased toughness via cavitation which relieves the triaxial stress and allowed the nylon 6 matrix to shear yield and thereby dissipate more energy. Cha, Y. J., Lee, C. H., and Choe, S. (1998) studied phase morphology and mechanical properties of the blends of Nylon 6 with scrap poly(vinyl butyral) (PVB) film and poly[styrene-block-(ethylene-co-butene)-

block-styrene] (SEBS). They found the average particle sizes in all over the blend compositions for Nylon 6/PVB were slightly increased with PVB content, but the dispersed phase is tightly adhered to the matrix phase, with PVB content in the range of 20-35% by weight of PVB. Elongation at break and notched Izod impact strength of all the blends were enhanced, which implies good interfacial adhesion. The rubberlike PVB film adhering to the Nylon 6 phase was the role of an improved impact strength and toughness. In particular, the optimum PVB content for the best impact strength is found to be in the vicinity of 20-35%, and this composition exhibits better moisture resistance than the other blend compositions. All of the blends up to 35% PVB show higher mechanical properties than those of Nylon 6 blended with conventional impact modifier SEBS. Thus, plasticized PVB film, which is recycled from the process of automobile safety glasses, is applicable as an impact modifier or a toughening agent of Nylon 6.

Phinyocheep, P., Saelao, J., and Buzare • , J. Y. (2007) studied the melt blending of poly(ethylene terephthalate) (PET) and natural rubber (NR) in twin screw extruder. They reported that increased toughness of the PET/NR blend with increasing the amount of NR. The impact strength of the PET/NR at 80/20 blend was increased up to seven fold when compared to that of pure PET. This should come from the interaction between the carbonyl group of PET with the abnormal groups such as hydroxyl function in NR, resulting in improving the compatibility of the studied blends, hence increasing the toughness.

Kilwon, C., JaeHo, Y., and Chan Eon, P. (1998) explored the toughening behavior of rubber toughened PMMA enables us to recognize the effect of the particle size in different fracture tests. They published that in the case of the impact test, maximum impact strength was obtained around a rubber particle size of 0.25 µm, regardless of the rubber phase contents. The blends containing 0.15 or 2 µm panicles showed only a slight improvement in impact strength. On the other hand, by the three points bending test, the blends containing the 2 µm particles showed quite a large improvement in fracture toughness.

Ochi, M., and Shimaoka, S. (1999) researched on the toughness of silicone-modified epoxy resin. Aramid silicone block copolymer was used as a compatibilizer. Fine silicone phases could be uniformly and stably dispersed in epoxy matrix by the addition of the block copolymer grafted with epoxy oligomers. The block copolymer that acts as a good compatibilizer was mainly concentrated in an interfacial area around the silicone phase. The thickness of the interphase depended on the architecture of the block copolymer and decreased with an increase in the chain length of the epoxy segment.

Epoxy resin blended with silicone rubber particles was published by Miwa, M., Takeno, A., Hara, K., and Watanabe, A. (1995). The dependency of the volume fraction of rubber particles and temperature of the Young's modulus and tensile strength of particulate blends was investigated. They found at all temperatures, both the Young's modulus and tensile strength decreased as the volume fraction of silicone rubber particles increased, with the decrease becoming more obviously seen with the falling temperature. These decreasing tendencies were estimated using various previously proposed equations. Furthermore, the volume fraction and temperature superposition held for the Young's modulus and tensile strength of the blends. The shift of volume fraction of silicone rubber particles was required to obtain master curves for the Young's modulus and tensile strength. A volume fraction of silicone rubber particles of 5-10% appears to be the most suitable for obtaining a blend in which the decrease in Young's modulus and the tensile strength.

Yanagase, A., and Ito, M. (2004) worked on silicone based impact modifiers. The modifiers were composed of silicone/acrylic rubber cores and grafted acrylic shells. The silicone emulsion that was used to produce the silicone based impact modifiers was prepared via two routes: emulsion polymerization and bulk polymerization of octamethyltetracyclosiloxane. The silicone based impact modifiers were blended with engineering resins such as PVC, polycarbonate (PC), poly(butylenes terephthalate) (PBT), and PC/PBT alloy. The impact strength under standard conditions and after weathering test conditions for the blends of the silicone-based impact modifiers were investigated with respect to two commercially available acrylic and methyl methacrylate/butadiene/styrene impact modifiers. The results showed good weather ability and good toughness under low temperature conditions for the silicone based impact modifiers. Kim, S.-R., and Kim, D.-J. (2008) also investigated the PC/silicone oil blended, two types of silicone oil, poly(dimethyldiphenyl siloxane) (PDMDPS) and poly(dimethyl siloxane) (PDMS), were added to polycarbonate (PC), and the morphological, mechanical, rheological, and thermal changes of the PC/silicone oil were investigated. SEM showed that the dispersed droplets of the silicone oils in the PC matrix and the size of the dispersed phases were enlarged with increasing amounts of silicone oil. A transition from brittle to ductile failure was observed with increasing PDMDPS. The impact strength of neat PC at -30°C was 8.0 kg$_f$ cm/cm, which increase to 52 kg$_f$ cm/cm with the addition of PDMDPS. It appeared that, at low temperature, the phenyl group in PDMDPS was more effective for toughening. The blending of PC with PDMDPS provided a practical way to develop a combination of high tensile strength and impact strength at a low temperature with applicable comprehensive properties.

Further, Zhou, W., and Osby, J. (n.d.) studied the PC/PDMS blends prepared by reactive blending of polycarbonate and hydroxyl terminated polydimethylsiloxane of ultrahigh molecular. By properly tuning the molecular weight of polycarbonate, a remarkable improvement in low temperature impact toughness was found with just about 5 wt% of PDMS incorporation. They found that the blend was able to maintain its superior impact toughness from room temperature down to as low as -40°C with essentially no reduction in noticed Izod toughness at low temperature. The extremely low glass transition temperature of PDMS plus a well dispersed morphology in the matrix polycarbonate is suspected to have a very effective impact modification to the base polycarbonate material, which lowers the ductile-to-brittle transition temperature. Cheah, K., and Cook, W. D. (2003) also attempted blending bisphenol-A polycarbonate include polycarbonate high molecular weight linear, high molecular weight branched and low molecular weight linear and their blends for impact measurements. They found that the dart impact energy showed only the low molecular weight polymer underwent a brittle to ductile transition at -30°C and all the blends were toughed at room temperature. The enhanced stress triaxiality inherent in the notched Izod test and caused the impact strength at room temperature to decrease almost linearly with blend composition.

The mechanical properties of rubber modified HDPE was studied by Bartczak, Z., Argon, A. S., Cohen, R. E., and Weinberg, M. (1999). The rubbers were either ethylene propylene copolymers (EPDM) or ethylene octene copolymers (EOR) and blended into HDPE at volume fractions up to 0.22. They found the notched toughness of the rubber-modified HDPE increases by more than 16 folds.

Chiu, H. T., and Chuang, C. Y. (n.d.) studied polyamide blends with TPU (thermoplastic polyurethane) and POE-g-MA (maleic anhydride grafted polyethylene- octene elastomer). The impact strength and the viscosity of PA blended with two elastomers were investigated. They found that POE-g-MA improved the low viscosity of PA and TPU during the blending process, and also their compatibility. Thus, the 80PA/20TPU/20POE-g-MA blend had better tensile stress and elongation than 80PA/ 20TPU blend, and furthermore POE-g-MA significantly improved the impact strength of PA, even to super toughness grade.

In thermoset systems, Mazali, C. A. I., and Felisberti, M. I. (2006) investigated silicone based additives as modifiers for vinyl ester resin. The additives were fine powders made up of about 50 wt % polydimethylsiloxane and 50 wt % silica. They found the flexural modulus of composites containing 5 wt % additive was lower than that for the cured resin. The impact resistance of the composites also depended on the curing conditions but not on the composition or size of the particle of the additive. The fractured morphologies of specimens subjected to impact resistance tests were different for samples cured in the presence or in the absence of DMA, which suggested that it influenced the mechanism of network formation.

2.3.2 Biodegradable polymers

Yuan, Y., and Ruckenstein, E. (1998) explored the toughened polylactic acid (PLA) by 5 wt% of a poly(e-caprolactone) (PCL) diol and triol based polyurethane (PU) network. The extent of crosslinking of the PU was varied by changing the ratio between diol and triol. The effects of the PU content and its crosslink density on the mechanical properties and the toughness of PU/PLA blends were investigated. A maximum toughness of PLA can be achieved by introducing 5 wt% of a properly crosslinked polyurethane network. The toughness of 18 MJ/m^3 was an order of magnitude higher than that of pure PLA. Lower toughness was occur when the polyurethane was linear or overly crosslinked. Hashima, K., Nishitsuji, S., and Inoue, T. (n.d.) circulated the toughened PLA by SEBS with the aid of reactive compatibilizer EGMA. The aging resistance and HDT were improved by incorporating PC. Properties of the high performance PLA alloy were shown that the high performance was maintained after the annealing at high temperature and it did not depend on the molding temperature; i.e., the high temperature molding, 80°C, was not required for the PLA alloy. The outstanding ductile nature seemed to come from the negative pressure effect of SEBS that dilated the PLA/PC matrix to enhance the local segment motions.

The mechanical, morphological and thermal properties of PLA and LLDPE toughened PLA nanocomposites were investigated by Balakrishnan, H., Hassan, A., Wahit, M. U., Yussuf, A. A., and Razak, S. B. A. (n.d.). The objective of the study was to develop a novel toughened PLA nanocomposite. The LLDPE toughened PLA nanocomposites consisted of PLA/LLDPE blends at the composition of 100/0 and 90/10 with MMT content of 2 phr and 4 phr were prepared. The Young's and flexural modulus improved with increasing content of MMT indicating that MMT effectively increased the stiffness of LLDPE toughened PLA nanocomposite even at low content. LLDPE also improved the impact strength of PLA nanocomposites with a sacrifice of tensile and flexural strength. The tensile and flexural strength was decreased with increasing content of MMT in PLA/LLDPE nanocomposites. The impact strength and elongation at break of LLDPE toughened PLA nanocomposites also declined steadily with increasing loadings of MMT. The crystallization temperature and glass transition temperature dropped gradually while the thermal stability of PLA improved with addition of MMT in PLA/LLDPE nanocomposites. The storage modulus of PLA/LLDPE nanocomposites below glass transition temperature increased with increasing content of MMT. X-ray diffraction and transmission electron microscope studies revealed that an intercalated LLDPE toughened PLA nanocomposite was successfully prepared at 2 phr MMT content.

Chen, B.-K., Shen, C.-H., Chen, S.-C., and Chen, A. F. (n.d.) revealed the improvement of the flexibility and strength of PLA. Urethane structure polymer materials were prepared. PLA was reacted with a small amount of methacryloyloxyethyl isocyanate (MOI) to obtain a ductile PLA with markedly improved mechanical properties. It was found that elongation at break increased by 20 times when compared to neat PLA. Impact resistance, notched, improved 1.6 times. Thus, this modified PLA biodegradable polymer might have greater applications as a biomedical material with increased mechanical properties.

Afrifah, K. A., and Matuana, L. M. (n.d.) studied ethylene/acrylate copolymer in toughening of the semicrystalline and amorphous PLA through melt blending. The ethylene/acrylate impact modifier effectively improved the impact strength of the blends, regardless of the PLA type. The blends showed the decreasing in tensile strength and modulus with increasing the impact modifier content. In contrast, the ductility and elongation at break increased significantly. The relatively low temperature obtained for the PLA blends renders the ethylene/acrylate copolymer impact modifier, a desirable additive, to toughen PLA for use in cold temperatures.

2.4 Crosslinking of polymers

There are several methods to improve the properties of polymers especially the chemical properties such as solvent resistance. One of the well known procedures is chain crosslinking. There several publications reported on the networking reactions of commercial polymers. The selected papers are summarized and categorized in this section.

2.4.1 Radiation crosslink

Jia, Z., Zhang, K., Tan, J., Han, C., Dong, L., and Yang, Y. (2009) enhanced the stability of plasticized poly(L-lactic acid) (PLLA) with poly(ethylene glycol) (PEG) by γ-ray crosslink process. In their study, plasticized PLLA (PLLA/PEG 80/20 wt/wt) was crosslinked under Co^{60} γ-ray in the presence of triallyl isocyanurate (TAIC) as crosslinking agent. They found that the mechanical properties of the plasticized PLLA were strengthened through networking formation. Both yield strength and elastic modulus of the samples increased after the 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 retained after suitable crosslinking.

Pure poly(viny1 alcohol) (PVA) films and five PVA films doped with $(CH_3COO)_2Pb.3H_2O$ was investigated by Sharaf, F., El-Eraki, M. H. I., El-Gohary, A. R., and Ahmed, F. M. A. (1995). The optical and mechanical properties before and after irradiation by γ-rays. They found before the irradiation that the refractive index, the band tail width and the tensile strength increased while the optical gap decreased as the concentration of lead acetate was increased. After irradiation, these optical and mechanical properties exhibit the cyclic effects.

Planes, E., Chazeau, L., Vigier, G., and Fournier, J. (2009) worked on the ethylene propylene diene monomer (EPDM) elastomers with different crosslink densities in order to evaluate the influence of gamma irradiation on their properties. They concluded that in the case of a major phenomenon of chain scissions, the consequences were a decrease in the modulus and also a decrease in the strain at break. The decreased in the strain at break was opposite to what was expected for materials with increasing in average chain length between crosslinks. Using the calculations, a novel interpretation of the ultimate properties of the elastomer as a function of its architecture was proposed.

Hill, D. J. T., O'Donnell, J. H., Perera, M. C. S., and Pomery, P. J. (1995) presented the effect of high energy radiation on halogenated butyl rubbers using electron spin resonance and nuclear magnetic resonance spectroscopies and gas chromatography. They found that during high energy irradiation most of the radicals were found to be generated on the halogenated isoprene units. A higher radiation yield for chain scission was observed in chlorinated butyl rubber than in brominated butyl rubber. This was due to the ready abstraction of hydrogen from the main chain by the chlorine radicals to give main chain radicals which were known to contribute to scission in butyl rubbers. However, in both polymers, crosslinking predominates over scission up to a limiting dose.

2.4.2 Chemical crosslink

Improve the thermal stability and mechanical properties of PLA by crosslinking via chemical treatment of the melt by adding small amounts of crosslinking agent triallyl isocyanurate (TAIC) and dicumyl peroxide (DCP) published by Yang, S. l., Wu, Z. H., Yang, W., and Yang, M. B. (2008). A series of crosslinked PLA materials with different gel fraction and crosslink density were prepared. Crosslinking structures can be effectively introduced into PLA by the initiation of DCP in the presence of a small amount of crosslinking agent (TAIC). They found that the thermal and mechanical properties of chemically crosslinked PLA had been mainly determined by the gel fraction and crosslinked density. With the introduction of crosslinking structure, the tensile strength was improved. The T_m shifted to lower temperature and the thermal stability was improved. Crosslinking was also responsible for the improved tensile modulus and tensile strength.

Han, C., Bian, J., Liu, H., Han, L., Wang, S., Dong, L., et al. (n.d.) explored a silane-grafting water-crosslinking approach to develop the crosslinked poly(*L*-lactide) (XPLLA) 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. Gel fractions were evaluated in order to calculate the crosslinking reaction kinetics and crosslinking density. Various techniques were used to investigate the effect of silane water crosslinking on the thermo mechanical properties, hydrolysis resistance and biodegradation of PLLA. Thermal stability and mechanical properties, hydrolysis resistance was significantly enhanced as a result of silane water crosslinking of PLLA. Moreover, the biodegradation of silane water crosslinked PLLA was retarded compared with neat PLLA.

Polylactic acid (PLA) blend with Polycaprolactone (PCL) was studied by Semba, T., Kitagawa, K., Ishiaku, U. S., and Hamada, H. (2006). Dicumyl peroxide (DCP) was added into the blend system to improve its ultimate tensile strain.

They found that the value of ultimate tensile strain peaked at low DCP concentration. The samples at low DCP contents show yield point and ductile behavior under tensile test. The impact strength of the optimum composition was 2.5 times superior to neat PLA, and ductile behavior such as plastic deformation was observed at its fracture surface.

Bengtsson, M., Oksman, K., and Stark, N. M. (2006) reported that silane crosslinked wood polyethylene composites produced by reactive extrusion and subsequently manufactured into rectangular profiles. The silane crosslinked composites were stored in a sauna at 90°C to increase the degree of crosslinking. Toughness of the silane crosslinked composites was significantly higher than for the non-crosslinked composites. Improved adhesion between the wood and polyethylene phases was most likely the reason for the improved toughness of the crosslinked composites. There was no significant difference in flexural modulus between the crosslinked and non-crosslinked composites. In addition, impact test showed that the impact strength of the crosslinked composites was considerable higher than the non-crosslinked. The effect of temperature on the impact strength of the composites indicated slightly higher impact strength at -30°C than at 0° and at 25°C, and then an increase in impact strength at 60°C. Moreover, scanning electron microscopy on the fracture surface of the crosslinked composites revealed good adhesion between the polyethylene and wood phases.

Kamphunthong, W., and Sirisinha, K. (n.d.) researched on silane crosslink of ethylene octene copolymer (EOC) together with the addition of particular filler to improve the thermal and mechanical properties. The effects of filler surface characteristics on siloxane network structure developed and final properties of the crosslinked products were discussed. The decomposition temperature of EOC increased in more than 50°C after modification. Only crosslinked composites were able to withstand the high temperature environment of aging test which was beyond the melting temperature of the matrix polymer. The crosslinked composites filled with calcium carbonate show superior properties to those with silica, due to a higher crosslink density and tighter network structure formed. However, an advantageous influence of both silane coupling and crosslink reaction in the silica filled composites was seen to enhanced tensile strength and modulus of the materials.

2.4.3 Hybrid crosslinks

The organic/inorganic hybrid coatings were formulated using multifunctional vinyltrimethoxysilane (VTMS) oligomers and acrylated polyester (AP) that was achieved by He, J., Zhou, L., Soucek, M. D., Wollyung, K. M., and Wesdemiotis, C. (2007). A radical photoinitiator was added to the VTMS/AP formulation and the films were crosslinked via UV radiation. It was found that the tensile and scratch data of VTMS oligomer dramatically increased hardness and scratch resistance. The VTMS oligomer also increased the storage modulus, glass transition temperature, and crosslinked density. The morphology of films and the particle size were observed using atomic force microscopy (AFM). The data indicated that the average silica particle size was~90 nm and the particles were well dispersed in the organic phase. It was postulated that the VTMS oligomer functioned effectively as a hyperbranched crosslinker, surface modifier, and reactive diluent.

Chen, J., Asano, M., Maekawa, Y., and Yoshida, M. (2008) prepared the crosslinked hybrid polymer electrolyte membrane (PEM) with high chemical stability. Silane monomer, namely *p*-styryltrimethoxysilane (StSi), was first grafted into poly(ethylene-*co*-tetrafluoroethylene) (ETFE) film by γ-ray preirradiation. It was found that the proton conductivity of the crosslinked hybrid PEM reached 0.11 S/cm at room temperature, and had better mechanical properties. Proton conductivity higher than 0.11 S/cm was obtained but this hybrid PEM became brittle due to the high degree of grafting and crosslinking. Since an increase in proton conductivity resulted in a decrease in chemical stability and an increase in methanol permeability, there was a trade-off among the proton conductivity, chemical stability, and methanol permeability with respect to application in fuel cells.

From the review of the literatures, there is no scientific work concerning the preparation of PLA compound for low temperature application by any mean. It will be exciting research for exploring the possibility to produce this biopolymer to utilize at the extreme low temperature. Blending with silicone together with silane reactive crosslink will enhance the properties of the compound in order to achieve the research goal.

CHAPTER III

EXPERIMENTAL

3.1 General background

The blends between PLA and silicone rubbers were investigated. Not only the polymer and rubbers were used in compounding but other ingredients such as filler, processing aids and silane coupling agent also employed. The performance testing by mean of tensile, impact test and thermal properties by mean of heat deflection temperature (HDT) were conducted. The descriptions of materials, experimental procedures and samples testing are given in more detail as follows.

3.2 Materials

Table 3.1 summarizes the reagents used and their function in the PLA/Silicone compounding process in this study. The extrusion grade poly(lactic acid) (PLA), 2002D, with a density of 1.24 g/ml was purchased from Nature Works®. The typical physical properties of the polymer reported in the manufactured data sheet are shown in Table 3.2. Two types of silicone were employed for compounding. Silicone I (DC: 732 RTV) and silicone II (SILASTIC(R) 3483). The first one is single component, moisture cured at room temperature silicone. The later was two components rubber system. They were vulcanized at room temperature by using triethylenetetramines (TETA) as amine curing agent. Both silicones were purchased from Dow Corning Corporation. Their cured properties are shown in Table 3.3. The silane, *gamma*-aminopropyltriethoxysilane, Silquest A-1100, APS, manufactured from Crompton

Corporation was individually used as coupling agent. Their properties provided by the supplier are concluded in Table 3.4. High viscous liquid, aliphatic polyester polyol, Rayelast A 8770, available from IRPC Polyol Co., Ltd, was used as processing aid and also as plasticizer in the compounding process. The technical data for this aliphatic polyester polyol is summarized in Table 3.5. Talc, JetFine 3CA , having the average 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 incorperated as heat/processing stabilizer. They were supplied from Ciba Specialty Chemicals Corporation. Properties of the heat/processing stabilizers used in this research work are shown in Tables 3.6-3.7, respectively. Those chemicals described above were used as received.

Table 3.1 The reagents and their function in PLA/silicone compound.

Chemical materials	**Function**
Poly(lactic acid), 2002D	Polymer matrix
Silane: A-1100	Coupling agent
Polyester polyols, Rayelast A 8770	Processing aids and plasticizer
Silicone	Low temperature toughener
Irgafos 168 and Inganox 1076	Heat/processing stabilizer
Talc	Filler
Triethylenetetramines	Silicone curing agent

Table 3.2 The properties of poly(lactic acid), 2002D.

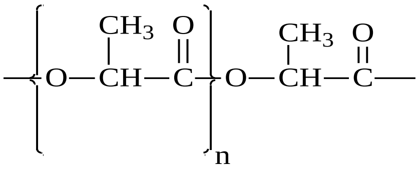
Properties	**Value**
Structure	 $-\left[O-\overset{CH_3}{\overset{\vert}{C}}H-\overset{O}{\overset{\Vert}{C}}\right]_n-O-\overset{CH_3}{\overset{\vert}{C}}H-\overset{O}{\overset{\Vert}{C}}-$
Specific gravity	1.24
Melt index, g/10 min at 190/2.16	4 - 8
Tensile strength at break, psi (MPa)	7,700 (53)
Tensile 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 Properties of silicone rubbers.

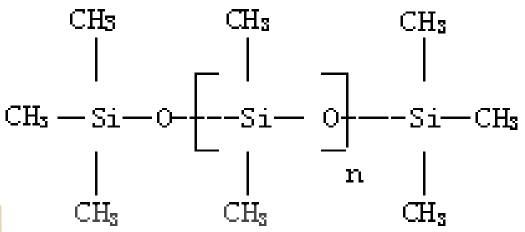
Properties	Unit	Silicone I (DC : 732 RTV)	Silicone II (SILASTIC 3483)
Structure		 $CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$	
Chemical name		Polydimethylsiloxane	Polydimethylsiloxane
Color		White or Clear	White
Mixed viscosity	mPa.s	-	16,000
Working time at 23°C	minutes	20	90 - 120
Specific gravity		1.04	1.15
Hardness (Shore A)		25	13
Tensile strength	MPa	2.3	3.9
Elongation at break	%	540	680
Tear strength	kN/m	-	25

Table 3.4 The properties of *gamma*-Aminopropyltriethoxysilane (Silquest A-1100, APS).

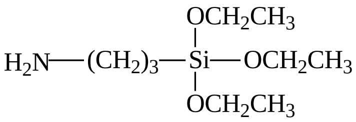
Properties	**A-1100**
Chemical name	*gamma*-aminopropyl triethoxysilane (APS)
Structure	 $H_2N{-}(CH_2)_3{-}\overset{OCH_2CH_3}{\underset{OCH_2CH_3}{Si}}{-}OCH_2CH_3$
Appearance	Clear, colorless
Specific gravity at 25°C	0.95
Flash point (°C)	96
Boiling point (°C)	220

Table 3.5 The properties of Polyester polyol, Rayelast® A 8770.

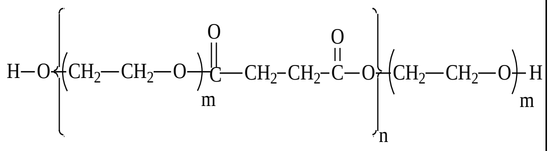
Properties	**Value**
Structure	 $\mathrm{H{-}O{-}\left[(CH_2{-}CH_2{-}O)_m{-}\overset{O}{\overset{\Vert}{C}}{-}CH_2{-}CH_2{-}\overset{O}{\overset{\Vert}{C}}{-}O\right]_n{-}(CH_2{-}CH_2{-}O)_m{-}H}$
Appearance	Light clear yellowise liquid
Viscosity at 60°C, cps	1500 - 1800
Hydroxyl value, mg KOH/g	54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

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

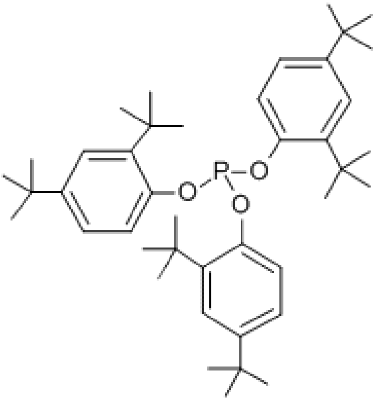
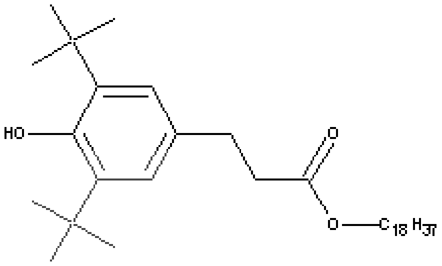
Properties	**Value**
Structure	
Appearance	White powder
Purity	99.0% min
Melting point	183-187°C
Volatility	0.3%
Clarity of solution	Clear
Acid value (mgKOH/g)	0.3% max
Anti-hydrolyze (90°C,water,14hrs)	Qualified
Transmittance	(425nm) 98% min; (500nm) 98%min
Applications	IRGAFOS 168 is a hydrolytically 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.

3.3 Experimental procedures

3.3.1 Specimen preparation

The schematic diagram illustrated in Figure 3.1 is summarized the complete experimental procedure for preparing the PLA/silicone compounding test specimen used in this study. PLA pellets were dehumidified at 80^{o}C for at least 2 hours in the vacuum oven beforehand. It was then premixed with desired amounts of silicone, silane and polyester polyol. The silicone content was in the range 0.5 - 8.0 phr. The silane content was in the range 0.2 - 1.5 phr. The polyol content was in the range 1 - 5 phr. In the PLA/silicone melt blending process, the dried PLA and silicone was premixed by mechanical stirring for 1 min and then the vigorously mixed, by high speed mechanical stirring, liquid mixture between viscous polyol and silane was added and again thoroughly stirred by high speed mixture for at least 1 min. Finally, the fine powder of heat and processing stabilizer was incorporated and again vigorously stirred. In case of talc filler was needed, it was added in this stage. By doing so, the liquid component and fine powder particle (s) was evenly and completely coated onto the polymer pellet.

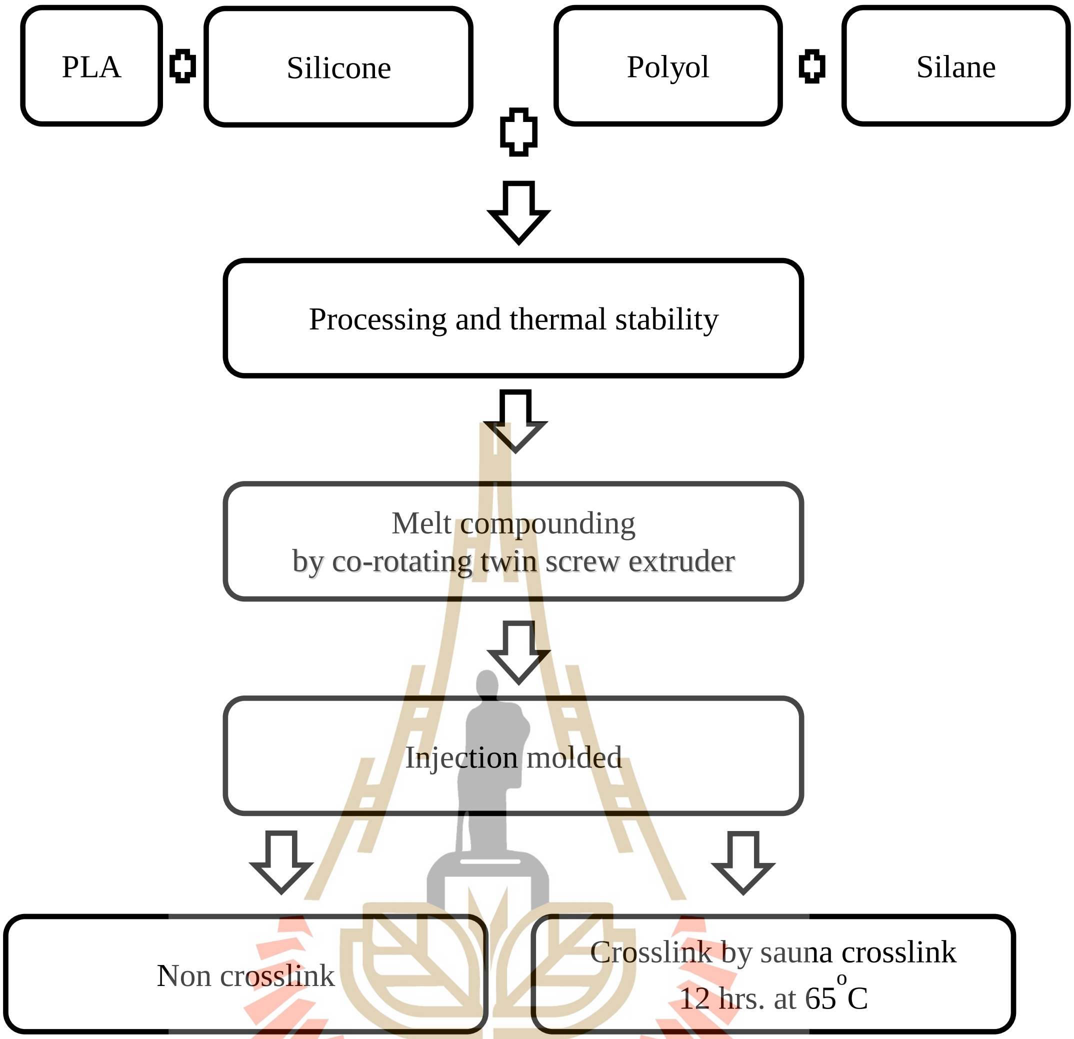


Figure 3.1 Schedule diagram for PLA/silicone compounding.

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 screws are consisted of 3X3 kneader blocks. Screw speed of 25 rpm and temperature profile of 140, 150, 160, 170, 180°C from feed zone to die head zone were constantly and electronically controlled. The extruded strand was allowed to cool down under the atmospheric condition. The compound was granulated by the pelletizer.

PLA/silicone compound and neat PLA pellets were dried in vacuum oven at 80°C for at least 2 hours to remove the excess moisture and molded into test specimen by using injection molding machine (Chuan Lih Fa Model CLF-80T). The barrel temperature was set at 150, 160, 170, 180°C from feed zone to nozzle zone and mold temperature was controlled at 30°C. The mold cycle was approximately 50 seconds.

The molded specimens were equally divided into two sets of sample. The first set was allowed to anneal at room temperature for overnight prior to conduct the testing. This sample was assigned as the original sample. The other was incubated at 65^{o}C in sealed and moisture saturated oven for 12 hrs. The incubation process, or sauna treatment, was conducted in order to accelerate the competition of silane/water crosslink condensation reaction. This type of sample was again assigned as the sauna cured or cured sample.

For manufacturing the PLA/silicone films, film blowing machine (A.R Product Model AH 40) was employed. The barrel temperature ranging from 160, 170, 175, 180°C from feed zone to die zone was constructed. Diameter of the spiral die was 50 mm and the blow up ratio (B/R) at 4 was controlled. The LDPE film also was obtained and used as reference. The tensile testing in both machine direction (MD) and transverse direction (TD) was performed.

3.4 Characterization and testing

3.4.1 Tensile test

For determining the tensile properties of the PLA compound, the standard test, ASTM D638, was followed. The Instron^{TM} universal testing machine, model 5565 with the standard load cell of 5 kN, was used. The constant strain rate of cross head speed was electronically controlled at 50 mm/min. The dimension of dumbbell shaped specimens, type II, of 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 the obtained test values were averaged for each set of sample. The tensile properties comprised of tensile strength, % strain at break, and Young's modulus (E), were reported.

3.4.2 Izod impact test

The impact test samples were prepared by injection molding in the rectangular shaped. The specimens were annealed overnight at room temperature after injected. Vice versa, the sauna cured samples were completed by incubating in moisture saturated oven at 65^{o}C for at least 12 hours. The specimens was machine notched using standard engine lathe notcher with a notch angle of 45° having a radius of 0.25 mm and depth of 2.54 mm. Notched Izod impact strength was analyzed according to ASTM 256 using an Atlas Impact Pendulum testing machine model BPI. The impact pendulum energy of 2.7 J was used for the notched mode impact test. For the unnotched type testing, the specimen was strike with the calibrated impact pendulum of 5.4 J. There were two test conditions for the impact measurement; room and sub zero temperature, respectively. For room temperature testing, the temperature was controlled at approximately 25°C. But at sub zero temperature testing, the sample was immersed in liquid mixture of liquid nitrogen and methyl alcohol for cooling for at least 5 minutes. Then, the sample was quickly and immediately transferred onto the testing equipment and tested. By doing this, the material still chilled at temperature below 0°C. The impact strength (kJ/m^2) is calculated from the failure energy, or absorbed energy, divided by the samples cross section area. Minimum of five specimens was tested for each sample and used for average value. Table 3.8 shows the typical temperature of liquid mixtures that are normally used for cooling purpose.

Table 3.8 Temperature of the common cooling mixtures. (Blatchley and Ronald C., 1997)

Mixture	T (°C)
Cacl$_2$.6 H_2O/ice (1:2.5)	–10
Nacl/ice (1:3)	–20
Carbon tetrachloride/CO_2	–23
Acetonitrile/CO_2	–42
Cacl$_2$.6 H_2O/ice (1:0.8)	–40
Acetone/CO_2	–78
Methanol/N_2	–98
Liquid N_2	–196

3.4.3 Rheological measurement

The rheological properties of PLA/silicone blends by means of melt flow index (MFI) and melt viscosity were performed. Shear viscosity of PLA/silicone blends at shear rate ranging from 10 to 1000 s^{-1} was obtained using a capillary rheometer from Kayeness model D5052M. The compound pellet was dried in a vacuum oven at 80°C for 4 hours before tested. The polymer were melted at 180°C with the melting time of 240 s. The zero shear viscosity (η_o) was calculated using

Power law’s model.

Melt flow index (MFI) of PLA blends were obtained using Kayeness melt flow indexer model 4004 at melting temperature of 180ºC with a load of 2.16 kg. The melt time of 240 s was chosen and at least 3 cuts with the desired cut time were obtained and weighed. The standard MFI unit (g/10 mins) was averaged.

3.4.4 Heat deflection temperature

In according to ASTM D648, Heat deflection temperature (HDT) was examined using Atlas Testing Machine, Model HDV1 at the heating rate of 2±0.2°C/min, rate A. The temperature of liquid silicone heat transfer media was raised from ambient temperature to the observed value. The injected rectangular cross section specimen with approx 127 mm in length, 12.9 mm in depth, and 3.2 mm in width were employed for testing. Three specimens were placed on the three point bending configuration at span length of 100 mm, with the calculated adding weight at the assigned standard load of 0.455 MPa and immersed in the heat transfer media. 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 the average value obtained from 3 tested specimens.

3.4.5 Morphological investigation

The morphology of the fractured surface of the PLA compound specimens taken from notched Izod impact testing were examined by scanning electron microscope (SEM) technique using the JEO SEM model JSM 6400. The fractured surface of specimen was obtained by cutting at the thickness of 5 mm below the fractured surface. It was placed on the sample holder and primed by coating with silver paint. The fractured surface was again thin film coated with gold by ion sputtering for 5 min.

3.4.6 Biodegradability

The biodegradability testing of samples were conducted by using simulated landfill chamber. Within chamber, it was filled with composted soil at 60^{o}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 3.1.

$$\text{Weight loss (\%)} = \frac{(W_0 - Wt)}{W_0} \times 100 \qquad (3.1)$$

where W_0 = Weight of test sample before burial

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

3.5 Analysis of DOE using Design Expert^{TM}

The experimental design on PLA/silicone blends using 2^k factorial experimental design was performed to analyze the significant effect of compound ingredients, or parameters by mean of the statistical point of view, on the properties of PLA/silicone blends. The *k* is the parameters to evaluate effects on the given respond (s). Normally, each parameter is divided into two level; high (+) and low (-). The numbers of experimental trials are equal to 2^k and the design matrix with combination of that parameter and it level is constructed. Table 3.9 given below is an example of the matrix with k = 3 and 8 individual runs are designed.

According to the 2^k factorial approach with k = 3, eight run were designed to evaluating the statistical effects of the recipe composition factor on the given responds. The effect of the factor is define as the change in response produce (Y) by a change in the level of the factor such high (+) and low (-) level. It is called main effect (E_f) and calculated as follow from equation 3.2.

$$E_f = \frac{\Sigma Y_{E+}}{n/2} - \frac{\Sigma Y_{E-}}{n/2} \qquad (3.2)$$

where E_f = main effect of factor

y_{E+} = the responses of high level factor

y_{E-} = the responses of low level factor

Table 3.9 Example of 2^k factorial design matrix with k = 3.

Run	**A**	**B**	**C**	**AB**	**AC**	**BC**	**ABC**	**Response (Y_i)**
1	-	-	-	+	+	+	-	Y_1
2	+	-	-	-	-	+	+	Y_2
3	-	+	-	-	+	-	+	Y_3
4	+	+	-	+	-	-	-	Y_4
5	-	-	+	+	-	-	+	Y_5
6	+	-	+	-	+	-	-	Y_6
7	-	+	+	-	-	+	-	Y_7
8	+	+	+	+	+	+	+	Y_8

Analysis of variance (ANOVA) and regression techniques are useful to determine if there is a statistically significant difference between treatments and levels of variables. After calculating the main effect and interaction effect of factors then graph plotting between normal probability and effect of factor into normal probability plot. The significant effect from the normal plot is again evaluation by ANOVA by statistical mean. In this work the commercial computer software, Design Expert^{TM} version 7, was using to assist the statistical calculation. The level of significant (α) was assigned at 0.05 or 95% confidential. Base on *P*-value from statistical calculation if the calculated *P*-value is less than 0.05, it is implied that statistical model and also the given factor were significant. Finally, the accepted factor derived from ANOVA was used to calculate the predicted regression model for properties of PLA/silicone blends.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Design of experiment 1 : effect of two components silicone, silane and polyester polyol contents

Initially, the effect of two components silicone system as main blending ingredient, silane as coupling agent and polyester polyol as plasticizer contents on the properties of PLA/silicone compound by mean of the statistical approach will be discussed. The MFI, tensile properties, impact strengths and HDT obtained from both original and sauna cured of the compound samples are used as the main design responds. To verify the properties of the blend at sub zero temperatures, only notched impact strength was examined.

Three parameters; silicone (**A**), silane (**B**) and polyester polyol (**C**) contents was erected. Each parameter was divided into two levels; high (+1) and low (-1), respectively. In each level, it was also divided into two sub levels as shown in Table 4.1. For example, silane content at 0.5 and 1.0 phr, corresponded to 100 g of PLA, were assigned as low levels, vice versa 2.0 and 3.0 phr were given as high levels, respectively. According to the rule of design, $2^3 = 8$, eight runs of PLA/silicone compound ingredients were constructed as demonstrated in Table 4.2. The actual mixing batch size was based on 500 g of PLA. The heat and processing stabilizer was constantly added at 1.0 phr into each formula.

Table 4.1 The parameters and levels of the DOE.

Parameters	High level (+)		Low level (-)	
(A) Silicone (phr)	+3.0	+2.0	-1.0	-0.5
(B) Silane (phr)	+1.5	+1.0	-0.5	-0.2
(C) Polyol (phr)	+5.0	+4.0	-2.0	-1.0

Table 4.2 Design matrix and compound formula of PLA/silicone blends.

Run no.	PLA (g)	Silicone (A) (g) (phr)	Silane (B) (g) (phr)	Polyol (C) (g) (phr)	Stabilizer (g) (phr)
1	500	2.5 (-0.5)	2.5 (-0.5)	10 (-2.0)	5 (1)
2	500	5.0 (-1.0)	1.0 (-0.2)	25 (+5.0)	5 (1)
3	500	5.0 (-1.0)	7.5 (+1.5)	5 (-1.0)	5 (1)
4	500	2.5 (-0.5)	5.0 (+1.0)	20 (+4.0)	5 (1)
5	500	10.0 (+2.0)	1.0 (-0.2)	5 (-1.0)	5 (1)
6	500	15.0 (+3.0)	2.5 (-0.5)	25 (+5.0)	5 (1)
7	500	15.0 (+3.0)	5.0 (+1.0)	10 (-2.0)	5 (1)
8	500	10.0 (+2.0)	7.5 (+1.5)	20 (+4.0)	5 (1)

Table 4.3 Rheological and tensile properties for design of experiment.

Runs	**MFI (g/10min)**	**Tensile strength (MPa)**		**Elongation at break (%)**		**Young's modulus (GPa)**	
		Original	**Cured**	**Original**	**Cured**	**Original**	**Cured**
PLA	2.86	52.38±0.93	59.48±1.57	4.33±0.26	4.94±0.42	2.58±8.07	2.67±0.96
1	2.07	43.91±3.26	47.69±5.83	4.49±0.86	6.54±1.12	2.49±0.07	2.33±0.07
2	2.43	38.23±2.18	41.04±2.32	4.39±1.56	8.77±2.32	2.48±0.08	2.21±0.09
3	2.64	38.99±1.36	45.21±2.23	6.05±0.73	9.33±3.35	2.52±0.08	2.43±0.08
4	2.43	37.49±0.87	43.10±2.03	6.97±2.04	8.19±1.58	2.50±0.06	2.23±0.13
5	2.45	34.28±1.08	40.95±2.04	7.56±3.35	16.81±0.78	2.52±0.13	2.48±0.13
6	3.22	29.52±3.77	38.60±2.45	9.17±2.23	12.45±3.18	2.45±0.85	2.31±0.14
7	3.28	31.63±1.33	39.87±1.30	12.92±3.84	12.87±3.24	2.53±0.02	2.39±0.07
8	2.48	34.43±1.82	42.27±0.70	5.11±3.46	9.97±3.28	2.39±0.18	2.38±0.15

Table 4.4 Impact and thermal properties for design of experiment.

Runs	Unnotched impact strength (kJ/m^2)		Notched impact strength (kJ/m^2)		Low temperature notched impact strength (kJ/m^2)		HDT (^oC)	
	Original	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**
PLA	15.97±2.35	21.15±2.41	2.49±0.48	3.45±0.98	2.60±0.62	3.20±0.42	51.67±0.58	52.40±0.72
1	20.33±3.03	22.24±2.09	2.55±0.21	3.25±0.71	5.98±0.68	5.37±0.31	49.27±0.64	59.33±0.58
2	21.54±0.80	23.99±2.91	3.07±0.64	3.05±0.23	3.68±1.06	5.00±0.36	48.07±0.50	57.80±1.64
3	22.02±3.32	23.22±2.06	2.31±0.16	2.96±0.41	4.97±0.81	6.45±0.54	49.33±0.58	57.67±0.58
4	26.02±6.67	28.85±3.75	2.38±0.15	3.44±0.26	4.90±0.91	3.68±0.43	47.93±0.70	60.00±1.00
5	29.75±3.19	32.78±2.66	3.68±0.85	6.34±0.37	6.05±0.60	6.40±0.18	48.53±0.50	57.93±0.31
6	26.02±2.26	36.45±6.85	2.81±0.76	5.68±0.29	6.07±0.68	6.77±0.35	47.33±0.58	58.00±0.40
7	25.35±2.87	30.35±4.27	3.54±0.59	5.93±0.40	5.25±0.93	7.38±0.22	48.52±0.42	60.33±1.15
8	20.64±1.22	26.07±2.49	3.69±0.62	3.93±0.12	5.58±1.21	5.65±0.59	47.80±0.72	58.67±2.31

Tables 4.3 and 4.4 are summarized of the test results of the PLA/Silicone compound derived from the formula given in Table 4.2. General observation, the tested values reveal that the mechanical and thermal properties of the blends samples undergone sauna incubation were obviously higher than the original ones, except the tensile modulus which are lower after incubation. It is emphasized that the silane induced condensation reaction which lead to branched or crosslinked structure had been probably taken place during the brewing process and hence effecting to the test properties. More further information regarding to the existing in the outcome of the silane condensation reaction that lead to non linear chain will be presented later on.

4.1.1 Effect of parameters on MFI of PLA/silicone compounds

Rheological properties by mean of melt flow index, obtained at 180/2.16, of the PLA/silicone blends are summarized in Table 4.5. The MFI of the blends are generally in the range of pure PLA. Taken MFI result into the calculation of the standard effects for the individual parameter and also the interacted parameters by assisting of Design Expert^{TM} and convert the effect into the normal probability values, consequently, plotting of the normal % probability with the calculated standard effects is shown in Figure 4.1. The plot indicates that all the effect values are linearly lined with their probability at 95% of confidential. They are illustrated that the parameters and their levels used probably has no influence on the MFI of the PLA/silicone blends. Moreover, the pareto chart that is plotted between calculated *t*-value of the standard effects and their rank, illustrated in Figure 4.2, also strengthen that the given parameters and their levels have no sign of the significant effect on the melt behavior of the blends because their calculated *t*-values are below the critical value ($t_{crit.}$ = 2.44691). Taken both normal plot and pareto chart, it can state that there are no significantly affects of design parameters and their level of design to the MFI of PLA/silicone compound.

Table 4.5 MFI result of PLA/silicone compounds.

Test	**PLA (phr)**	**Silicone (A) (phr)**	**Silane (B) (phr)**	**Polyol (C) (phr)**	**Stabilizer (phr)**	**MFI at 180/2.16 (g/10 min)**
1	500	0.5 (-)	0.5 (-)	2.0 (-)	1	2.07
2	500	1.0 (-)	0.2 (-)	5.0 (+)	1	2.43
3	500	1.0 (-)	1.5 (+)	1.0 (-)	1	2.64
4	500	0.5 (-)	1.0 (+)	4.0 (+)	1	2.43
5	500	2.0 (+)	0.2 (-)	1.0 (-)	1	2.45
6	500	3.0 (+)	0.5 (-)	5.0 (+)	1	3.22
7	500	3.0 (+)	1.0 (+)	2.0 (-)	1	3.28
8	500	2.0 (+)	1.5 (+)	4.0 (+)	1	2.48

However, to validate the above conclusion, ANOVA testing was also taken into analysis. The figures of the ANOVA result is given in Table 4.6. According to the statistical conclusion, the designed parameters or perhaps levels of design for manufacturing the PLA/silicone compounds are not significantly affected to the MFI of the PLA blends as it is indicated by the calculated *p*-value, 0.1210, of the model more than the critical value, 0.05. Therefore, on parameter even though the silicone content (**A**), has an effect to the flow properties of the polymer.

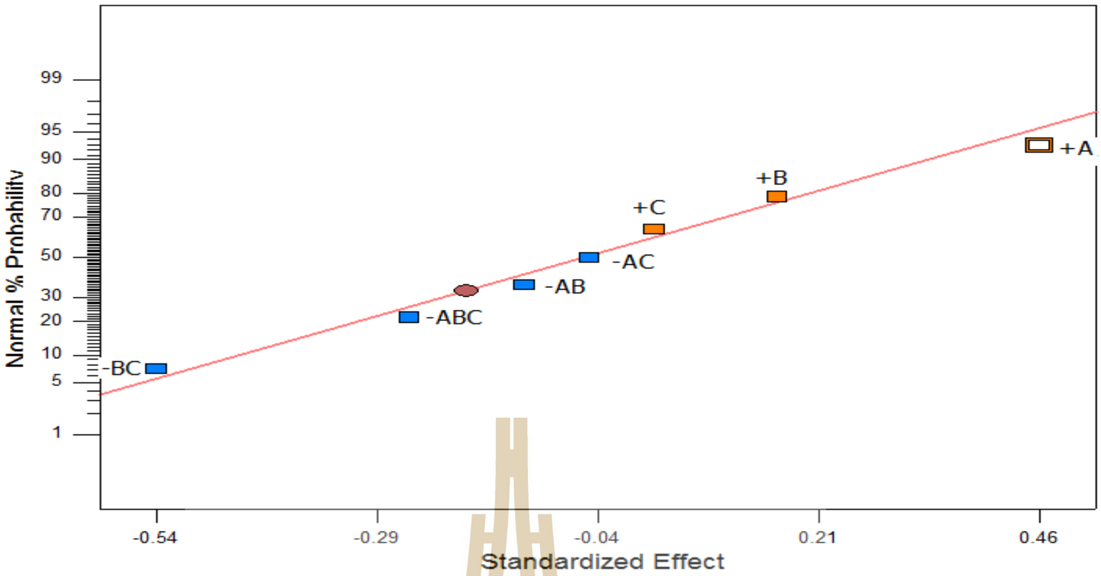


Figure 4.1 Normal probability plot of MFI.

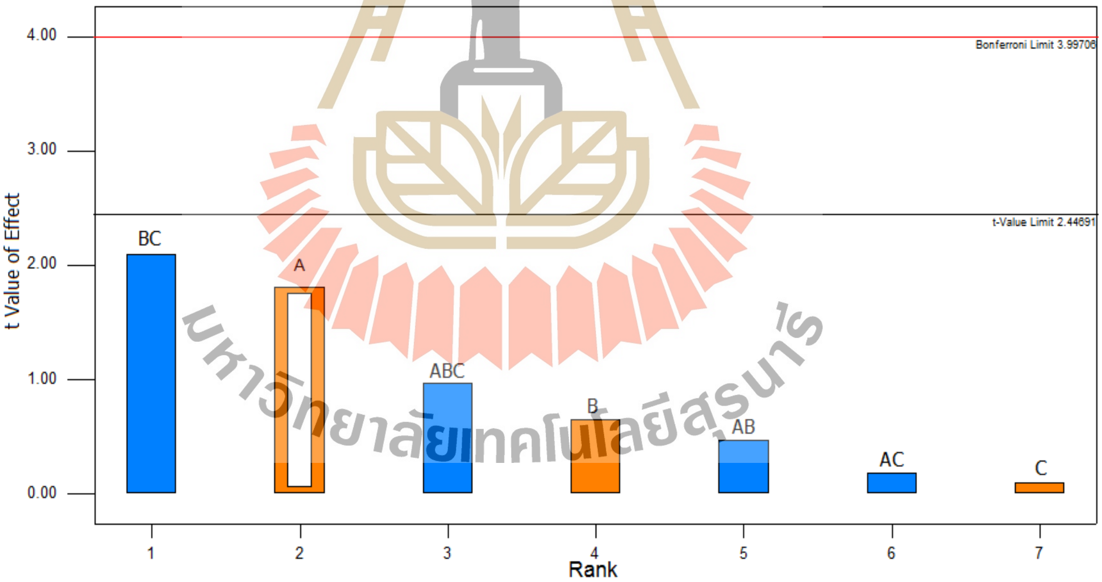


Figure 4.2 Pareto analysis chart of MFI.

Table 4.6 ANOVA conclusion for MFI.

Analysis variance table of MFI						
Source	**Sum of squares**	**df**	**Mean square**	**F value**	***p*-value prob>F**	**Conclusion**
Model	0.4297	1	0.4297	3.2604	0.1210	not significant
A-silicone	0.4297	1	0.4297	3.2604	0.1210	
Residual	0.7907	6	0.1318	-	-	
Cor total	1.2204	7	-	-	-	

4.1.2 Effect of tensile properties of PLA/silicone compounds

Tensile strength, elongation at break and modulus, obtained at constant strain rate of the cross head speed at 50 mm/min are summarized in Table 4.7. General observation, it is seen that the test values obtained from sauna cured sample are slightly higher than the sample without curing. The crosslink network though the silane/water condensation reaction might responsible for the increasing. In other aspect, the increasing in crystallinity and chemical interaction of PLA/silicone matrix while incubation at temperature above the T_g, 65°C, for 12 hours, so temperature above the T_g polymer chain can be vibrates for linking with other chain of polymer via silane crosslink agent.

Taken the tensile strength result into the calculation of the standard effects for the individual parameter and also the interacted parameters by assisting of Design Expert^{TM} and convert the effect into the normal probability values, consequently, plotting of the % normal probability with the calculated standard effects is constructed and shown in Figure 4.3 for original samples. The plot indicates that silicone **(-A)** parameter is out of linearly trend line. It is illustrated that the parameter and its levels, contents, used probably has strongly influenced on the tensile strength of the PLA/silicone blends.

The pareto chart that is plotted between calculated t-value of the standard effects and their ranks, illustrated in Figure 4.4, also given that the parameter and its level has significant effect on the tensile strength of the blends because their calculated *t*-values were above the critical value ($t_{crit.}$ = 2.4469). Taken both normal plot and pareto chart, it can suggest that silicone content has significantly affects on the tensile strength of PLA/silicone compound before sauna cured.

Table 4.7 Tensile result of PLA/silicone compounds.

Test run	Tensile strength (MPa)		Elongation at break (%)		Modulus (GPa)	
	Original	Cured	Original	Cured	Original	Cured
1 (-,-,-)	43.91±3.26	47.69±5.83	4.49±0.86	6.54±1.12	2.49±0.07	2.33±0.07
2 (-,-,+)	38.23±2.18	41.04±2.32	4.39±1.56	8.77±2.32	2.48±0.08	2.21±0.09
3 (-,+,-)	38.99±1.36	45.21±2.23	6.05±0.73	9.33±3.35	2.52±0.08	2.43±0.08
4 (-,+,+)	37.49±0.87	43.10±2.03	6.97±2.04	8.19±1.58	2.50±0.06	2.23±0.13
5 (+,-,-)	34.28±1.08	40.95±2.04	7.56±3.35	16.81±0.78	2.52±0.13	2.48±0.13
6 (+,-,+)	29.52±3.77	38.60±2.45	9.17±2.23	12.45±3.18	2.45±0.05	2.31±0.14
7 (+,+,-)	31.63±1.33	39.87±1.30	12.92±3.84	12.87±3.24	2.53±0.02	2.39±0.07
8 (+,+,+)	34.43±1.82	42.27±0.70	5.11±3.46	9.97±3.28	2.39±0.18	2.38±0.15

To validate the above comment, ANOVA testing was also taken into account. The figures concluded from the ANOVA result is given in Table 4.8. According to the statistical conclusion, the designed parameter and levels of silicone **(-A)** for manufacturing the PLA/silicone compounds are significantly affected to the tensile strength of the PLA blends as it is indicated by the calculated *p*-value, 0.0084, of the model less than the critical value, 0.05. Therefore, silicone content (**A**), has negatively and significantly effect on the tensile strength of the original blends sample.

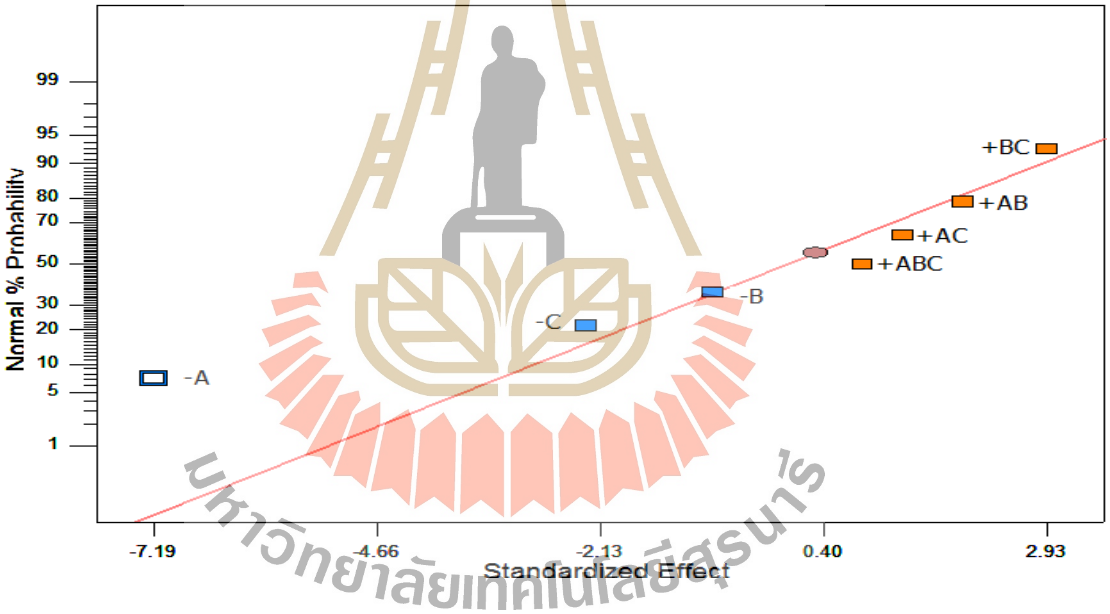


Figure 4.3 Normal probability plot of tensile strength (original).

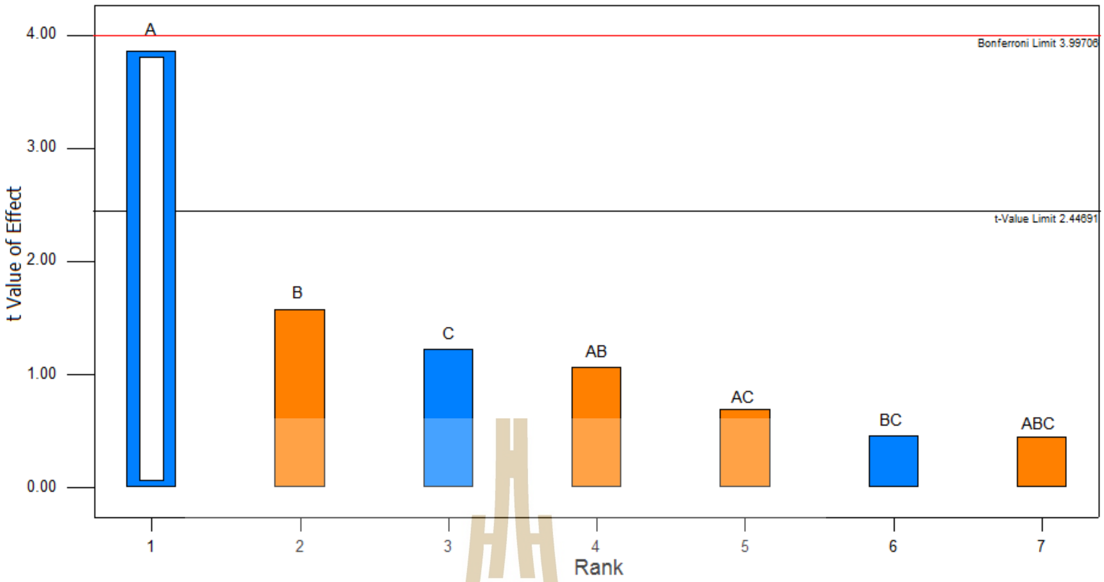


Figure 4.4 Pareto analysis chart of tensile strength (original).

Table 4.8 ANOVA conclusion for tensile strength (original).

Analysis of variance table of tensile strength (original)						
Source	**Sum of squares**	**df**	**Mean square**	**F value**	***p*-value prob>F**	**Conclusion**
Model	103.3922	1	103.3922	14.8443	0.0084	significant
A-silicone	103.3922	1	103.3922	14.8443	0.0084	
Residual	41.7908	6	6.9651	-	-	
Cor total	145.1830	7	-	-	-	

Exact examination for the sample after sauna incubation, the normal plot is illustrated in Figure 4.5. Based on the analyzed result, it is seen that there is no parameter that has the tendency to be the significant effect to the tensile strength of PLA/silicone after sauna curing as all the calculated effect values are lined on the linear trend. It is pointed out that the parameters and their levels used for compounding the PLA/silicone probably have no influence on the tensile strength of the cured samples. Moreover, the pareto chart that as illustrated in Figure 4.6, also strengthen that the given parameters and their levels have no significant effect on the tensile strength of the PLA/silicone cured samples. Again, because their calculated t-values are below the critical value ($t_{\text{crit.}}$ = 2.44691). To confirm this proposition, the ANOVA testing was performed and the test result is summarized in Table 4.9. According to the statistical conclusion, the designed parameters and levels of design parameters for manufacturing the PLA/silicone compounds are not significantly affected to the tensile strength of the PLA blends as it is indicated by the calculated p-value, 0.9822, of the model above the critical value, 0.05.

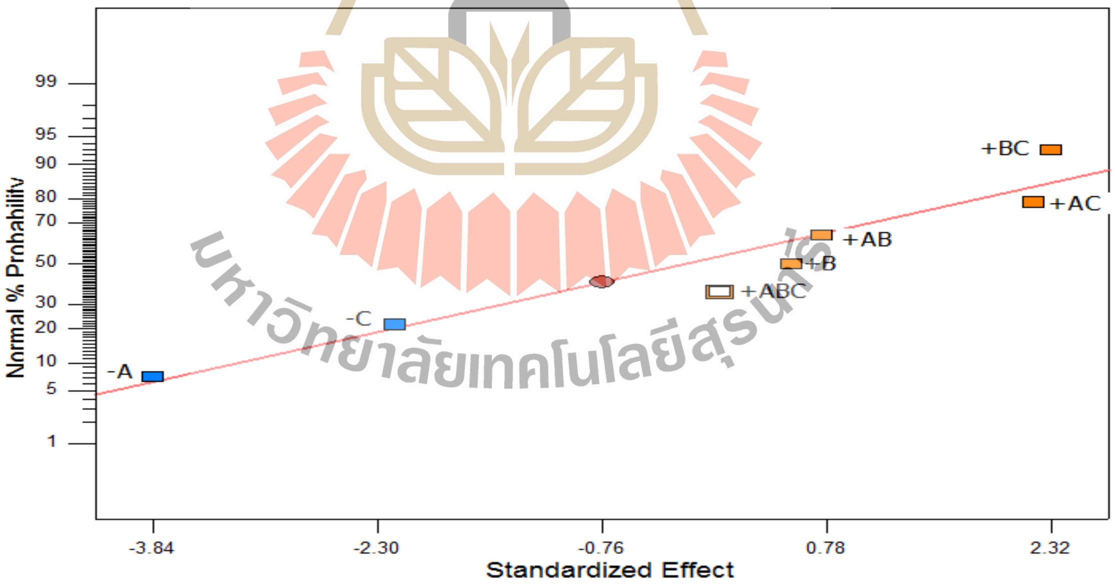


Figure 4.5 Normal probability plot of tensile strength (cured).

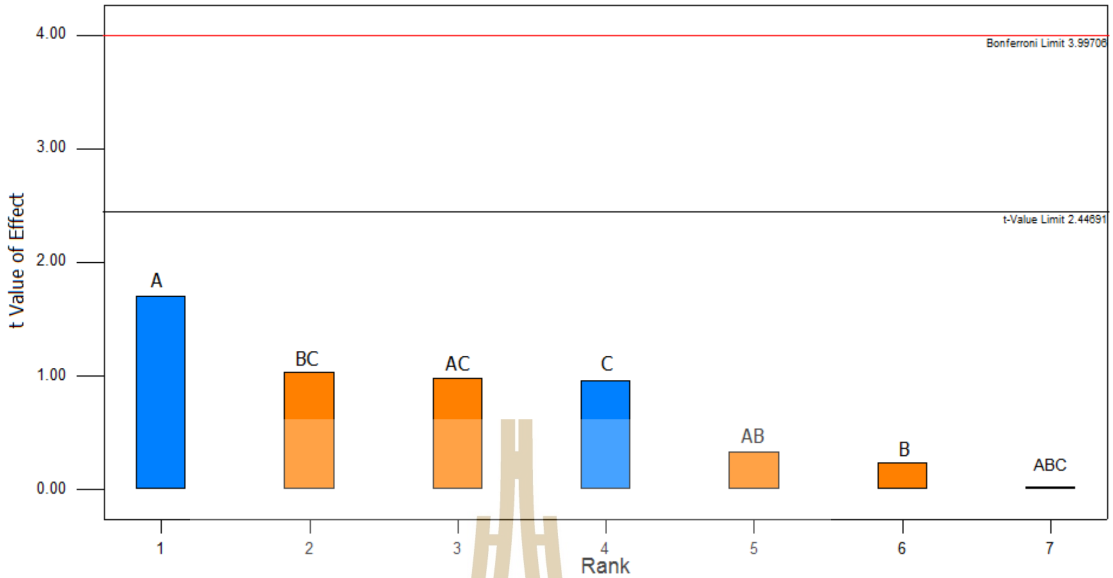


Figure 4.6 Pareto analysis chart of tensile strength (cured).

Table 4.9 ANOVA conclusion for tensile strength (cured).

Analysis of variance table of tensile strength (cured)						
Source	**Sum of squares**	**df**	**Mean square**	**F value**	***p*-value prob>F**	**Conclusion**
Model	0.0055	1	0.0055	0.0005	0.9822	not significant
ABC	0.0055	1	0.0055	0.0005	0.9822	
Residual	61.1470	6	10.1912	-	-	
Cor total	61.1525	7	-	-	-	

The normal plot of the standard effect of the elongation at break of PLA/silicone original samples are given in Figure 4.7. The plot indicates that all the effect values of silicone (+A) and silane (+B) are out of the linear line. They are hinted that these parameters and their levels used probably have obvious influence on the % elongation of the PLA/silicone blends. However, the pareto chart presented in Figure 4.8, is also contradicted that the suspicious parameters and their levels have no significant effect on the % elongation of the blends because their calculated *t*-values are below the critical value ($t_{crit.}$ = 2.44691). Taken both normal plot and pareto chart, it can preliminary conclude that all the desired parameters has no significantly effect to the % elongation of original PLA/silicone sample. The ANOVA conclusion is given in Table 4.10. According to the result, it is strengthen that the designed parameters and the given levels of content for manufacturing the PLA/silicone compounds are not significantly affected to the % elongation of the PLA/silicone blends without silane/water crosslink reaction as it is indicated by the calculated *p*-value, 0.2528, of the model more than the critical value, 0.05.

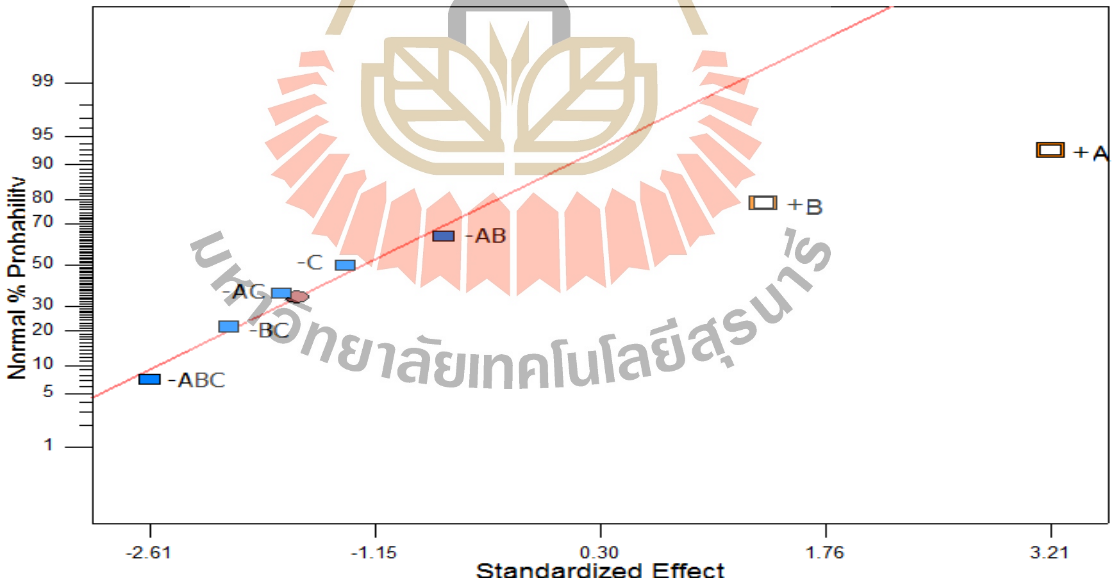


Figure 4.7 Normal probability plot of elongation at break (original).

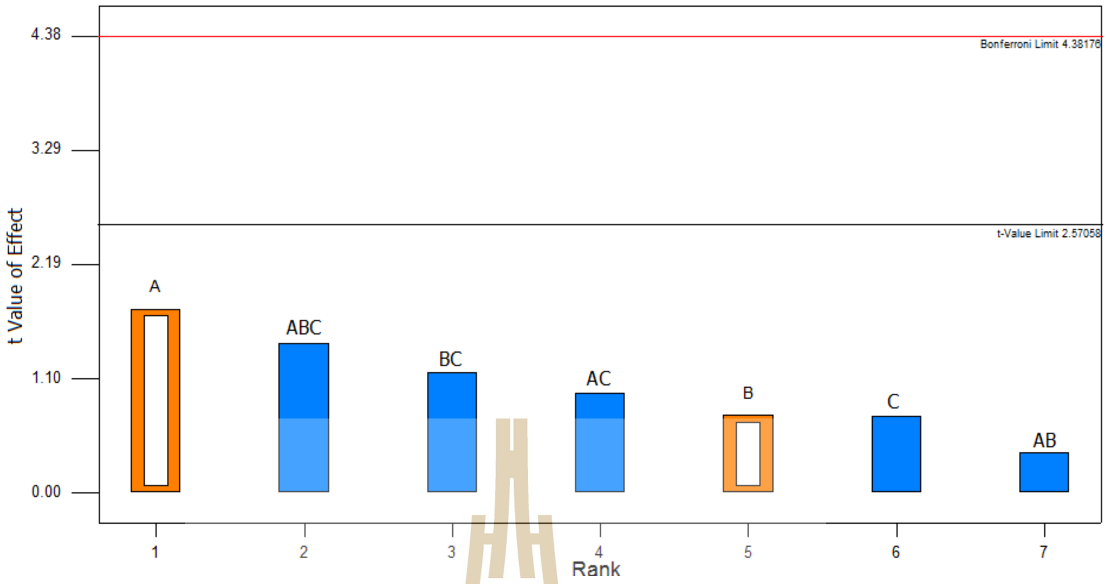


Figure 4.8 Pareto analysis chart of elongation at break (original).

Table 4.10 ANOVA conclusion for elongation at break (original).

Analysis of variance table of elongation at break (original)						
Source	**Sum of squares**	**df**	**Mean square**	**F value**	***p*-value prob>F**	**Conclusion**
Model	24.3717	2	12.1858	1.8335	0.2528	not significant
A-silicone	20.6725	1	20.6725	3.1105	0.1381	
B-silane	3.6992	1	3.6992	0.5566	0.4892	
Residual	33.2305	5	6.6461	-	-	
Cor total	57.6022	7	-	-	-	

Analyzing on cured sample, the normal plot is given in Figure 4.9. The similar consequences as discussed above are adopted. It is seen that silicone (+A) has strong potential to be the significant effected on the % elongation of PLA/silicone after sauna curing as its calculated effect values is out of the linear line. Moreover, the pareto chart in Figure 4.10 also strengthen that the parameter and its levels probably has significant effect on the % elongation of cured PLA/silicone. Because it is calculated *t*-values are above the critical value ($t_{crit.}$ = 2.44691). The conclusion is confirmed by the ANOVA testing given in Table 4.11. The calculated *p*-value of silicone parameter is 0.0202 which less than the critical value, 0.05. Therefore, adding silicone at high contents will significantly give rise to the PLA/silicone compound having high elongation at break after sauna cured process.

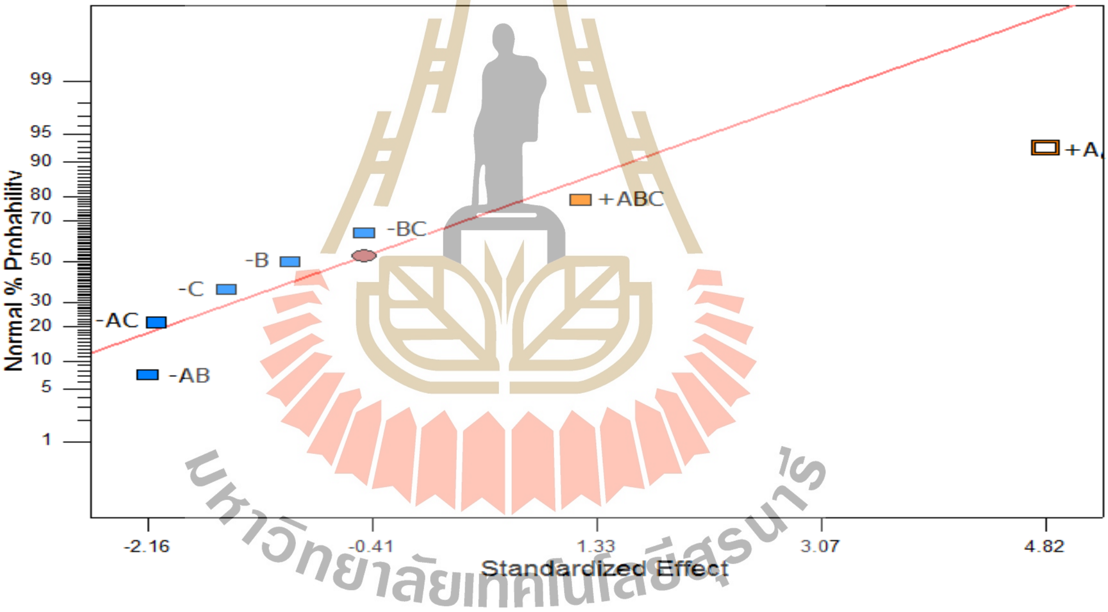


Figure 4.9 Normal probability plot of elongation at break (cured).

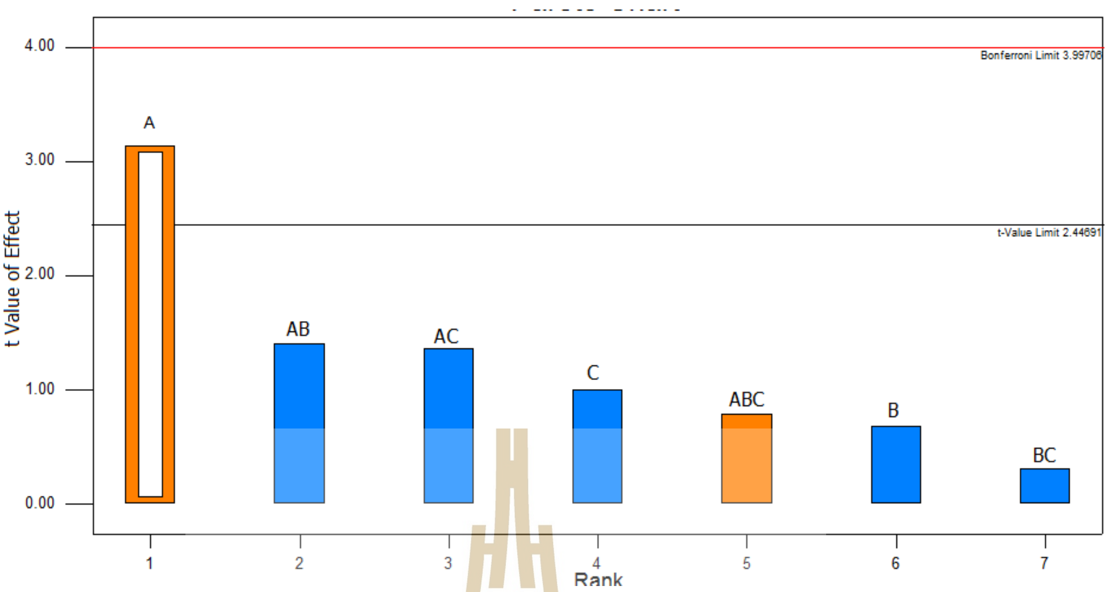


Figure 4.10 Pareto analysis chart of elongation at break (cured).

Table 4.11 ANOVA conclusion for elongation at break (cured).

Analysis of variance table of elongation at break (cured)						
Source	**Sum of squares**	**df**	**Mean square**	**F value**	***p*-value prob>F**	**Conclusion**
Model	46.4166	1	46.4166	9.8163	0.0202	significant
A-silicone	46.4166	1	46.4166	9.8163	0.0202	
Residual	28.3712	6	4.7285	-	-	
Cor total	74.7878	7	-	-	-	

The normal plot of tensile modulus is exhibited in Figure 4.11. It is seen that all of the calculated standard effects derived from the parameter (s) are almost lined on the straight line except the amount of polyester polyol (-C), which its negative effect values, is slightly out of the group. It is suspected to be the significant effect on the tensile Young's modulus of the original PLA/silicone compound. In Accordance, the pareto chart shown in Figure 4.11 reinforce that this parameter, polyol content (-C), is significant effect on the modulus of the blend sample because its calculated *t*-values are above the critical. The ANOVA results given in Table 4.12 conclude that the parameter used in the PLA/silicone compounding is significantly affected to the modulus of the PLA blends. It is mean that mixing the polyester polyol into the PLA/silicone at low level it will result in the PLA/silicone material having higher modulus.

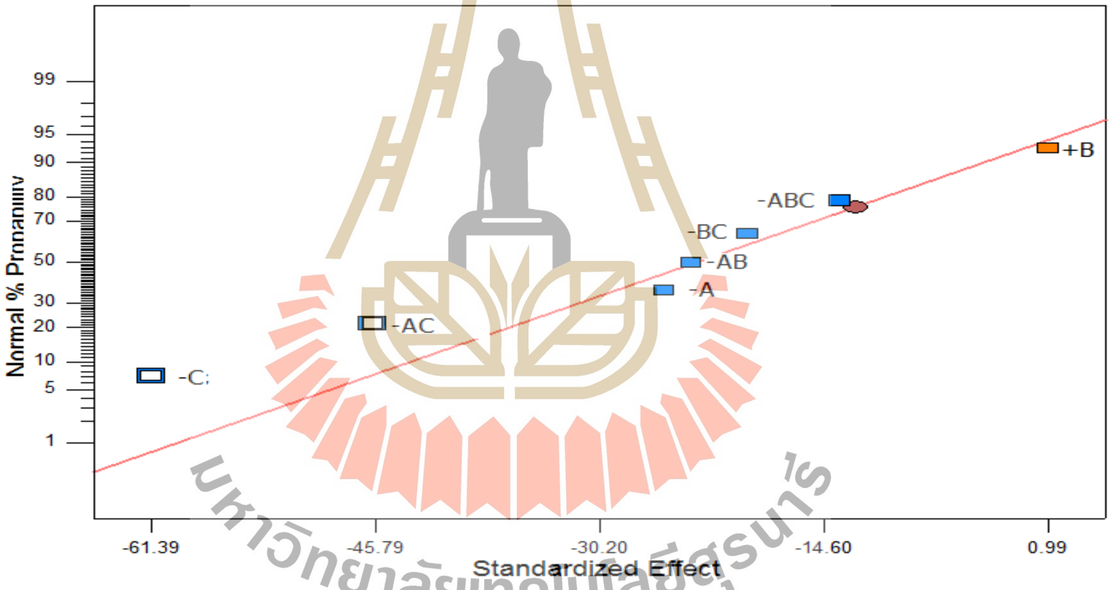


Figure 4.11 Normal probability plot of tensile modulus (original).

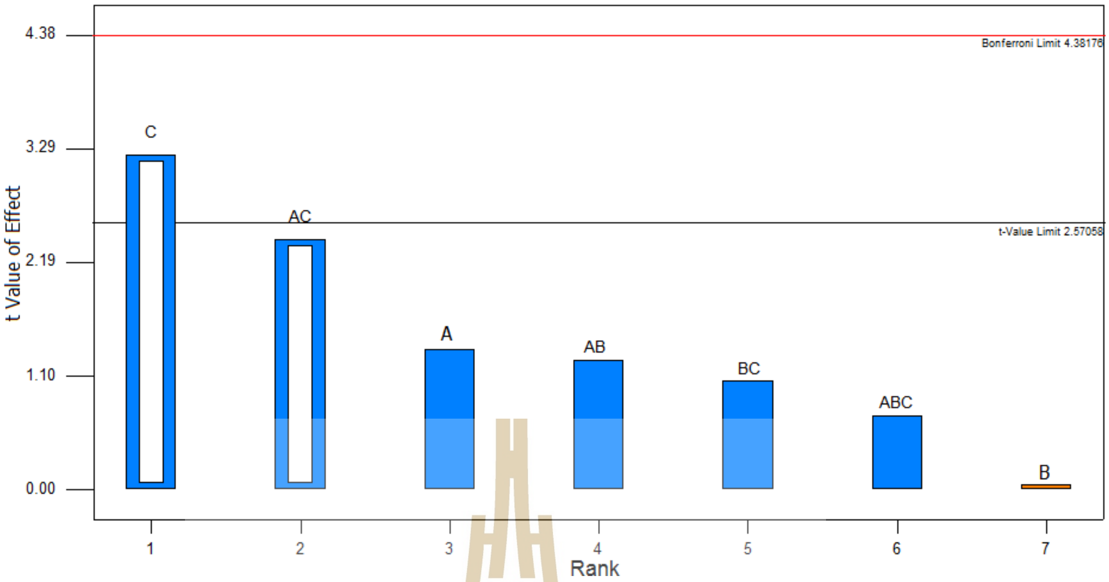


Figure 4.12 Pareto analysis chart of tensile modulus (original).

Table 4.12 ANOVA conclusion for tensile modulus (original).

Analysis of variance table of modulus (original)						
Source	**Sum of squares**	**df**	**Mean square**	**F value**	***p*-value prob>F**	**Conclusion**
Model	11763.79	2	5881.90	8.1204	0.0269	significant
C-polyol	7536.85	1	7536.85	10.4052	0.0233	
AC	4226.94	1	4226.94	5.8356	0.0604	
Residual	3621.66	5	724.33	-	-	
Cor total	15385.45	7	-	-	-	

For the sauna cured specimen, the normal plot and the pareto chart of the modulus are presented in figure 4.13 and 4.14, respectively. It is seen that all of the calculated standard effects derived from the parameter (s) are almost lined on the linear trend line except for the amount of polyester polyol (-C), which is negative effect, is obviously out of the trend. It is suspected to be the significant effect on the Young’s modulus of the cured PLA/silicone compound. In According with the pareto chart support that this parameter, polyol content, is significant effect on the modulus of the blend sample because its calculated *t*-values is just above the critical value. To confirm this proposition, the ANOVA testing was performed and the result is given in Table 4.13. According to the statistical conclusion, the parameters used in the PLA/silicone compounding are significantly affected to the modulus of the PLA blends as the calculated *p*-value, 0.0449, for the designed model is less than the degree of confidence. It is also meant that mixing the polyester polyol into the PLA/silicone material at low level, it will result in the PLA/silicone material having higher modulus.

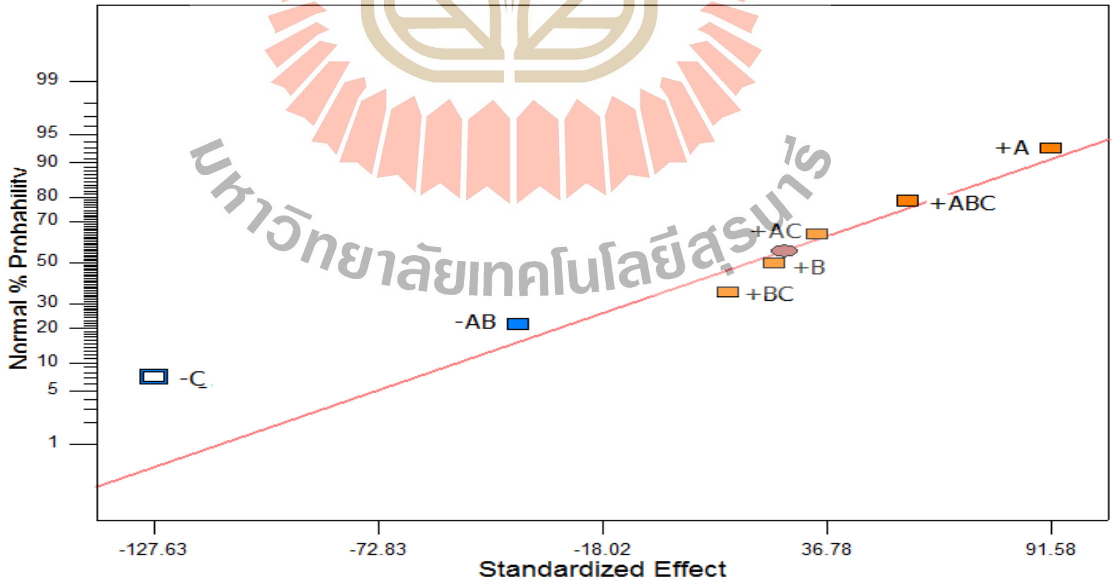


Figure 4.13 Normal probability plot of tensile modulus (cured).

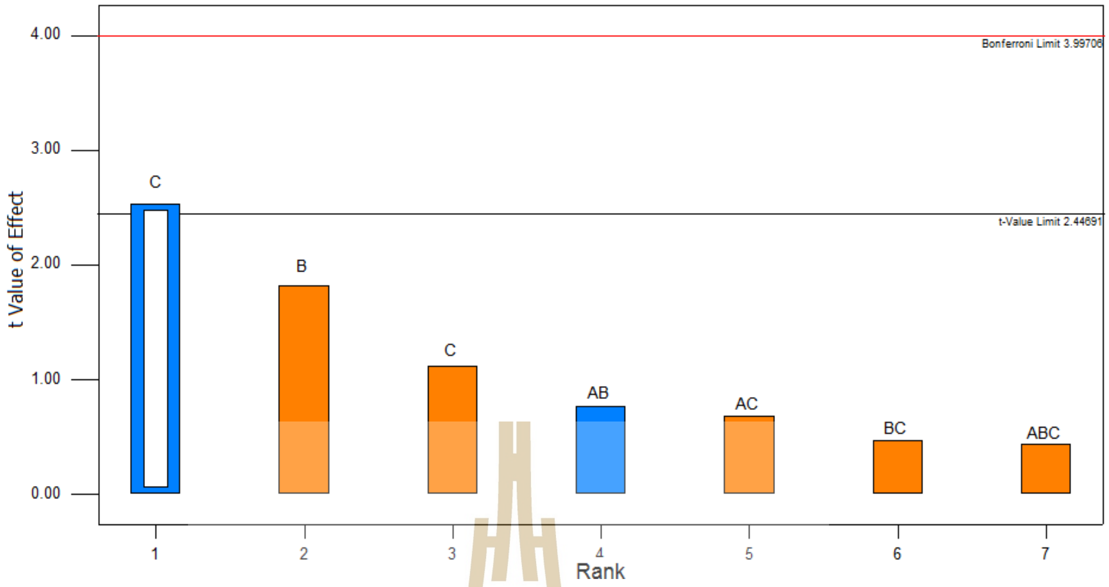


Figure 4.14 Pareto analysis chart of tensile modulus (cured).

Table 4.13 ANOVA conclusion for tensile modulus (cured).

Analysis of variance table of modulus (cured)						
Source	**Sum of squares**	**df**	**Mean square**	**F value**	***p*-value prob>F**	**Conclusion**
Model	32581.39	1	32581.39	6.3863	0.0449	significant
C-polyol	32581.39	1	32581.39	6.3863	0.0449	
Residual	30610.72	6	5101.79	-	-	
Cor total	63192.11	7	-	-	-	

4.1.3 Effect of impact properties of PLA/silicone compounds

Table 4.14 summarizes the impact strength of PLA/Silicone compound derived from the formula given in Table 4.2 for both at room and sub zero temperatures.

Table 4.14 Impact result of PLA/silicone compounds.

Test Run	**Unnotched impact strength (kJ/m^2)**		**Notched impact strength (kJ/m^2)**		**Low temperature notched impact strength (kJ/m^2)**	
	Original	**Cured**	**Original**	**Cured**	**Original**	**Cured**
PLA	15.97±2.35	21.15±2.41	2.49±0.48	3.45±0.98	2.60±0.62	3.20±0.42
1 (-,-,-)	20.33±3.03	22.24±2.09	2.55±0.21	3.25±0.71	5.98±0.68	5.37±0.31
2 (-,-,+)	21.54±0.80	23.99±2.91	3.07±0.64	3.05±0.23	3.68±1.06	5.00±0.36
3 (-,+,-)	22.02±3.32	23.22±2.06	2.31±0.16	2.96±0.41	4.97±0.81	6.45±0.54
4 (-,+,+)	26.02±6.67	28.85±3.75	2.38±0.15	3.44±0.26	4.90±0.91	3.68±0.43
5 (+,-,-)	29.75±3.19	32.78±2.66	3.68±0.85	6.34±0.37	6.05±0.60	6.40±0.18
6 (+,-,+)	26.02±2.26	36.45±6.85	2.81±0.76	5.68±0.29	6.07±0.68	6.77±0.35
7 (+,+,-)	25.35±2.87	30.35±4.27	3.54±0.59	5.93±0.40	5.25±0.93	7.38±0.22
8 (+,+,+)	20.64±1.22	26.07±2.49	3.69±0.62	3.93±0.12	5.58±1.21	5.65±0.59

General observations, the impact strength of the blends undergone sauna incubation are mostly higher than the ones without the curing process. It is emphasized that the silane induced condensation reaction via the moisture cure that lead to branch or crosslinked structure was probably taken place during the brewing process and hence higher in the test values.

Closer investigation, the normal plot of unnotched impact strength for the original sample is illustrated in Figure 4.15. Based on this statistical plot, it is seen that all the calculated standard effects can be averagely fitted onto the linear line. They are indicate that there are no significant effect of the parameters on the unnotched impact strength of the compound before sauna curing, Moreover, the pareto chart that is illustrated in Figure 4.16, also strengthen that the given parameters and their levels of content use in this study have no significant effect on the unnotched impact strength of the PLA/silicone original samples because their calculated *t*-values are below the critical value ($t_{crit.}$ = 2.44691). To confirm this conclusion, the ANOVA testing was evaluated and the result is summarized in Table 4.15. According to the conclusion, the designed parameters and levels of design parameters for manufacturing the PLA/silicone compounds are not significantly affected to the unnotched impact strength of the blends as it is indicated by the calculated *p*-value, 0.8991, of the model is above the critical value, 0.05.

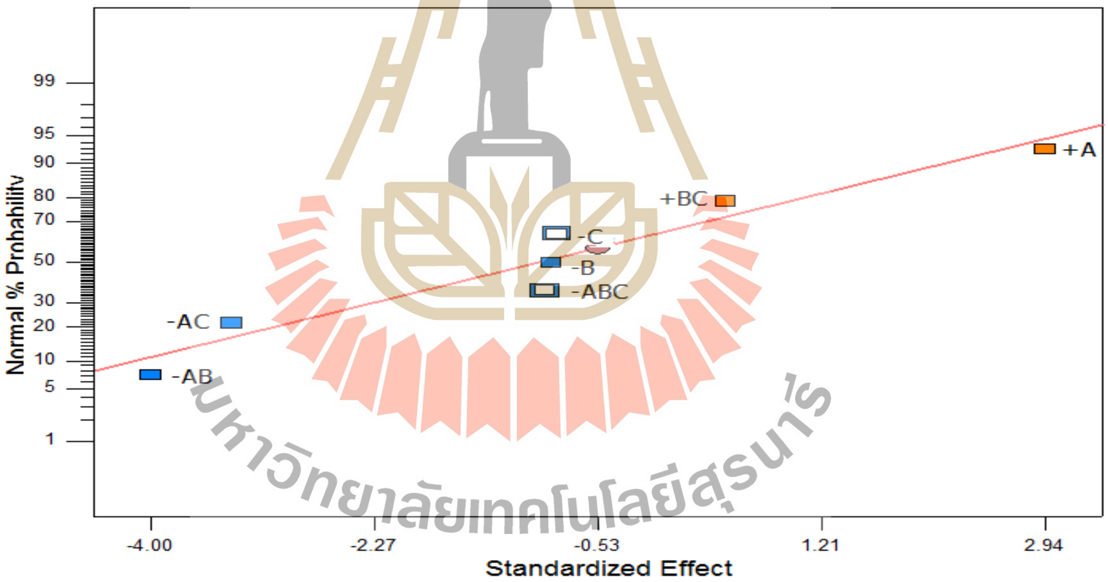


Figure 4.15 Normal probability plot of unnotched impact (original).

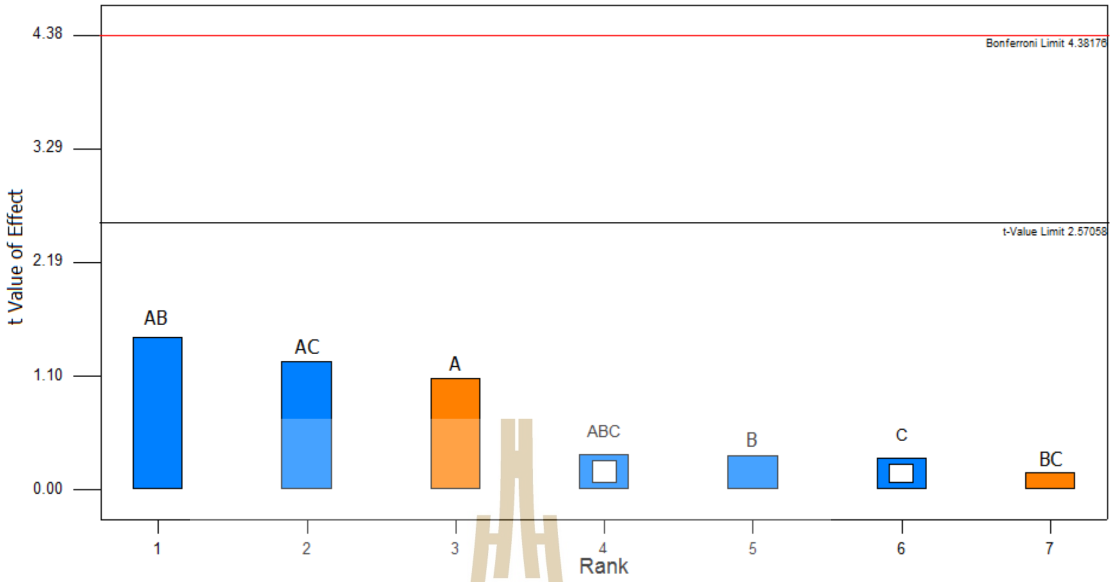


Figure 4.16 Pareto analysis chart of unnotched impact (original).

Table 4.15 ANOVA conclusion for unnotched impact (original).

Analysis of variance table of unnotched impact (original)						
Source	**Sum of squares**	**df**	**Mean square**	**F value**	***p*-value prob>F**	**Conclusion**
Model	3.2269	2	1.6135	0.1087	0.8991	not significant
C-polyol	1.4484	1	1.4484	0.0976	0.7673	
ABC	1.7785	1	1.7785	0.1198	0.7433	
Residual	74.2064	5	14.8413	-	-	
Cor total	77.4333	7	-	-	-	

For the unnotched impact strength of the sauna cured PLA/silicone samples Figure 4.17 and 4.18 show the normal plot and pareto chart derived from the statistical computation. The plot indicates that the positive effect values of silicone

(+A) and polyester polyol (+C) are beyond the linear trend line. They are hinted that these parameters and their content levels used in the compound formula probably and greatly influence on the unnotched impact strength of the blends. However, the pareto chart as given in Figure 4.18, is contradicted to those the suspicious parameters because the calculated t-values are below the critical value ($t_{crit.}$ = 2.44691). Taken both the normal plot and pareto chart, it can preliminary state that the +A and +C parameters have no significantly effect on the unnotched impact strength of sauna cured PLA/silicone blend. The ANOVA conclusion given in Table 4.16 strengthen that the designed parameters, A, B and C, and their levels of content for compounding the PLA/silicone are not significant affected to the unnotched impact strength of the blend in which undergo silane/water condensation reaction. It is indicated by the calculated p-value of the model and the parameters are higher than the critical value, 0.05.

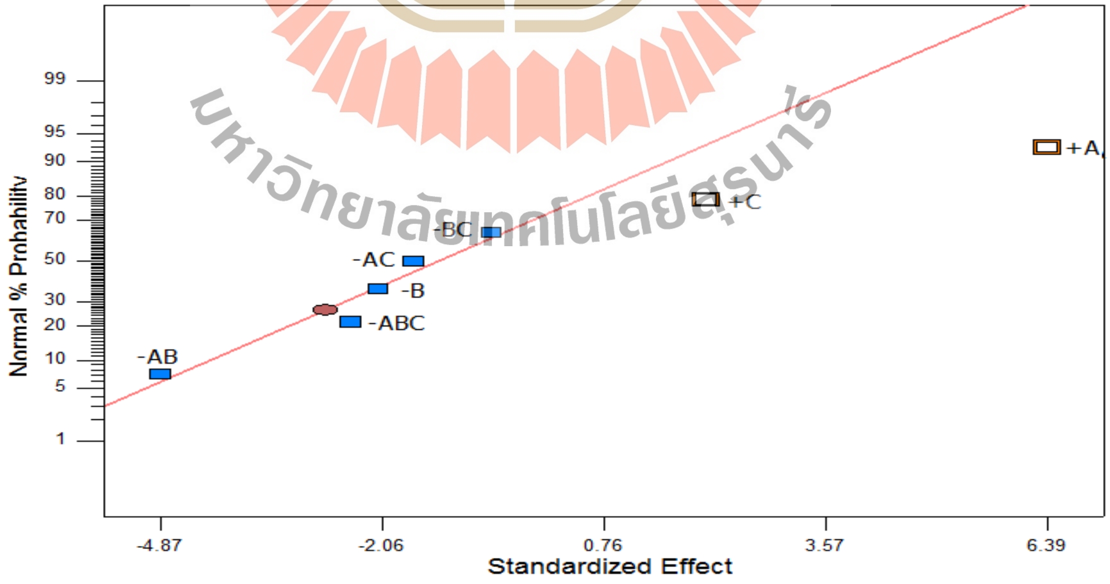


Figure 4.17 Normal probability plot of unnotched impact (cured).

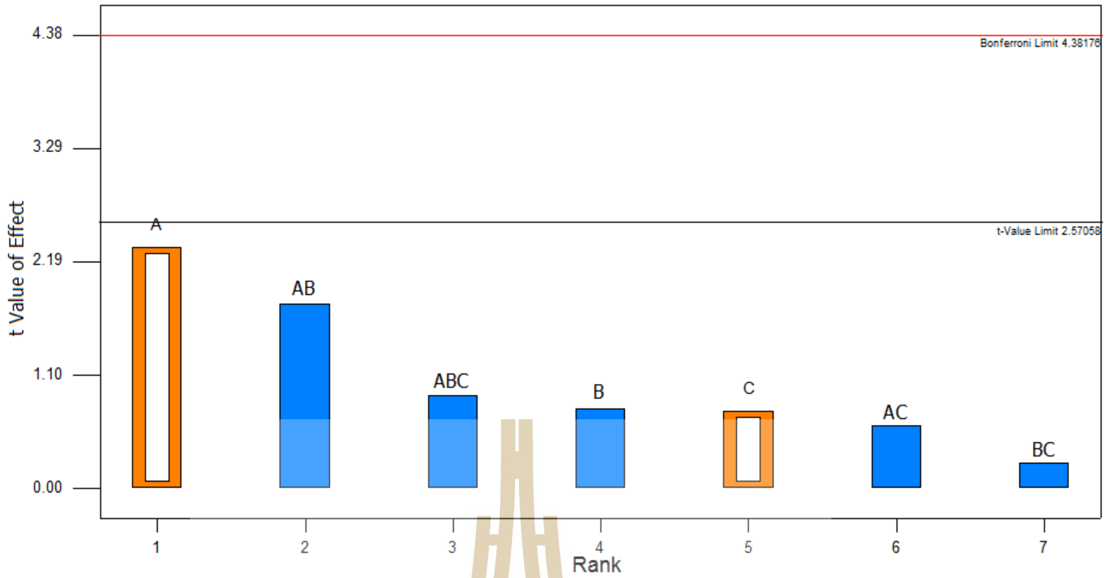


Figure 4.18 Pareto analysis chart of unnotched impact (cured).

Table 4.16 ANOVA conclusion for unnotched impact strength (cured).

Analysis of variance table of unnotched impact (cured)						
Source	**Sum of squares**	**df**	**Mean square**	**F value**	***p*-value prob>F**	**Conclusion**
Model	89.9501	2	44.9751	3.0046	0.1390	not significant
A-silicone	81.5492	1	81.5492	5.4480	0.0669	
C-polyol	8.4009	1	8.4009	0.5612	0.4875	
Residual	74.8435	5	14.9687	-	-	
Cor total	164.7937	7	-	-	-	

Figure 4.19 and 4.20 are the normal plot and pareto chart of the notched impact strength of PLA/silicone blend before sauna curing. The similar consequences as discussed above are adopted. It is seen in the normal plot that only

silicone content (+A) has strongly and potentially to be the significant effected to the notched impact strength of PLA/silicone as its calculated effect values is out of the linear line. Furthermore, the pareto charts, in Figure 4.20, also strengthen that *t*-values of the suspected parameter and its levels is above the critical value ($t_{crit.}$ = 2.44691). It probably has significant effect on the notched impact strength of the original PLA/silicone blend. Considering the ANOVA analysis given in Table 4.17, it shown that the calculate *p*-value of the designed experiment and also the silicone parameter is 0.0195. It is lower than the critical value at 0.05. Therefore, it can conclude that adding silicone at high level of contents, above 3 phr. will has the positive and significant effect to the notched impact strength of the PLA/silicone compound.

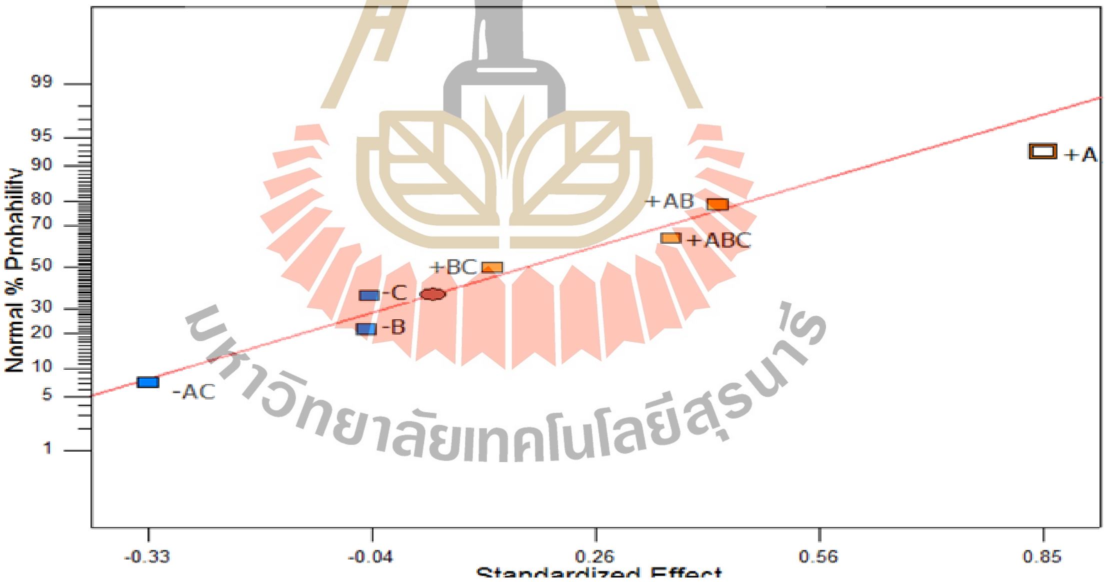


Figure 4.19 Normal probability plot of notched impact (original).

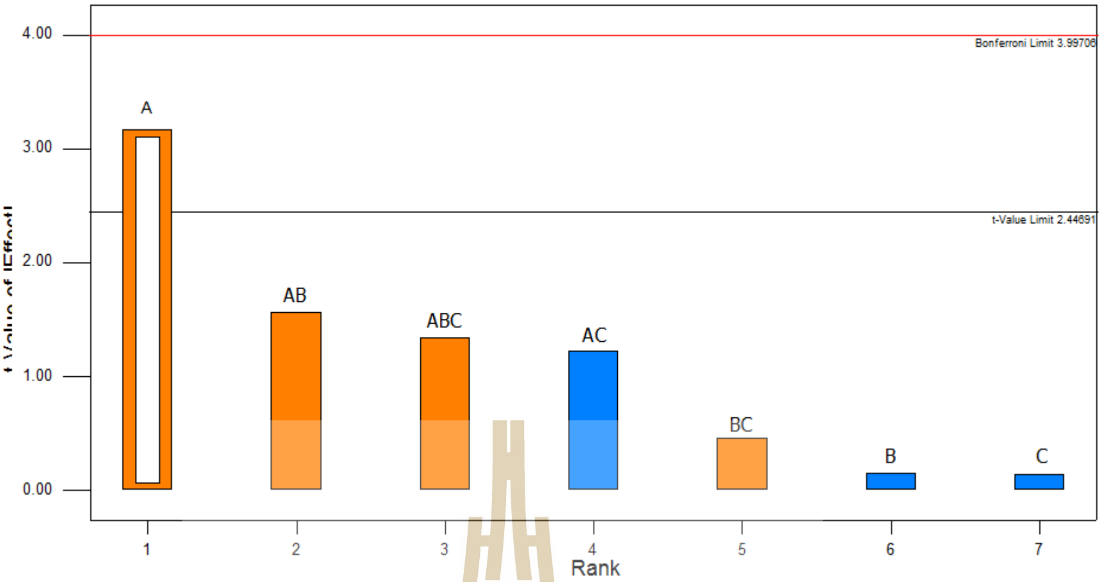


Figure 4.20 Pareto analysis chart of notched impact (original).

Table 4.17 ANOVA conclusion for notched impact (original).

Analysis of variance table of notched impact (original)						
Source	**Sum of squares**	**df**	**Mean square**	**F value**	***p*-value prob>F**	**Conclusion**
Model	1.4544	1	1.4544	9.9949	0.0195	significant
A-silicone	1.4544	1	1.4544	9.9949	0.0195	
Residual	0.8731	6	0.1455	-	-	
Cor total	2.3274	7	-	-	-	

Figure 4.21 and 4.22 are the normal plot and pareto chart of the notched impact strength of PLA/silicone blend after sauna curing. The similar consequences as discussed above are adopted. It is seen in the normal plot that only silicone content (+A) has strongly and potentially to be the significant effected to the

notched impact strength of PLA/silicone as its calculated effect values is out of the linear line. Furthermore, the pareto charts, in Figure 4.22, also strengthen that *t*-values of the suspected parameter and its levels is above the critical value ($t_{crit.} = 2.44691$). It probably has significant effect on the notched impact strength of the sauna cured PLA/silicone blend. Considering the ANOVA analysis given in Table 4.18, it shown that the calculate *p*-value of the designed experiment and also the silicone parameter is 0.0055. It is lower than the critical value at 0.05. Therefore, it can conclude that adding silicone at high level of contents, above 3 phr. will has the positive and significant effect to the notched impact strength of the PLA/silicone compound.

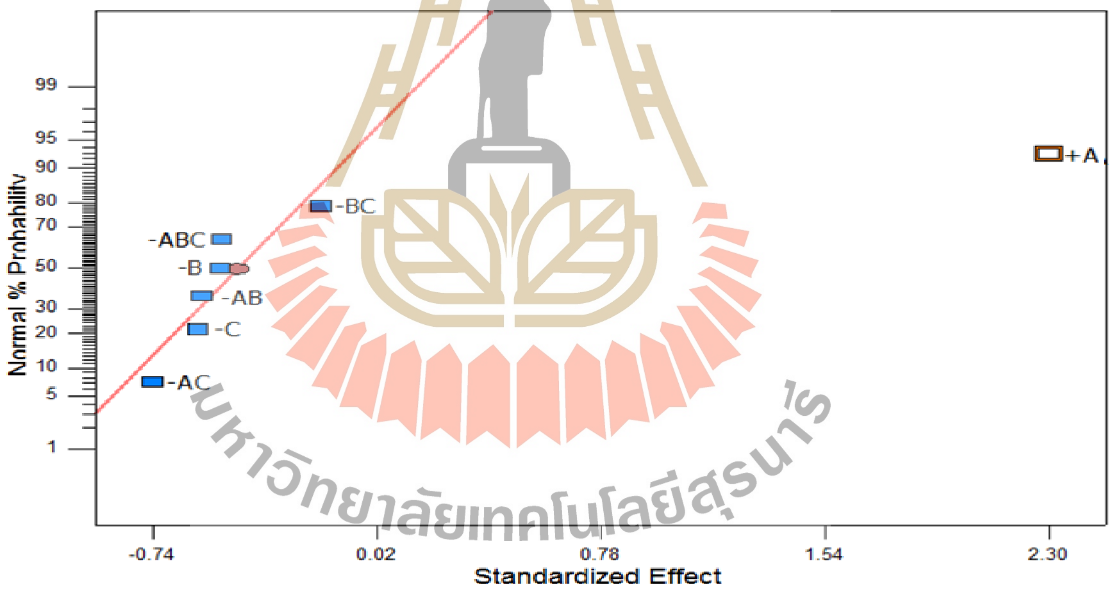


Figure 4.21 Normal probability plot of notched impact (cured).

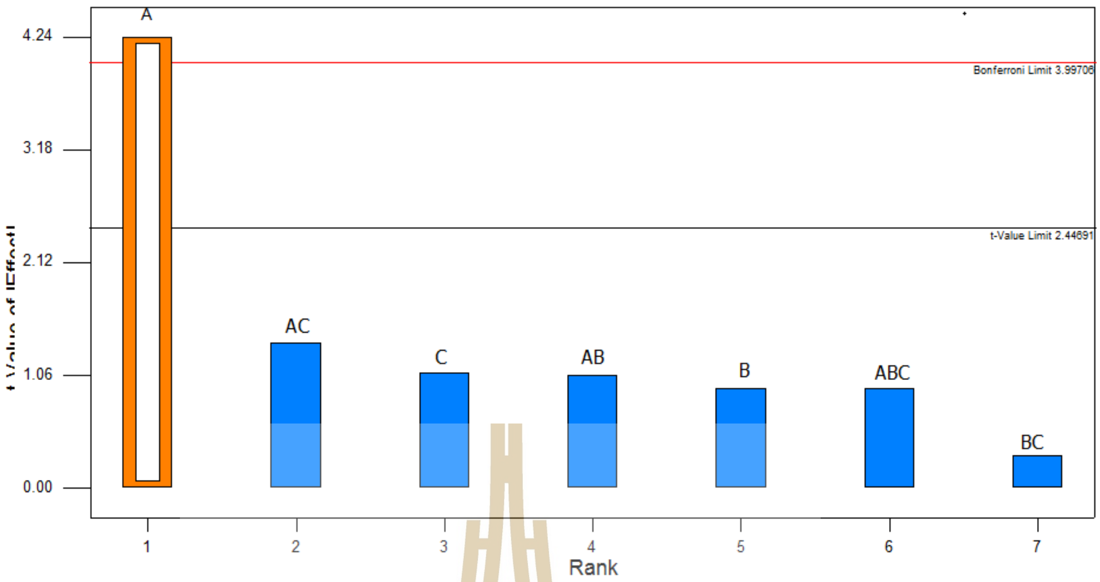


Figure 4.22 Pareto analysis chart of notched impact (cured)

Table 4.18 ANOVA conclusion for notched impact (cured).

Analysis of variance table of notched impact (cured)						
Source	**Sum of squares**	**df**	**Mean square**	**F value**	***p*-value prob>F**	**Conclusion**
Model	10.5616	1	10.5616	17.9428	0.0055	significant
A-silicone	10.5616	1	10.5616	17.9428	0.0055	
Residual	3.5318	6	0.5886	-	-	
Cor total	14.0934	7	-	-	-	

Similar outcome is observed for the notched impact result of the original samples of PLA/silicone performed at low temperature. The standard normal plot and pareto chart are reported in Figure 4.23 and 4.24, respectively. The standard effect plot shows that the silicone (+A) and interaction between silicone and silane (-

AB) are excluded from the linear regressed line. They are manifested that these parameters and their levels used probably have influence on, by statistical mean, the notched impact strength of the PLA/silicone blends at sub zero temperature of testing. In contrast, the pareto chart presented in Figure 4.24, contradicts that the parameters and their levels have no significant effect on the notched impact strength of the blends because their calculated *t*-values are below the critical value ($t_{crit.}$ = 2.44691). Combination both normal plot and pareto chart, it can preliminary say that the given parameters and their levels have no significant effect to the impact strength tested at low temperature of PLA/silicone without sauna incubation. Analysis of the data by the ANOVA, the statistical conclusion is given in Table 4.19. According to the result, it is strengthen that the designed model, the parameters and levels of content has no significant affected to the notched impact strength at low temperature as it is indicated by the higher calculated *p*-value, 0.1229 than the critical value.

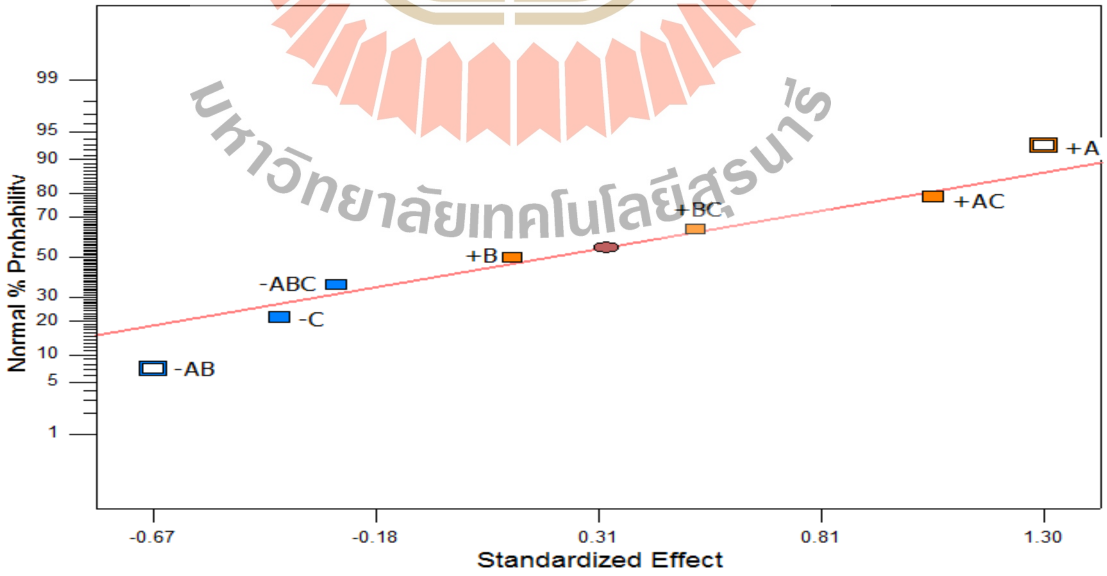


Figure 4.23 Normal probability plot of notched impact at low temperature (original).

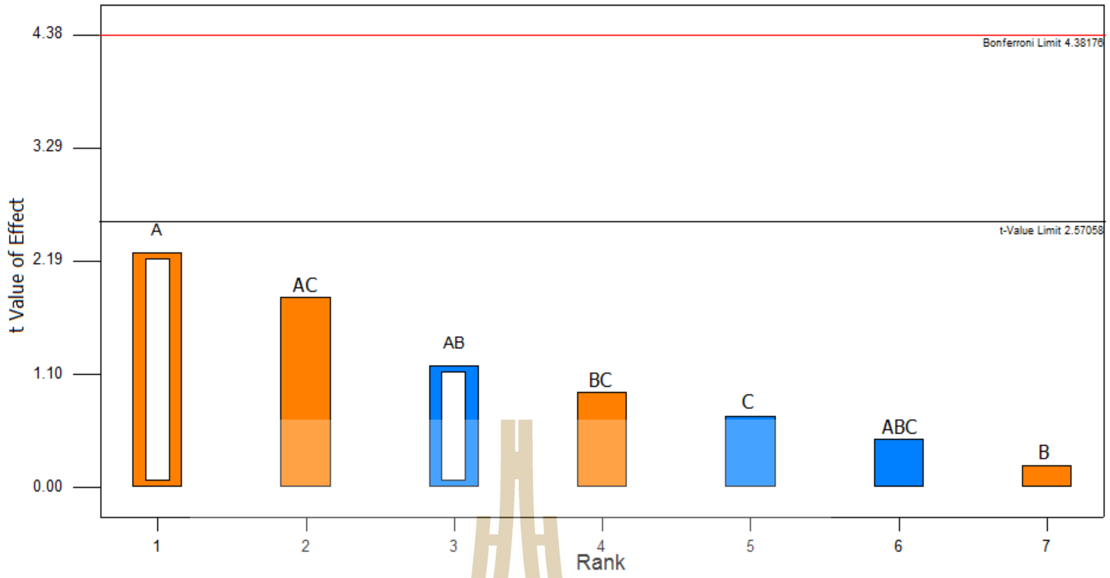


Figure 4.24 Pareto analysis chart of notched impact at low temperature (original).

Table 4.19 ANOVA conclusion for notched impact at low temperature (original).

Analysis of variance table of notched impact at low temperature (original)						
Source	**Sum of squares**	**df**	**Mean square**	**F Value**	***p*-value prob > F**	**Conclusion**
Model	4.27	2	2.14	3.28	0.1229	not significant
A-silicone	3.37	1	3.37	5.17	0.0720	
AB	0.9	1	0.9	1.39	0.2914	
Residual	3.25	5	0.65	-	-	
Cor total	7.52	7	-	-	-	

Figure 4.25 and 4.26 are the normal plot and pareto chart of the low temperature notched impact strength of PLA/silicone after sauna treatment, respectively. The similar statistical conclusion will be made. The standard plot

illustrates that only the interaction factor between silicone and silane (-AB) can not fit onto the linear trend line. It is pointed out that this parameter and also its level used in the compounding process has probably control the low temperature notched impact strength of the PLA/silicone blends. Nevertheless, the pareto chart presented in Figure 4.26, contradict the proposal. Because the calculated *t*-value of the suspicious parameter is lower than the critical value at 2.44691. It means that AB has no significant effect on the notched impact strength of the blends. Taken both normal plot and pareto chart, it can preliminary conclude that all the desired parameters has no significantly effect to the low temperature impact strength of PLA/silicone cured sample. Accordingly, the ANOVA conclusion given in Table 4.20 strengthen that the parameter is not significant effect to the low temperature notched impact strength due to the fact that the calculated *p*-value, 0.9644, of the designed model is far beyond the critical value. Within this design of experiment, the parameters and their levels assigned have no real influence on the low temperature notched impact strength of both uncured and cured of PLA/Silicone blends.

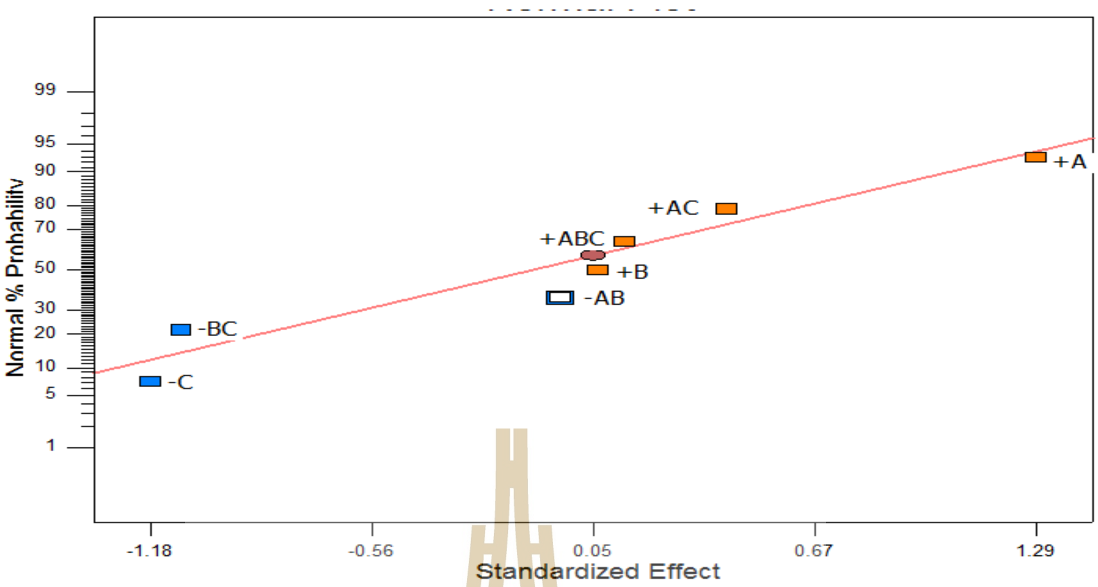


Figure 4.25 Normal probability plot of notched impact at low temperature (cured).

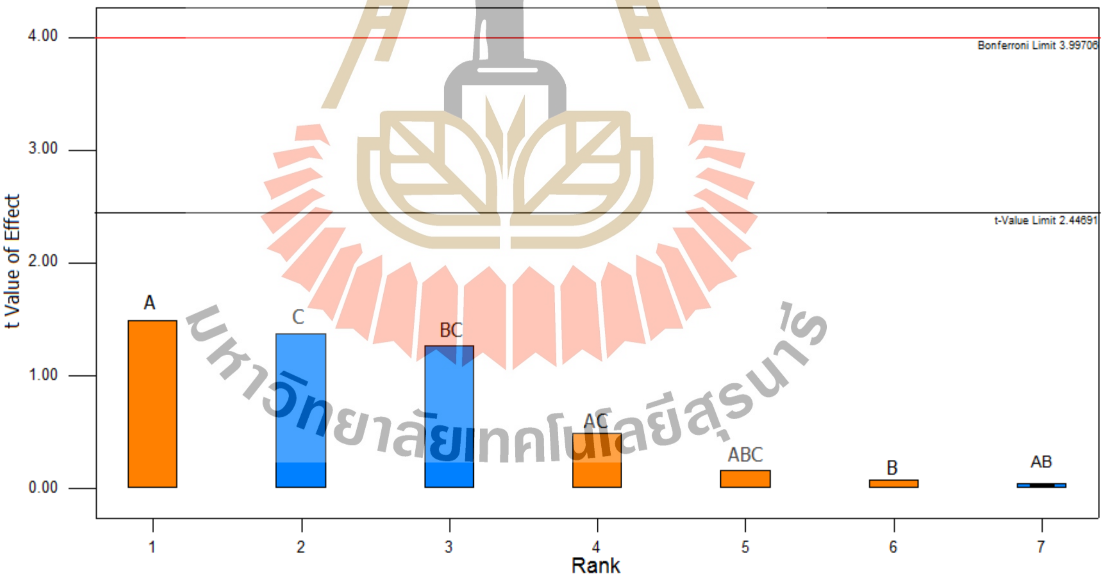


Figure 4.26 Pareto chart of notched impact at low temperature (cured).

Table 4.20 ANOVA conclusion for notched impact at low temperature (cured).

Analysis of variance table of notched impact at low temperature (original)						
Source	**Sum of squares**	**df**	**Mean square**	**F Value**	***p*-value prob > F**	**Conclusion**
Model	0.0032	1	0.0032	0.0022	0.9644	not significant
AB	0.0032	1	0.0032	0.0022	0.9644	
Residual	8.89	6	1.48	-	-	
Cor total	8.9	7	-	-	-	

4.1.4 Heat Distortion Temperature Analysis of PLA/silicone compounds

Heat deflection temperature (HDT), obtained at constant heating rate at 120°C/hour are summarized in Table 4.21.

Table 4.21 Thermal properties of PLA/silicone compounds.

Test	**PLA (phr)**	**Silicone (A) (phr)**	**Silane (B) (phr)**	**Polyol (C) (phr)**	**Stabilizer (phr)**	**HDT original (°C)**	**HDT cured (°C)**
1	500	0.5 (-)	0.5 (-)	2.0 (-)	1	49.27±0.64	59.33±0.58
2	500	1.0 (-)	0.2 (-)	5.0 (+)	1	48.07±0.50	57.80±1.64
3	500	1.0 (-)	1.5 (+)	1.0 (-)	1	49.33±0.58	57.67±0.58
4	500	0.5 (-)	1.0 (+)	4.0 (+)	1	47.93±0.70	60.00±1.00
5	500	2.0 (+)	0.2 (-)	1.0 (-)	1	48.53±0.50	57.93±0.31
6	500	3.0 (+)	0.5 (-)	5.0 (+)	1	47.33±0.58	58.00±0.40
7	500	3.0 (+)	1.0 (+)	2.0 (-)	1	48.52±0.42	60.33±1.15
8	500	2.0 (+)	1.5 (+)	4.0 (+)	1	47.80±0.72	58.67±2.31

General observation, it is seen that the test values obtained from sauna cured sample are obviously more or less 10 degrees higher than the sample without curing. The improvement in the HDT is probably due to the silane bonding during the silane/moisture condensation reaction in sauna treatment. As the result, the polymer chain could be either enlarge or crosslink and hence the thermal property is elevated.

Figure 4.27 and 4.28 illustrate the normal plot and pareto chart derived from the HDT respond for the PLA/silicone samples before sauna curing, respectively. It is obviously seen that the calculated effects derived from the silicone (-A) and polyester polyol (-C) contents, which are negative effect values, cannot be included into the group. As the result, they are the suspect to be the significant effect on the HDT of the original PLA/silicone compound. Reinforcing with the pareto chart, shown in Figure 4.28, there are no doubt that silicone (-A) and polyol (-C) contents are negative and also significant effect on the HDT of the blend because their calculated *t*-values are above the critical one. The ANOVA conclusion as given in Table 4.22 again strengthen that the parameters and levels used in this designed experiment have significant effect on the HDT as evidenced by the calculated *p*- value at 0.0006 which is below the degree of confidential. Consequently, the parameters -A and -C are negatively and significantly affect to the HDT of the PLA/silicone blends without moisture curing. It means that compounding PLA/Silicone polymer with low silicone, less than 1 phr, and low polyol, less than 2 phr, contents would give rise to the compound with higher HDT than the mixing at high level of contents.

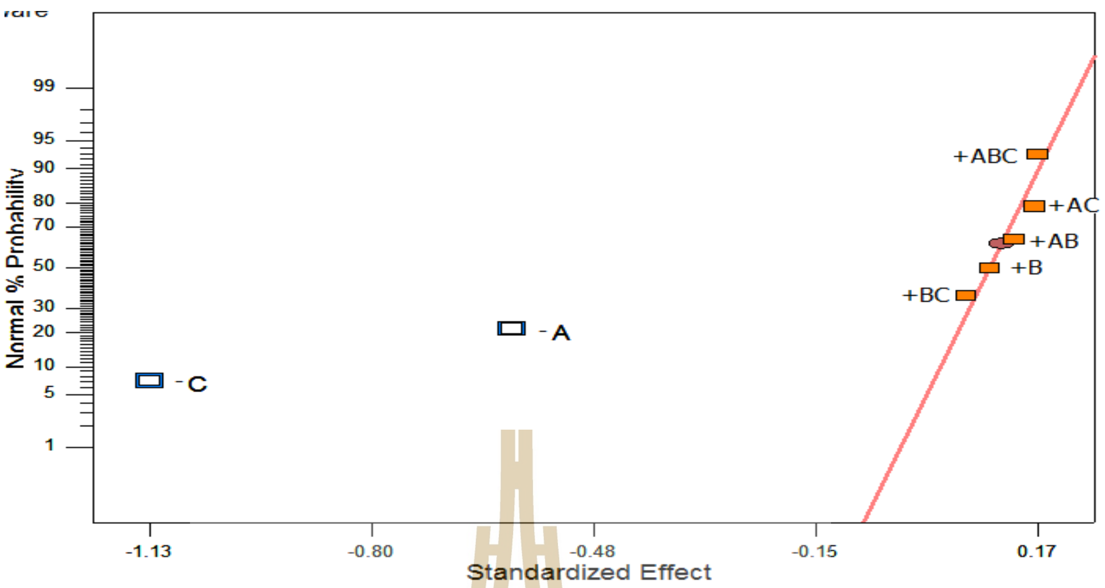


Figure 4.27 Normal probability plot of HDT (original).

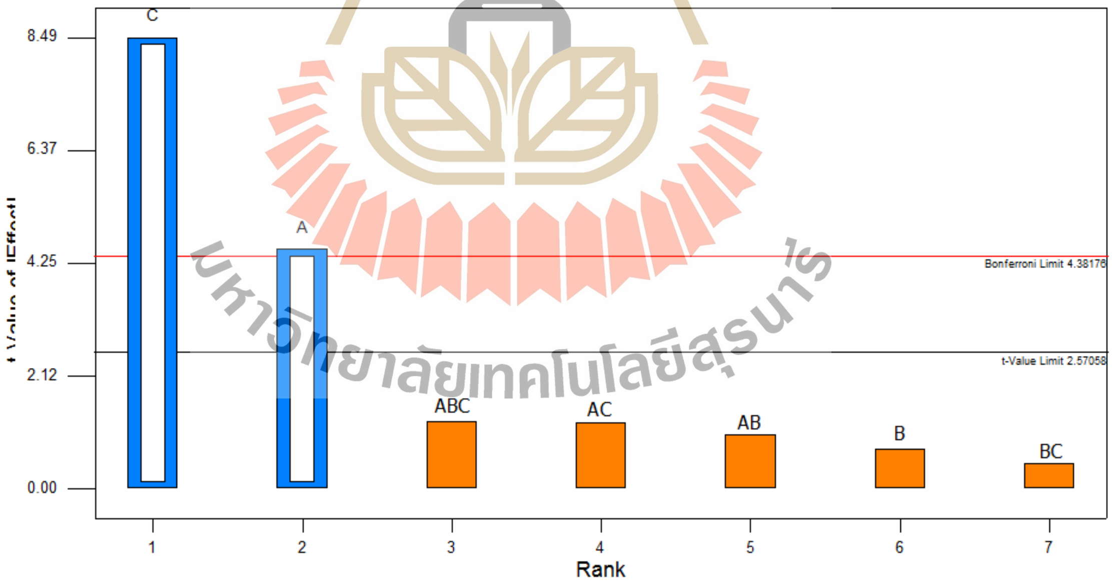


Figure 4.28 Pareto chart of HDT (original).

Table 4.22 ANOVA conclusion for HDT (original).

Analysis of variance table of HDT (original).						
Source	**Sum of squares**	**df**	**Mean square**	**F Value**	***p*-value prob > F**	**Conclusion**
Model	3.27	2	1.64	46.2	0.0006	significant
A-silicone	0.72	1	0.72	20.32	0.0064	
C-polyol	2.55	1	2.55	72.08	0.0004	
Residual	0.18	5	0.035	-	-	
Cor total	3.45	7	-	-	-	

On the other hand, in the statistical analysis of the samples after sauna incubation the results of normal plot and pareto chart reported in Figure 4.29 and 4.30, respectively. Unexpectedly, the standard plot illustrates that all of the calculated effects are almost lined on the same trend except the effect of silane (+B) content is slightly out of the rest. It points out that this parameter and also its level used in the compounding process has probably the positive control on the HDT of the PLA/silicone blends. Nevertheless, the pareto chart, presented in Figure 4.30, contradict the proposal. Because the calculated *t*-value of the suspicious parameter is lower than the critical value at 2.44691. It means that +B has no real significant effect on the HDT of the blends. Taken both normal plot and pareto chart, it cans preliminary say that all the given parameters have no significant effect to the HDT of the sauna cured PLA/silicone sample. According to the ANOVA conclusion given in Table 4.23, it strengthens that the designed parameters are not significant effect to the HDT due to the conclusion that the calculated *p*-value, at 0.2467, of the designed model is far greater than the critical value. Within this design of experiment, the parameters and their assigned levels have no real influence on the HDT of cured PLA/silicone blends.

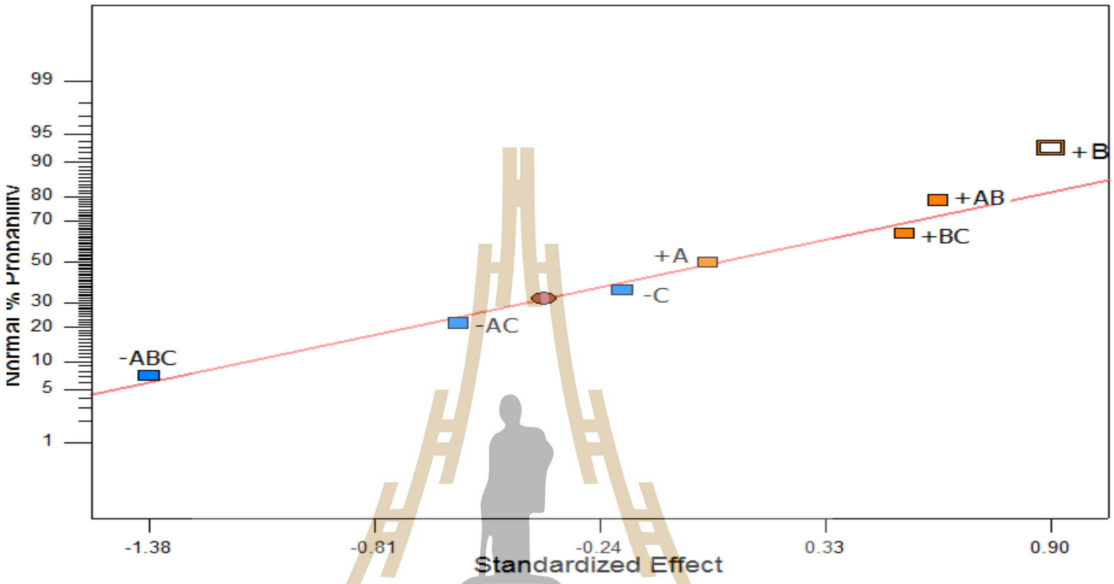


Figure 4.29 Normal probability plot of HDT (cured).

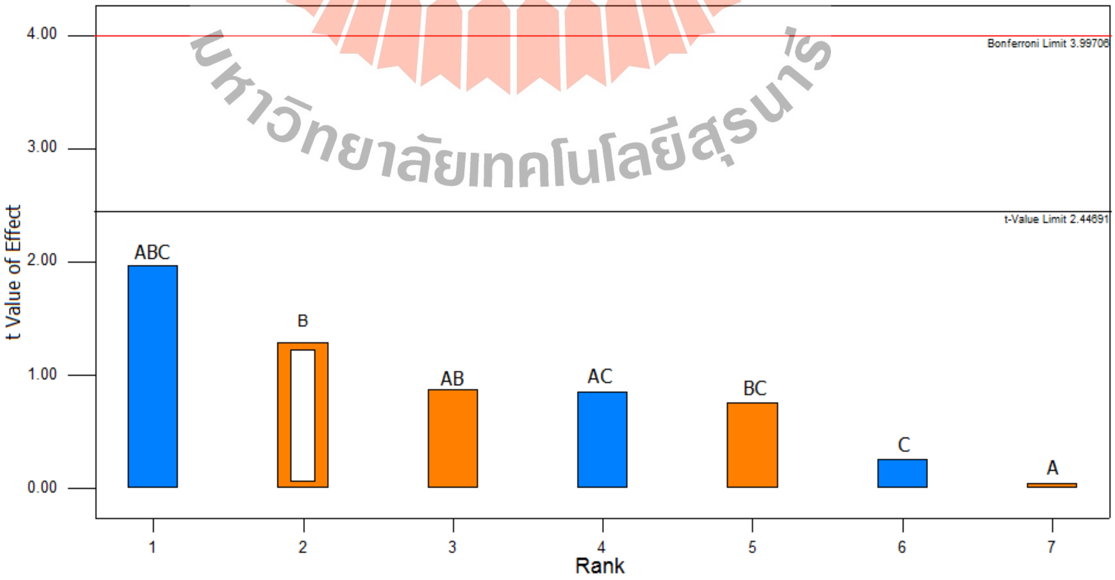


Figure 4.30 Pareto chart of HDT (cured).

Table 4.23 ANOVA conclusion for HDT (cured).

Source	Sum of squares	df	Mean square	F Value	*p*-value prob > F	Conclusion
Model	1.63	1	1.63	1.65	0.2467	not significant
B-silane	1.63	1	1.63	1.65	0.2467	
Residual	5.94	6	0.99	-	-	
Cor total	7.56	7	-	-	-	

4.1.5 Optimization

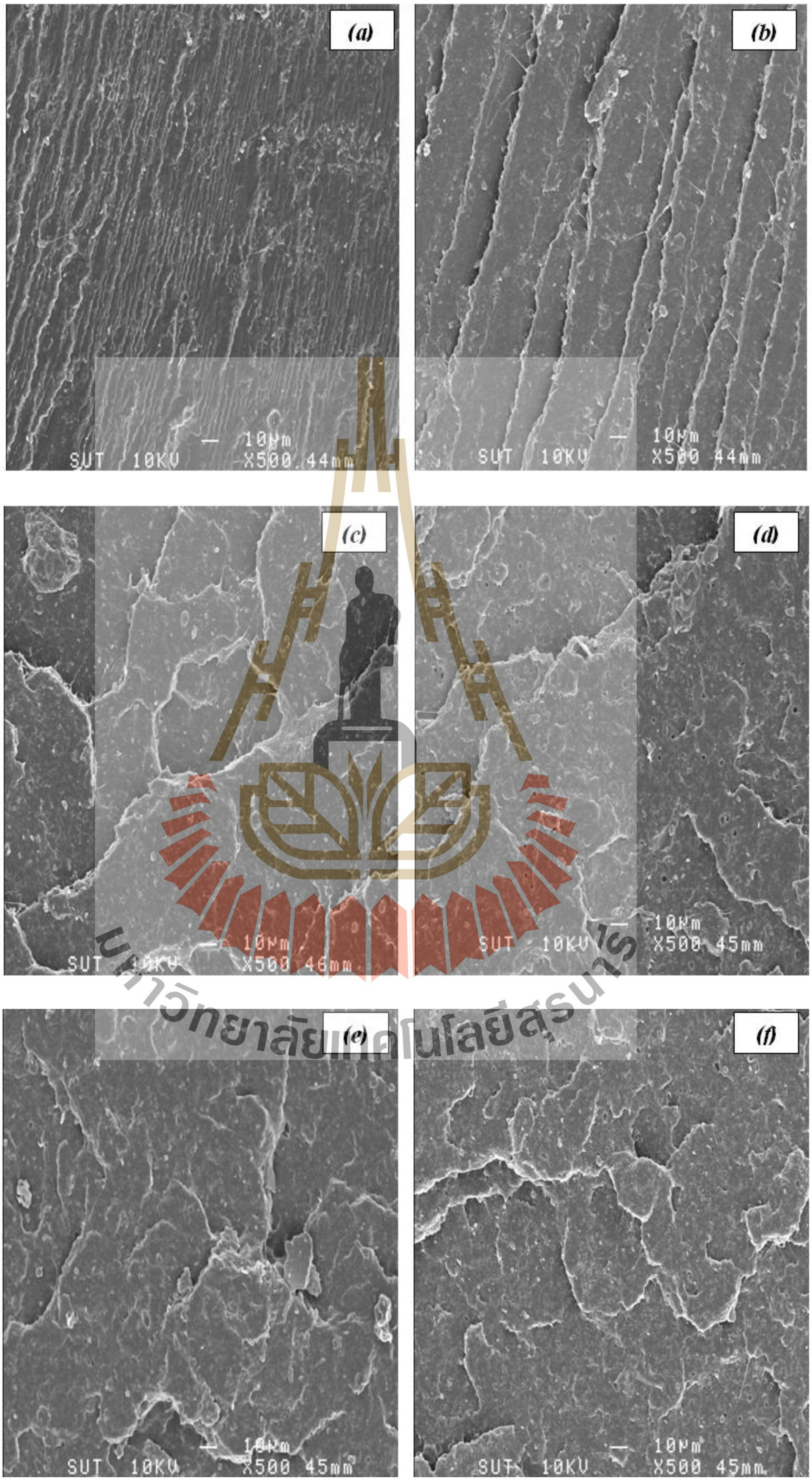
Taking the statistical conclusion presented before, the obtained regression models are the relations between the parameters and the respond properties are constructed and summarized in Table 4.24. These equations could be statistically used to predict the properties of the PLA/silicone blend to the desired value. For example, the equation for notched impact strength of the original is 3+0.43 (**A**). It is implied that maximized notched impact strength of PLA/silicone blend can be achieved if it is compounded in twin screw mixer and injected at 190^{o}C by using high level of silicone **(A** > 3 phr), accordingly. The rest can be estimated as the identical manner. By using the DOE approach, the optimal formulation of PLA/silicone for low temperature applications can be accomplished. For the further properties improvement of the PLA/Silicone blend, the formula which has the outstanding low temperature impact strength, run#5, is chosen. Not only the low temperature impact strength, the overall properties are also relatively high comparing the rest. This high silicone (+A), low silane (-B) and low polyester polyol (-C) contents formula will be further explored and will be discussed later on.

Table 4.24 The predicted regression model of the respond properties of PLA/silicone derived from the DOE.

Properties	**Regressed models**
Room temperature	
Original:	
Melt flow rate	No significant
Tensile strength	36.06-3.60 (A)
Elongation at break	No significant
Tensile modulus	2.49-30.69 (C)-22.99 (AC)
Notched impact	3+0.43 (A)
Unnotched impact	No significant
HDT	48.35-0.30 (A)-0.56 (A)
Sauna cured:	
Tensile strength	No significant
Elongation at break	10.62+2.41 (A)
Tensile modulus	2.35-63.82 (C)
Notched impact	4.32+1.15 (A)
Unnotched impact	No significant
HDT	No significant
Sub zero temperature	
Notched impact (original)	No significant
Notched impact (cured)	No significant

4.1.6 Morphological investigation of PLA/silicone compounds

Morphological observation by SEM in order to trace the fracture behavior evidences of the sample was conducted. The SEM photographs of the fractured surface of the PLA/silicone blends obtained from Run#1, 5, and 8, and also from the neat PLA are shown in Figure 4.31 (***a***) to 4.31 (***g***). Run# 1 and Run#8 samples are represented the blend formula which were derived from inclusively low levels and high levels parameters, respectively. But Run#5 formula showed the relative high in impact properties at both room and sub zero testing temperatures. Phase separation between PLA matrix and silicone rubber are obviously seen at high level of content, Run#8. On the other hand, the separation is hardly seen at 0.5 phr of the rubber content. When compare the impact strength as shown in Table 4.3, it was found that high content of silicone shows the better strength than lower silicone utilization. PLA/silicone obtained from all low level of contents result in lowest elongation The larger fracture trace, from SEM, for high silicone blend would be explained the result. However, comparing between Run#5 and Run#8, where only silane and polyol were reduced to low levels, and the impact value is increased especially after the sauna curing. It is indicates that the chain crosslinking via the silane/water condensation reaction had greatly contribution to the material brittleness. Whereas the size of phase separated silicone particle is retrained. This SEM results are in agreement with the previous DOE analysis which showed that silane and polyol, especially silane, had the negative effect to the impact strengths of cured PLA/Silicone blends. Taken from the SEM photograph, it is seen that finer fracture surface higher in material brittleness vice versa rougher had better toughness.


(a)
10µm
SUT 10KV X500 44mm
(b)
10µm
SUT 10KV X500 44mm
(c)
10µm
SUT 10KV X500 46mm
(d)
10µm
SUT 10KV X500 45mm
(e)
10µm
SUT 10KV X500 45mm
(f)
10µm
SUT 10KV X500 45mm

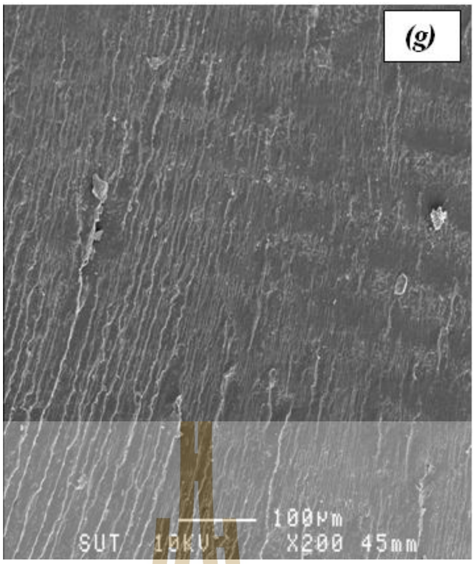


Figure 4.31 SEM micrograph of (***a***) run.1 (original), (***b***) run.1 (cured), (***c***) run.8 (original), (***d***) run.8 cured, (***e***) run.5 original, (***f***) run.5 cured (x500), (***g***) neat pla (x200).

Statistical study of PLA/silicone blend with adding silane as coupling agent and polyester polyol as plasticizer was found that silicone at high level of content can significantly improve the fracture toughness of the blends both at room and sub zero temperature. As expected, at high level of the rubber content, the tensile strength become lower but higher in the elongation at break. Silane/water reaction does fractionally and negatively influence on the fracture toughness by mean of the impact strengths especially when the material undergoes sauna treatment. The electron photographs are used to support the statement.

4.2 The effect of two components silicone system on PLA compound

From the previous experiment, the statistical responds and morphological results showed that the blend derived from run#5 had outstanding in toughness properties and also better in elongation value. It was compounded from high level of silicone, low level of silane and low level polyester polyol. Therefore, run#5 formula is interested in term of further mechanical properties improvement especially elongation as high as found in LDPE. From the DOE, it was found that the elongation property after sauna treatment of the blend was positive and significant achieved by the silicone content. Therefore, investigation of the maximum amount of the rubber addition is worth to explore.

In this experimental section, the blend formula from run#5, at low level of silane content, 1.0 phr, and low level of polyol content, 1.0 phr, with further varying silicone contents from 0 to 8 phr was examined. The designed formulae are summarized in Table 4.25. The test results obtained from injected specimen that were prepared from the given formula are also reported in Table 4.26 and 4.27.

Table 4.25 The designed formula with varying the two components silicone contents.

Run no.	PLA (g)	Silicone (g) (phr)	Silane (g) (phr)	Polyol (g) (phr)	Stabilizer (g) (phr)
1	700	0.0 (0.0)	7 (1.0)	7 (1.0)	7 (1.0)
2	700	14.0 (2.0)	7 (1.0)	7 (1.0)	7 (1.0)
3	700	28.0 (4.0)	7 (1.0)	7 (1.0)	7 (1.0)
4	700	42.0 (6.0)	7 (1.0)	7 (1.0)	7 (1.0)
5	700	56.0 (8.0)	7 (1.0)	7 (1.0)	7 (1.0)

Table 4.26 Rheological and tensile properties with increasing the silicone contents.

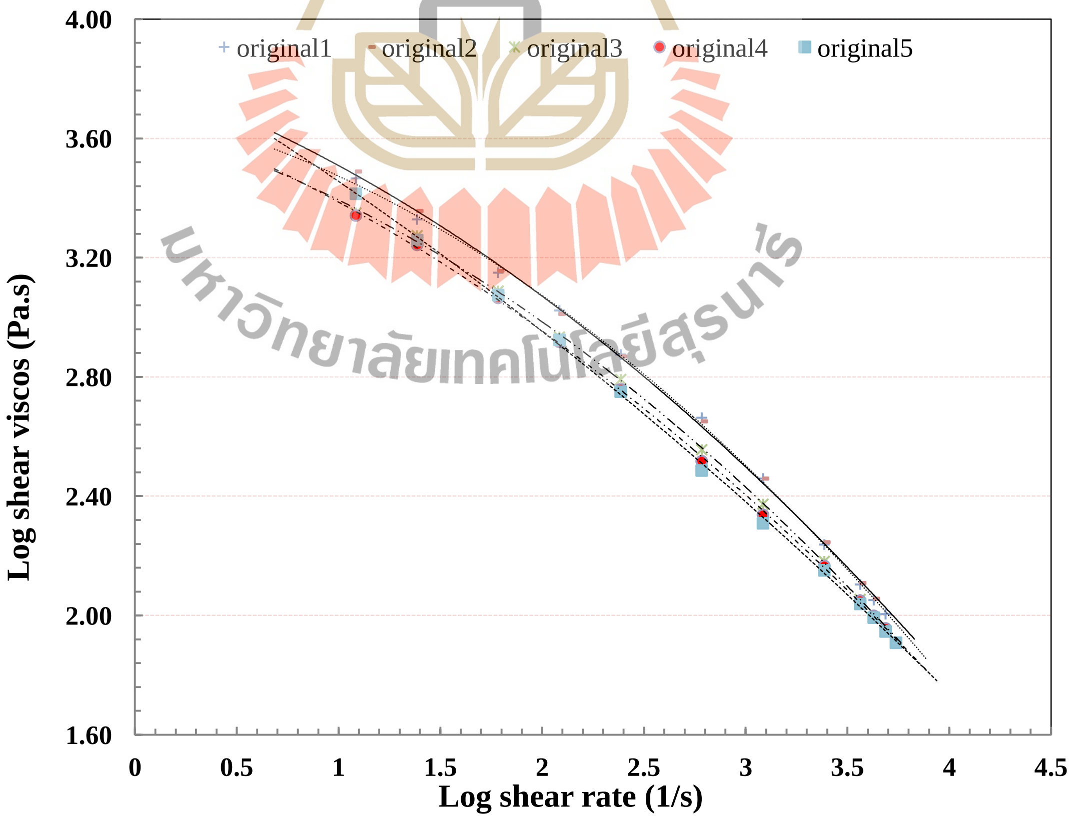
Silicone content (phr)	**η_o viscosity (Pa.s)**		**MFI (g/10min)**		**Tensile strength (MPa)**		**Elongation at break (%)**		**Young's modulus (GPa)**	
	Original	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**
LDPE	3698.28	3630.78	2.86±0.07	2.84±0.05	8.16±0.43	8.43±1.12	91.93±2.26	91.28±3.12	0.15±1.22	0.14±1.31
PLA	4655.47	4320.23	1.41±0.04	1.77±0.02	52.38±0.93	59.48±1.57	4.33±0.26	4.94±0.42	2.58±1.07	2.67±0.96
0.0	5495.41	3926.44	1.81±0.02	2.84±0.04	46.11±3.17	61.72±1.71	3.77±0.97	3.43±0.14	2.42±0.10	2.43±0.12
2.0	5067.36	4168.69	1.91±0.01	2.88±0.04	41.10±4.65	41.66±1.83	6.38±1.56	4.30±2.59	2.33±0.04	2.49±0.05
4.0	3854.78	2079.69	3.27±0.04	4.74±0.05	31.38±4.36	36.26±1.16	7.23±4.20	4.87±0.88	2.34±0.04	2.16±0.10
6.0	4083.19	2387.81	3.07±0.02	4.23±0.05	15.89±7.79	35.34±2.69	8.03±2.76	5.28±3.00	2.23±0.10	2.18±0.08
8.0	4881.59	2535.12	2.25±0.05	3.10±0.06	15.61±2.12	31.57±1.60	11.4±14.13	6.80±3.19	2.04±0.13	2.12±0.13

Table 4.27 Impact and thermal properties with increasing the silicone contents.

Silicone content (phr)	**Unnotched impact (kJ/m^2)**		**Notched impact (kJ/m^2)**		**Low temperature unnotched impact (kJ/m^2)**		**Low temperature notched impact (kJ/m^2)**		**HDT (^oC)**	
	Original	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**
LDPE	No break	No break	No break	No break	No break	No break	4.80±1.34	3.60±0.62	36.60±2.00	39.60±1.59
PLA	15.97±2.35	21.15±2.41	2.49±0.48	3.45±0.98	21.23±1.34	22.15±2.21	2.60±0.62	3.20±0.42	51.67±0.58	52.40±0.72
0.0	20.54±2.03	24.88±3.39	2.84±0.10	3.56±0.31	23.96±2.97	28.86±2.20	3.88±1.29	4.46±0.89	49.67±0.70	58.00±1.00
2.0	21.64±1.87	29.29±1.48	3.39±0.25	6.08±0.12	25.90±3.47	26.55±2.85	5.55±1.03	4.70±0.81	49.53±0.90	60.00±2.00
4.0	23.07±2.58	23.29±3.59	2.58±0.13	7.64±0.34	20.78±1.34	26.37±1.59	4.65±1.21	6.24±0.80	49.20±0.72	60.20±1.59
6.0	20.48±1.70	24.97±2.59	3.15±0.32	9.14±0.32	21.65±1.88	35.44±1.69	4.04±1.03	6.54±0.49	47.53±0.42	60.13±0.81
8.0	22.23±1.72	33.73±0.48	7.68±0.82	12.45±0.26	23.79±1.76	35.53±1.06	6.40±0.36	6.97±0.20	47.67±0.58	60.00±2.50

4.2.1 Shear viscosity versus silicone contents analysis

The shear stress and appearance shear rate plots performed at 180^{o}C of the blends at the given silicone contents are illustrate the Figure 4.32 (**a**) and 4.32 (**b**), for the original and cured sample, respectively. From the plots, the zero shear viscosities ($\boldsymbol{\eta_o}$) derived through the power law model are also obtained and reported in Table 4.26. It is seen that the $\boldsymbol{\eta_o}$ of the PLA blends are shows shear viscosity as a function of shear rate and illustrate shear thinning behavior. After sauna curing process the zero shear viscosity was lower than original sample. The decreasing in the viscosity through the sauna treatment might be due to the moisture residual in the compound that would cause the chain degradation via the hydrolysis during the polymer melting.



(a)

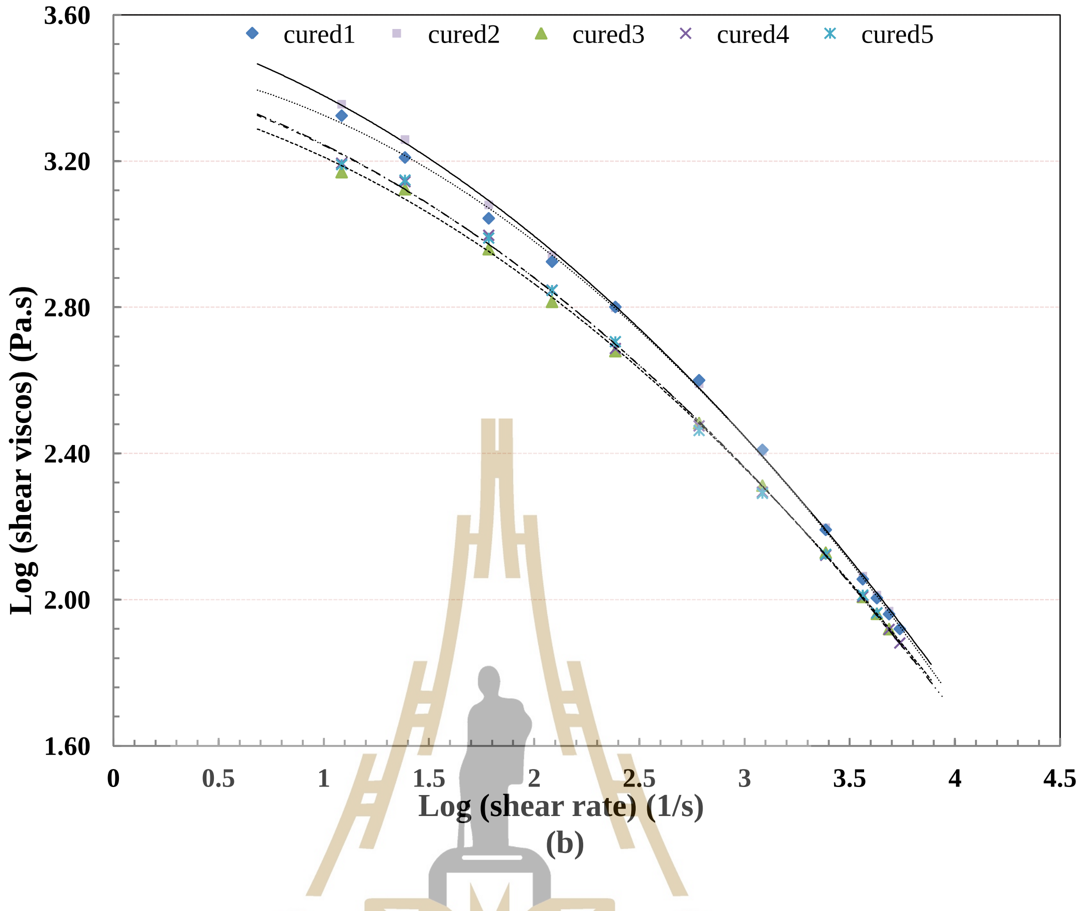


Figure 4.32 Shear viscosity plot of the PLA/silicone blends; (a) original and (b) after sauna treatment, respectively.

4.2.2 MFI versus silicone contents analysis

The rheological properties at constant load were measured by the melt flow index. The test results are recorded and plot as function of silicone content in Table 4.26 and Figure 4.33, respectively. MFI of PLA compounds show the tendency to increase with increasing the silicone content except at 6 to 8 phr where the test values are decreased. The similar trend is found in the cured samples. It also seen that the MFI is increased after the sauna incubation. The increasing in the MFI of the blends is probably explained by the fact that the silicone system used in this experiment is two components system. But there was no curing added into the compound system therefore, the added rubber remained completely uncured. Adding more uncured rubber into the compound ingredient, the rubber would act as plasticizer rather than thoughener. As the result, the viscosity of the material would become lower, higher in flow ability, at the higher rubber contents. Further adding the short chain rubber, phase separation would be occurred and hence lower in flow ability of the material.

4.2.3 HDT versus silicone contents analysis

Plotting the HDT of PLA/silicone blends as reported in Table 4.27 with the amount of silicone is shown in Figure 4.33. It is indicated that HDT of the PLA blends are lower than that obtained in pure PLA and PLA compound without addition of silicone, especially for the original samples. It is also observed that the HDT values are slightly decreased with increasing the silicone addition. However, condensation reaction via the silence/moisture incubation the samples are higher the HDT of the material and it overcome the negative effect of silicone characteristic. There is no obvious changing in the HDT of the PLA blend in correspondence the silicone contents of the sauna cured specimen. From the results found, it explained that the resistance of the material in the increasing in the environment temperature of these PLA blends is mainly come from the ability of the continuous phase to withstand the hazard temperature fluctuation.

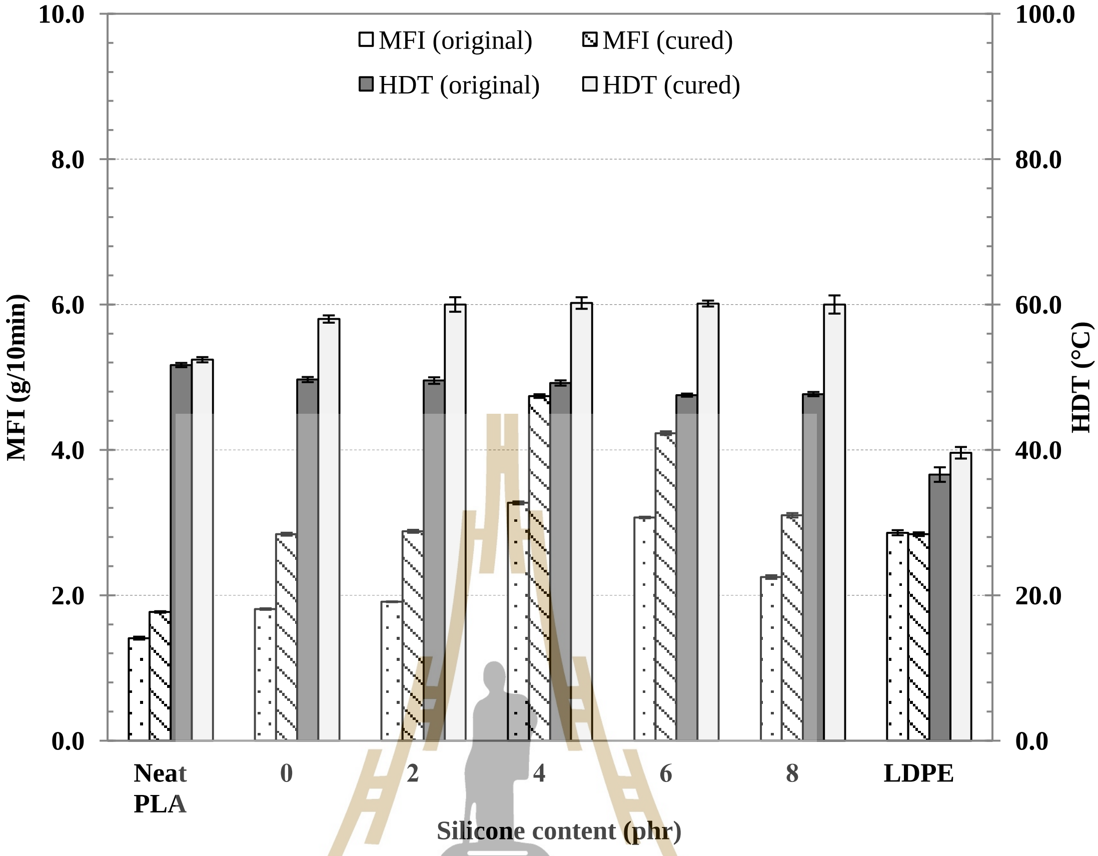


Figure 4.33 HDT and MFI of the compound as a function of silicone content.

4.2.4 Tensile properties versus silicone contents analysis

The plot of tensile strength and modulus with the silicone contents are shown in Figure 4.34. It is observed that tensile strength of the original and also cured sample are gradually decreased with increasing the silicone content. The tensile strength of the cured sample is higher than the original sample. The difference between the two is very obvious when higher silicone content is added. However there is no consistency between the modulus of the original and cured. But generally, sauna incubation give rise to the fractionally increase in the modulus. For the test result of elongation at break concluded in Figure 4.35. It is seen that the deformation at break of the compound is also increased with increasing the silicone content.

Silane/moisture condensation reactions lower the flexibility of the polymer compound.

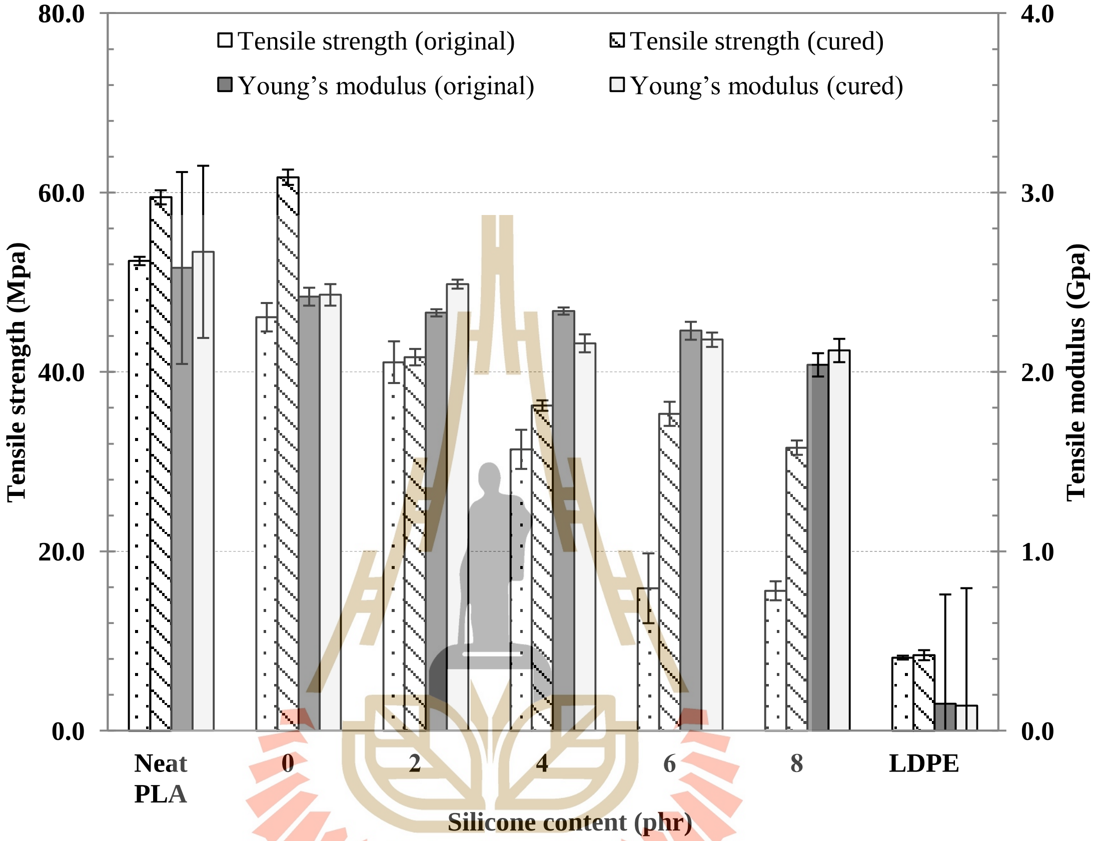


Figure 4.34 Tensile strength and tensile modulus of the compound as a function of silicone content.

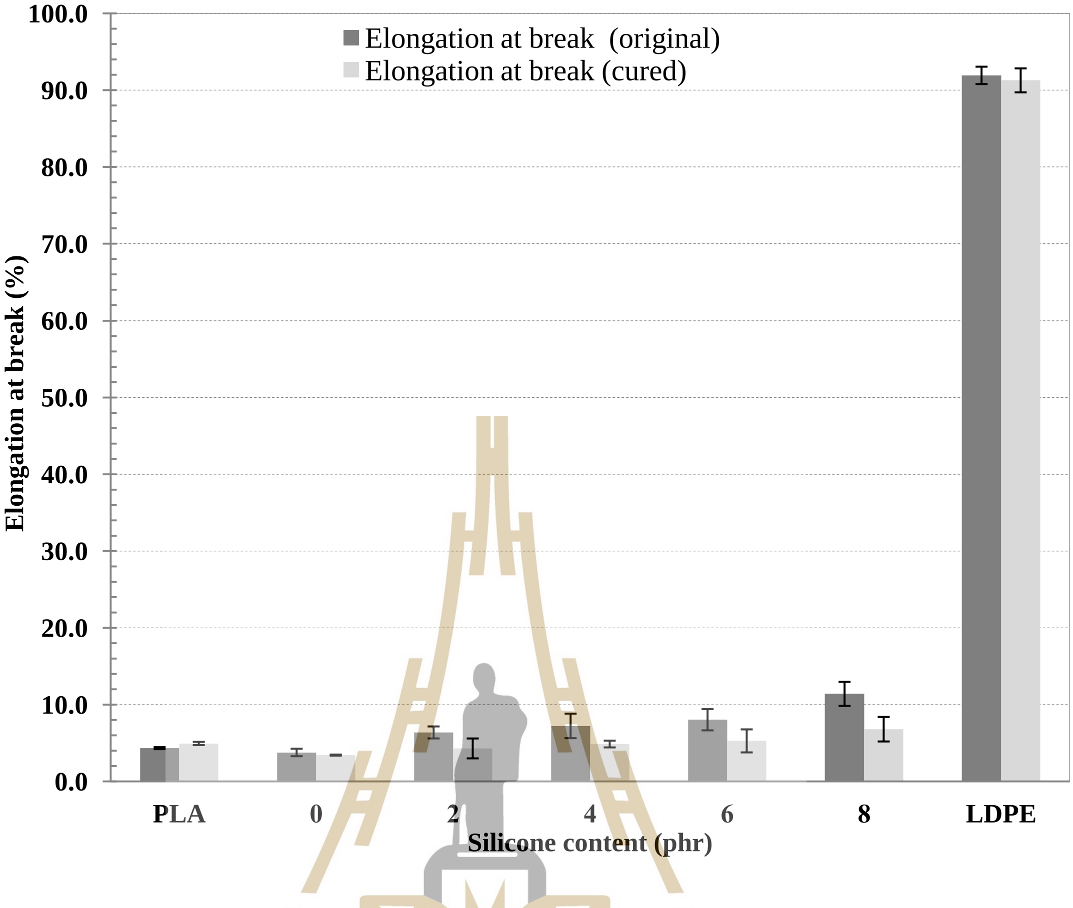


Figure 4.35 Elongation at break of the compound as a function of silicone content.

From the tensile properties, it reveals that there is obvious domination of the silicone rubber on the PLA/silicone compound. As the silicone content is increased, the elastomeric behavior; low strength and modulus, and high elongation at break, of the compound is noticed. Network forming via the silane/moisture reaction, probably in the rubber phase, causing the compound behave less rubbery. This observation will be further seen in later the impact properties.

4.2.5 Impact strength versus silicone contents analysis

The notched and unnotched impact test results performed at room temperature against the silicone contents as summarized in Table 4.27, they are also graphically presented in Figure 4.36. Similar to those previously found for the other tests, it is seen that the notched impact strength of the sauna cured compound is noticeably higher than the original sample for all compound. Closer observation, it also indicates that are increased with increasing the silicone content for both notched and unnotched impact strength with and without sauna curing. Within this experiment conducted, adding 8 phr of two packs silicone rubber into the PLA compound shows the maximum impact strengths. It reviews that the silicone rubber acts as the impact modifier, or impact energy absorber, for the compound. The highest value is still higher than the impact value obtained from the virgin PLA. But, it is lower than LDPE which is the polymer commonly used for manufacture the frozen food packaging. This polymer is reported as non break (nb) under the given impact energy, 2.7 joule.

The main purpose of this research work is to obtain the compound to manufacture frozen food packaging. Therefore, the impact test at the actual application condition, for below 0^oC, is important. The notched and unnotched impact strengths at low temperature, at approx. -98^oC, are plotted against the silicone contents and illustrated in Figure 4.37. The similar trend to those tested at room temperature is found. The impact strengths are slowly increased with increasing the silicone contents. However, with the compensation of silane/moisture reaction during sauna cure, the strength of the sample is significantly higher than the original and dramatically increased with adding more silicone rubber. Again, the highest test value is found at 8 phr of silicone concentration. The figure is not only higher than the number obtained from virgin PLA but also higher that the test value derived from the film grade LDPE.

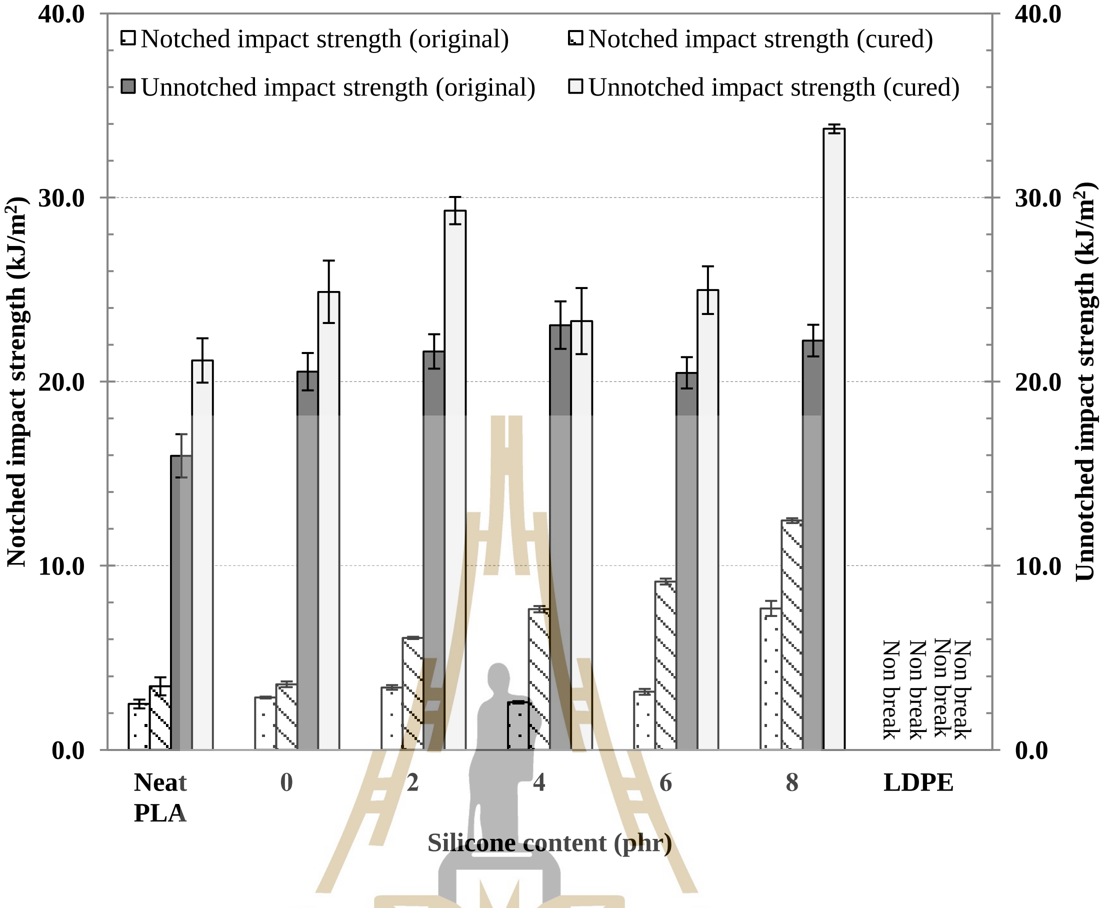


Figure 4.36 Impact properties of the compound as a function of silicone content.

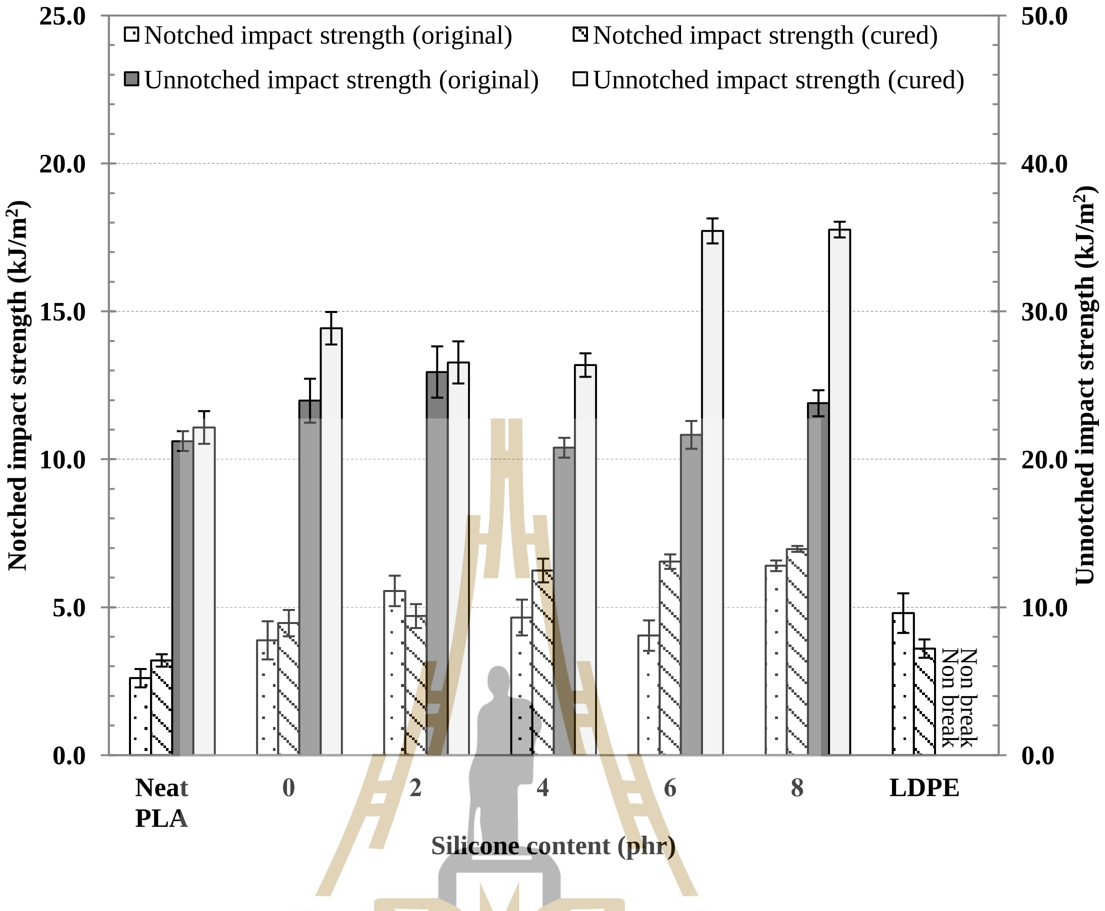
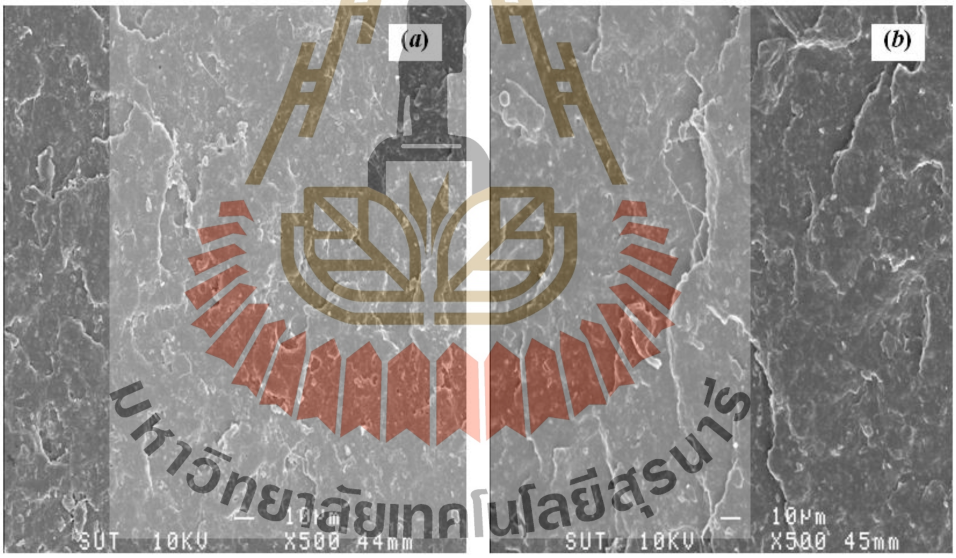


Figure 4.37 Impact properties at low temperature of the compound as a function of silicone content.

4.2.6 Scanning electron microscopy (SEM)

The miscibility between added silicone rubber and PLA is important not only the mechanical properties point of view but the appearance of the compound is also concerned. Clear or at least translucent packaging is prime desirable for food packaging. General observation, it is evidenced that the injected specimen from the compound is translucent. The clarity or light transmit ability is inversed with the silicone content. Therefore, the discussion of the miscibility between PLA and silicone rubber is verified by the phase homogeneity through the SEM technique.

Figure 4.38 (*a*) to 4.38 (*d*) are the SEM photographs obtained from fractured notched specimens of the compound with silicone contents at 4.0 phr and 8.0 phr for the original and sauna cured, respectively. From the phase separation on the surfaces of PLA/silicone compounded at high silicone, 8 phr, show signify rougher fracture surface. It indicates that the high silicone content specimen has the better impact strength than lower silicone one. From the picture, there is no significant different in the separated silicone phase between 4.0 and 8.0 phr of silicone addition which seen as ultra tiny separated particle. These dispersed droplets are believed to be the silicone rubber.



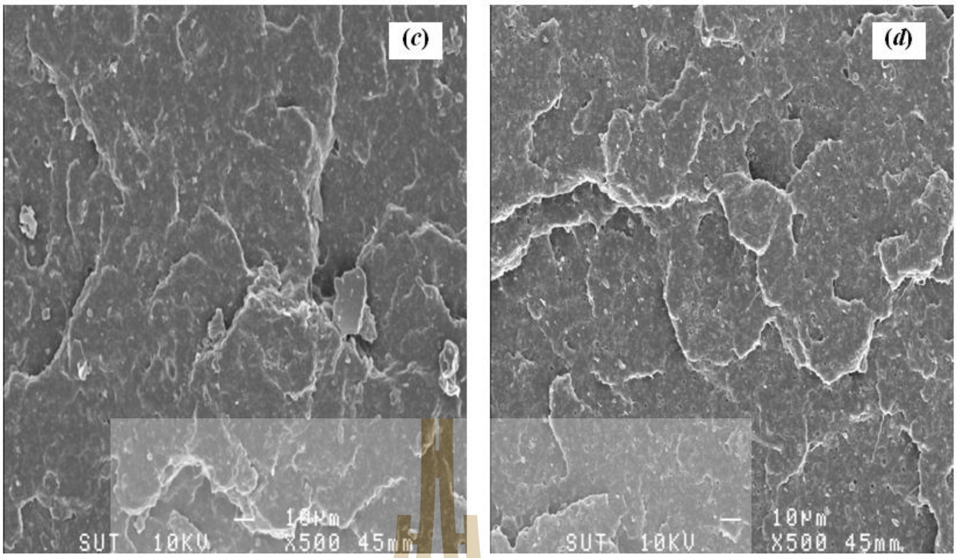


Figure 4.38 SEM micrograph of PLA/silicone compound with silicone contents; (*a*) 4 phr (original), (*b*) 4 phr (cured), (*c*) 8 phr (original) and (*d*) 8 phr (cured), respectively.

From the overall results summarized in Table 4.26 – 4.27 and also from the morphological investigation, it can state that the PLA/silicone compounds at silicone content varied from 0.0 - 8.0 phr are increased with increasing the rubber incorporation especially the toughness both at room temperature and sub zero temperature. With the assisting of the sauna incubation process, the properties are further improved. Moreover, the sample with 8.0 phr of silicone content demonstrates the highest properties value. The impact properties, in especially, of compound are increased after incubation. However, as silicone rubber employed in this experimental section is two packs silicone system but it was used without adding the curing agent, amine reagents. Next experiment, adding the TETA as silicone curing agent will be discussed.

4.3 Effect of TETA hardener for two component silicone on PLA/silicone compound

From the previous experiments, blending PLA with two component silicone system without adding the rubber curing agent, found that the mechanical and thermal properties of PLA compound is not as good as obtained from LDPE. In this section, adding amine, namely triethylenetetramines (TETA), as curing agent for the two component silicone system will be discussed. Proper cured silicone normally provides better mechanical, flexibility and thermal properties than the incomplete rubber. According to the rule of mixture, blending PLA with cured silicone would possibly enhance the properties of the compound especially those elongation at break. From the previous results, the mechanical value and morphological analysis showed that the blend PLA with 8 phr of silicone had decent properties especially at low temperature. Therefore, silicone content at this concentration was retained. Addition of curing agent, TETA, into the system is the major interested in term of the properties enhancement of the PLA/silicone compound.

The blend formula with silicone content of 8.0 phr, 1.0 phr of silane, 1.0 phr of polyol and 1.0 phr of processing stabilizer was adopted as shown in Table 4.28. The TETA, the silicone hardener, was varied from 0.1 to 1.0 phr in corresponded with amount of silicone used were assigned. The identical compounding processes as previously performed were repeated. The test results obtained from the injected specimen of the PLA/cured silicone compound are given in Table 4.29 and 4.30.

Table 4.28 The blend formula and TETA concentrations.

Run No.	**PLA (g)**	**Silicone (g) (phr)**	**TETA (g) (phr of silicone)**	**Silane (g) (phr)**	**Polyol (g) (phr)**	**Stabilizer (g) (phr)**
1	800	64.0 (8.0)	0.000 (0.0)	8 (1.0)	8 (1.0)	8 (1.0)
2	800	64.0 (8.0)	0.064 (0.1)	8 (1.0)	8 (1.0)	8 (1.0)
3	800	64.0 (8.0)	0.256 (0.4)	8 (1.0)	8 (1.0)	8 (1.0)
4	800	64.0 (8.0)	0.384 (0.6)	8 (1.0)	8 (1.0)	8 (1.0)
5	800	64.0 (8.0)	0.512 (0.8)	8 (1.0)	8 (1.0)	8 (1.0)
6	800	64.0 (8.0)	0.640 (1.0)	8 (1.0)	8 (1.0)	8 (1.0)

Table 4.29 Rheological and tensile properties of PLA/silicone with TETA contents.

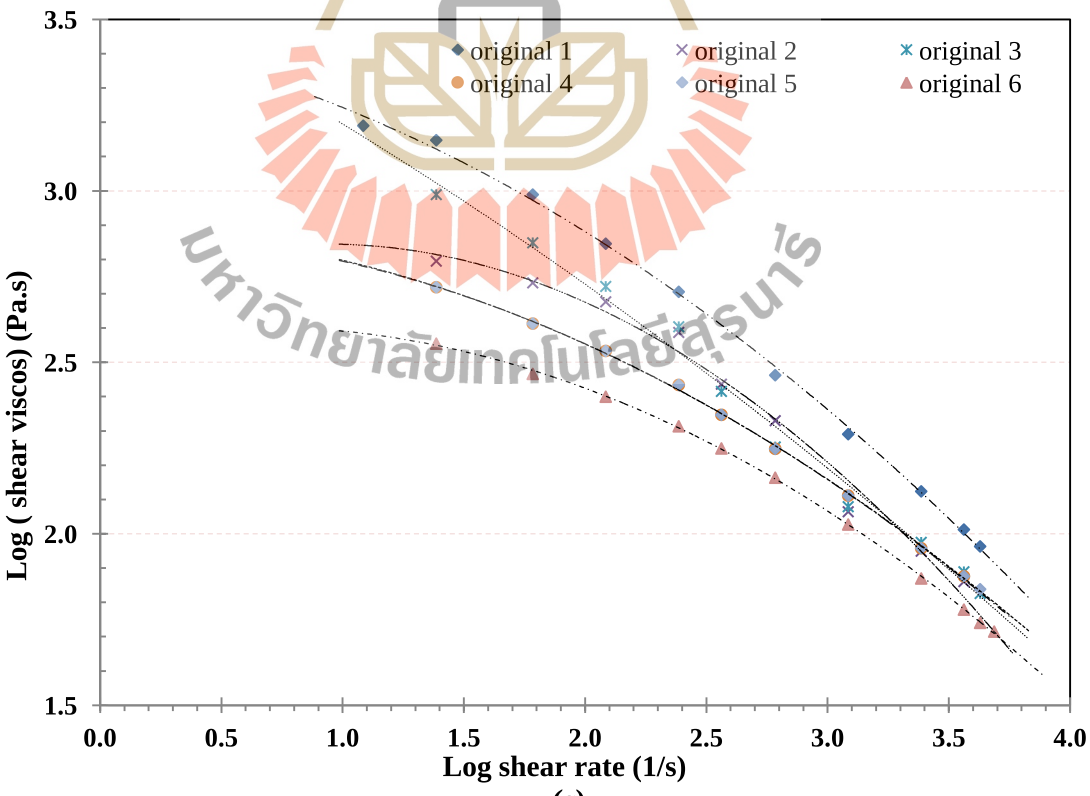
TETA content (phr)	η_o viscosity (Pa.s)		MFI (g/10min)		Tensile strength (MPa)		Elongation at break (%)		Young's modulus (GPa)	
	Original	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**
LDPE	3698.28	3630.78	2.86±0.07	2.84±0.05	8.16±0.43	8.43±1.12	91.93±2.26	91.28±3.12	0.15±1.22	0.14±1.31
PLA	4655.47	4320.23	1.41±0.04	1.77±0.02	52.38±0.93	59.48±1.57	4.33±0.26	4.94±0.42	2.58±1.07	2.67±0.96
0.0	3715.35	1905.46	2.25±0.05	3.10±0.06	15.61±2.12	31.57±1.60	11.4±14.13	6.80±3.19	2.04±0.13	2.12±0.13
0.1	1513.56	1676.08	3.98±0.18	3.48±0.08	23.63±6.26	33.45±2.19	13.59±4.76	13.35±7.62	2.24±0.91	2.14±1.09
0.4	676.08	1047.12	6.13±0.22	4.87±0.16	19.09±6.41	30.89±0.52	27.28±5.61	21.16±7.63	2.26±0.59	2.22±0.47
0.6	301.99	758.57	7.64±0.33	6.54±0.36	19.48±5.18	29.04±0.31	16.91±3.86	8.76±1.43	2.17±0.37	2.01±0.58
0.8	457.01	691.83	8.50±0.47	7.02±0.17	20.58±8.80	28.09±0.58	14.84±4.01	15.24±4.16	2.15±0.21	2.00±0.92
1.0	275.42	426.57	10.36±1.06	9.70±0.09	21.83±9.29	28.53±0.32	15.53±12.02	13.93±5.63	2.15±0.28	2.08±0.43

Table 4.30 Impact and thermal properties of PLA/silicone with TETA contents.

TETA content (phr)	**Unnotched impact (kJ/m^2)**		**Notched impact (kJ/m^2)**		**Low temperature unnotched impact (kJ/m^2)**		**Low temperature notched impact (kJ/m^2)**		**HDT (°C)**	
	Original	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**
LDPE	No break	No break	No break	No break	No break	No break	4.80±1.34	3.60±0.62	36.60±2.00	39.60±1.59
PLA	15.97±2.35	21.15±2.41	2.49±0.48	3.45±0.98	21.23±1.34	22.15±2.21	2.60±0.62	3.20±0.42	51.67±0.58	52.40±0.72
0.0	22.23±1.72	33.73±0.48	7.68±0.82	12.45±0.26	23.79±1.76	35.53±1.06	6.40±0.36	6.97±0.20	47.67±0.58	60.00±2.50
0.1	19.38±3.25	31.43±2.23	6.24±1.27	11.43±0.68	29.46±3.89	34.97±0.68	6.50±0.83	6.93±0.54	42.67±0.58	53.33±1.15
0.4	37.74±6.13	67.75±2.05	7.77±0.54	13.19±0.32	35.40±1.93	51.55±4.23	6.63±0.69	7.07±0.46	44.10±0.17	52.00±1.00
0.6	25.63±0.71	33.48±1.29	7.53±0.50	9.75±0.27	34.67±1.36	38.21±5.45	5.82±0.31	5.51±0.19	43.43±0.51	51.67±1.15
0.8	31.48±5.02	32.14±3.87	8.45±1.16	4.64±1.50	36.52±1.82	45.98±8.41	5.89±0.66	5.43±0.76	43.20±0.35	51.46±0.50
1.0	27.41±3.09	33.93±4.65	5.42±0.53	6.84±0.12	29.76±3.41	45.71±8.49	6.87±0.74	3.94±0.69	42.53±0.50	51.20±1.06

4.3.1 Shear viscosity versus TETA contents analysis

The shear viscosity and appearance shear rate plots performed at 180°C of the blends at the given silicone contents are present the Figure 4.39 (***a***) and 4.32 (***b***), for the original and cured sample, respectively. From the plots, the zero shear viscosities ($\boldsymbol{\eta_o}$) derived through the power law model are also obtained and reported in Table 4.29. It is seen that the $\boldsymbol{\eta_o}$ of the PLA blends are shows shear viscosity as a function of shear rate and illustrate shear thinning behavior. After sauna curing process the zero shear viscosity was higher than original sample because after the sauna incubation with the chain bonded via silane/moisture coupling reaction, probably crosslinking, the $\boldsymbol{\eta_o}$ of the compound would be decreased, higher in melt viscosity.



(a)

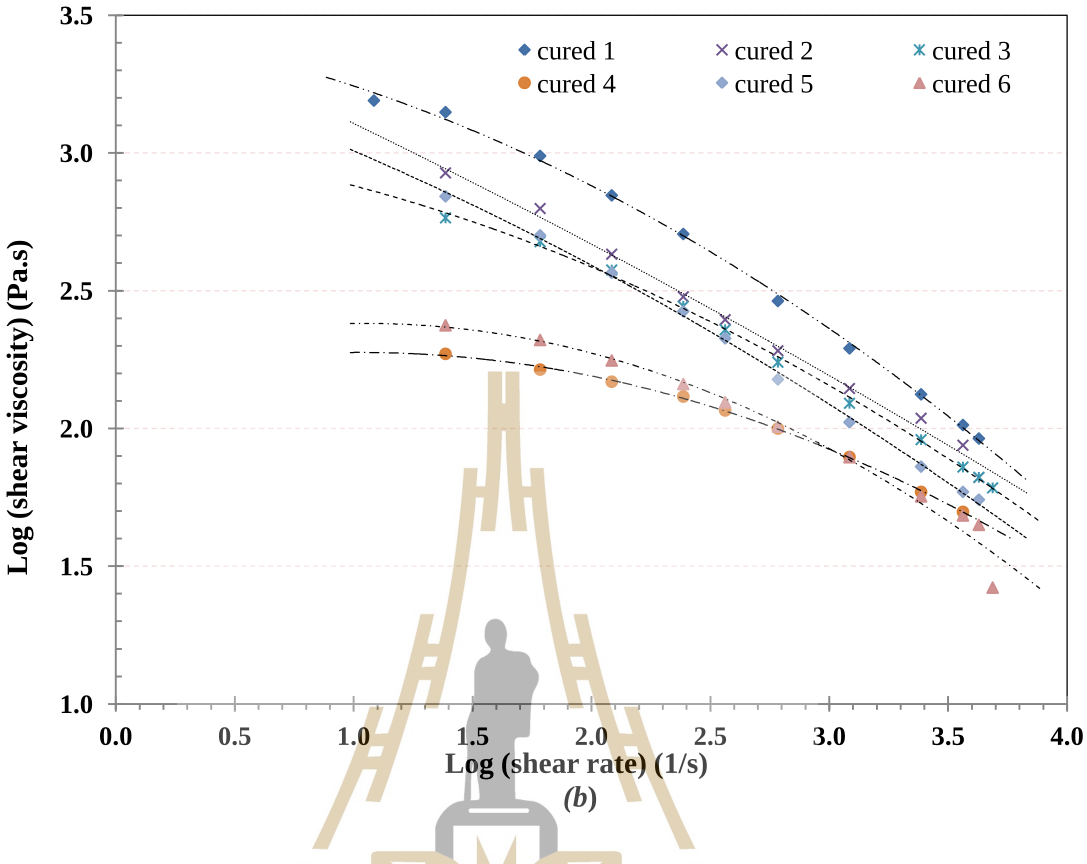


Figure 4.39 Shear viscosity plot of the PLA/silicone formula; (a) original samples and (b) sauna treated, respectively.

4.3.2 MFI versus TETA contents analysis

Not only the shear viscosity of the PLA/cured silicone compound was analyzed but also the rheological properties at the static load were measured by the melt flow index. The MFI of the compound with respect to the TETA curing agent content are given in Table 4.29 and plotted as shown in Figure 4.40. It is seen that MFI of the PLA compounds is linearly increased with increasing the TETA content for both original and cured samples. However, it is observed that the MFI is decreased after the sauna incubation. The increasing in the MFI of the blends with increasing the

TETA is probably explained by the hypothesis that the TETA added into the compound would not only act as the curing agent for the silicone rubber but the excess amount of TETA or unreacted TETA would also undergo aminolysis with PLA. Hence, the degraded polymer chain would become more liquidized. As the result, the viscosity of the material would be lower, higher in flow ability, at higher TETA contents. After the sauna incubation with the chain bonded via silane/moisture coupling reaction, probably crosslinking, the MFI of the compound would be decreased, higher in melt viscosity. This statement will be emphasis by the mechanical properties, especially toughness, later on.

4.3.3 HDT versus TETA contents analysis

HDT of PLA/silicone blends obtained from the design matrix formula and also of virgin PLA and blown film grad LDPE as reported in Table 4.30 are plotted with the amount of TETA is shown in Figure 4.40. It is observed that HDT of the compounds are slightly decreased with increasing the TETA content. Sauna curing causes the marginally increase in the HDT. When compare with the virgin polymers, it is found that HDT of the compounds without sauna cured are lower than neat PLA but higher than LDPE. However, condensation reaction via the silane/moisture incubation the samples has elevated the HDT of the material as high as found for the original polymer. Moreover, there is no obvious differ in the HDT of the PLA blends with correspondence to the increasing in TETA contents. Except for the sample prepared without TETA curing agent where the HDT is oddly high.

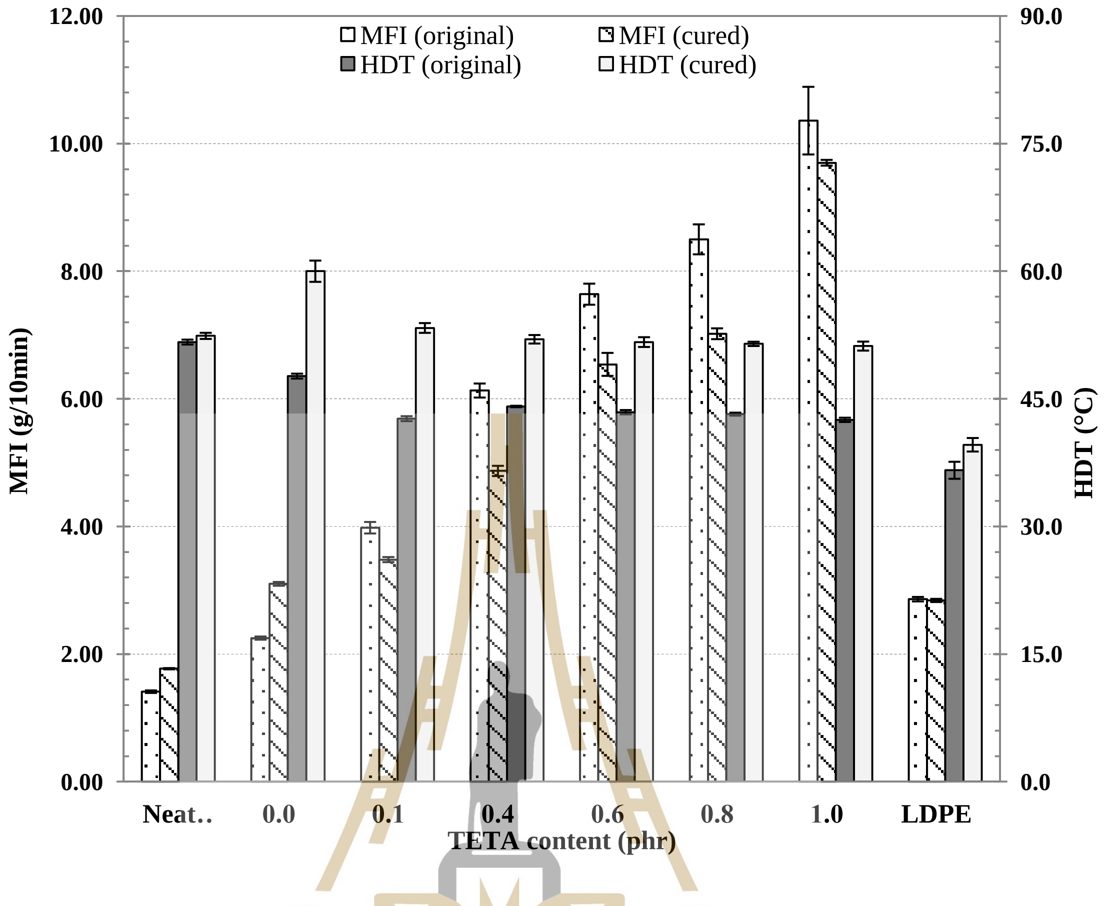


Figure 4.40 HDT and MFI of TETA cured PLA/silicone compounds.

From the results found, it can be explained that adding TETA as silicone curing agent does decrease the service temperature of the PLA/silicone blends. The decreasing might be due to the degradation of polymer chain via the aminolysis reaction between the excess amine and PLA chain as previously indicated by the MFI. But chain reconstruction occurred through the silane/moisture condensation reaction brought back the HDT to the higher value.

4.3.4 Tensile properties versus TETA contents

Figure 4.41 shows the plot of tensile strength and modulus of PLA/silicone blend with amount of TETA curing agent. It is observed that tensile strength of both original and cured samples are slightly decreased with increasing the TETA content. It is also seen that curing of the sample obviously increases the strength. The similar trend is found for the modulus properties with slightly decreasing in the test figure via the sauna treatment. For the elongation at break of the samples that are shown in Figure 4.42, it is seen that the strain at break is increased with increasing the TETA content to 0.4 phr after that it is decreased. The silane/moisture condensation reaction does generally lower the flexibility of the blends. However, in comparison between the PLA blends with PLA and LDPE, it is noticeably seen that the strength and modulus is much lower than neat PLA but vastly higher than LDPE, vice versa with the material flexibility.

From the tensile results, it reveals that there is obvious domination of adding TETA as silicone curing agent on the PLA/silicone compound. TETA addition enhances the tensile properties of the blend. Further adding the amine above 0.4 phr content, the inferior in the elastomeric behavior; low strength and modulus, and low elongation at break, of the compound is noticed. Network forming via the silane/moisture reaction, probably in the matrix phase, causing the compound behave less rubbery. The excess of TETA addition that might lead to the chain degradation probably used to explain the inferiorly of the tensile properties. This observation will be further refine in later the results.

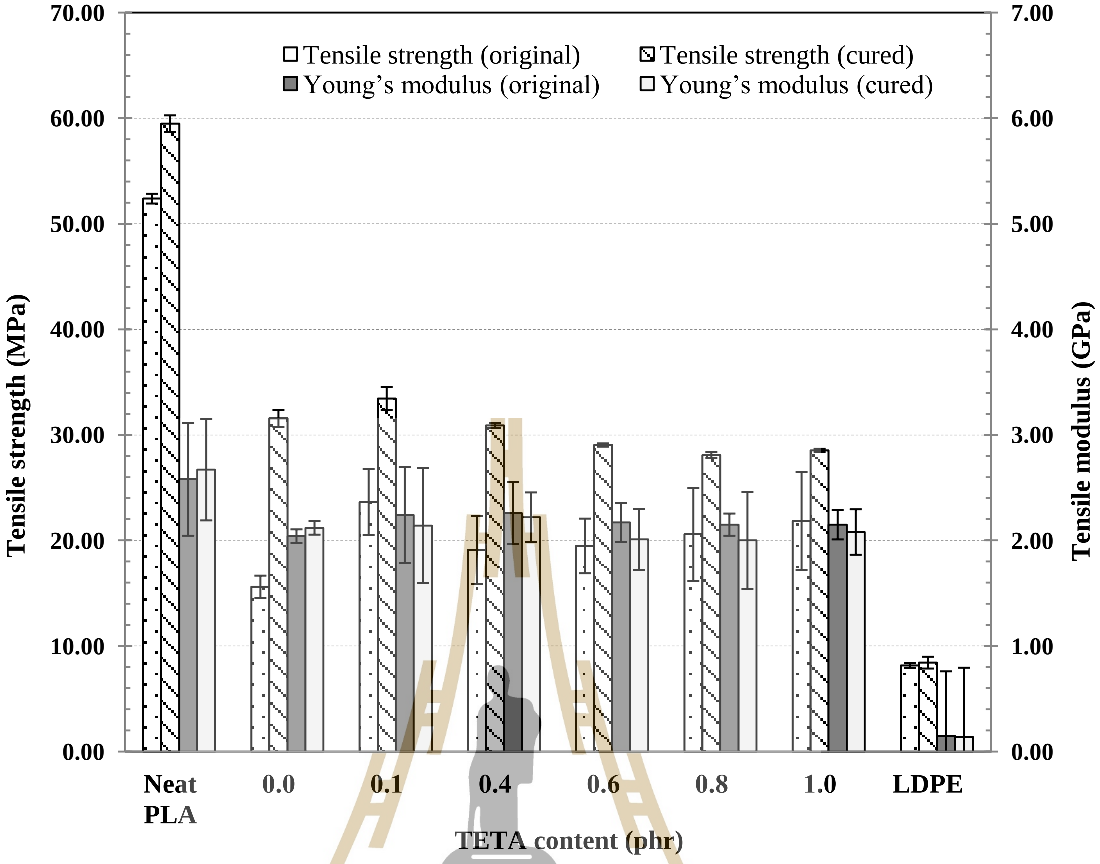


Figure 4.41 Tensile strength and modulus of TETA cured PLA/silicone compounds.

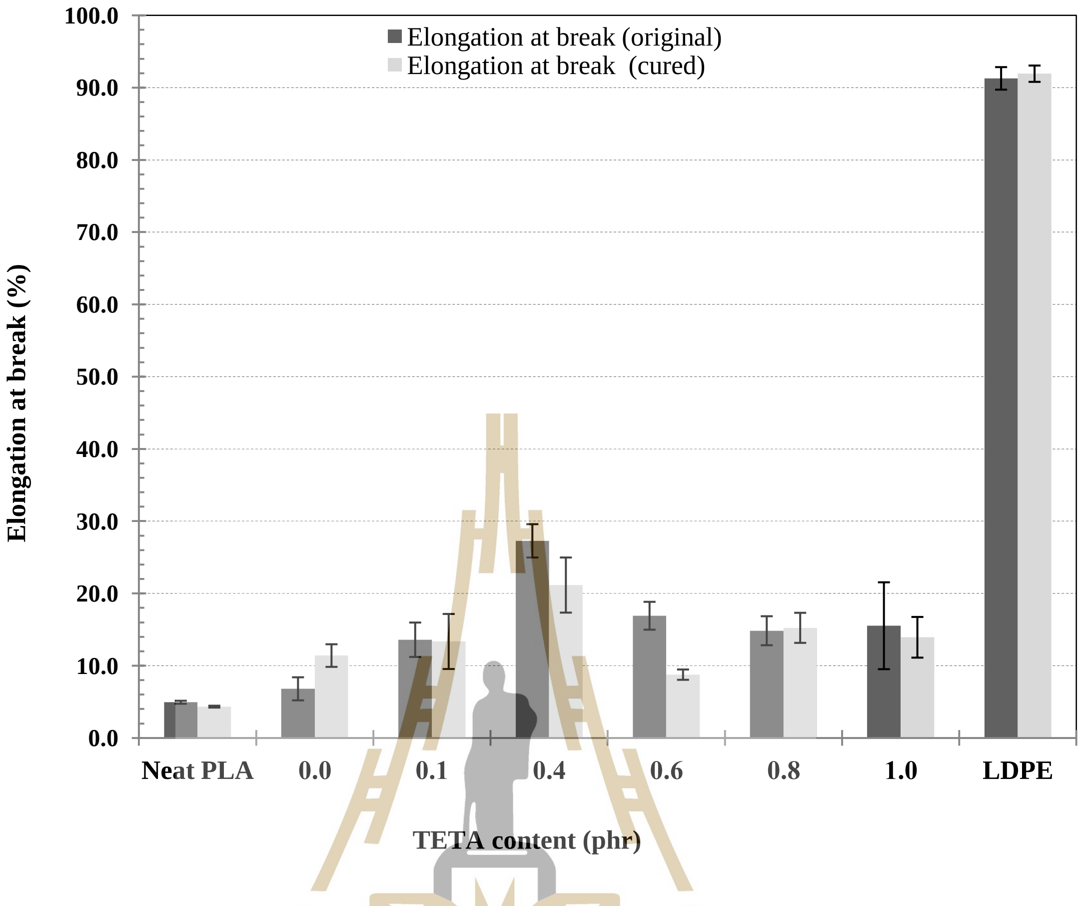


Figure 4.42 Elongation at break of TETA cured PLA/silicone compounds.

4.3.5 Impact strengths versus TETA contents

The notched and unnotched impact strength results conducted at room temperature against the TETA contents as summarized in Table 4.30 and they are also graphically represented in Figure 4.43. Similar to those previously found in the earlier discussions, it is seen that the notched and unnotched impact strengths are slightly increased with increasing the TETA contents, however, adding the amine beyond 0.4 phr the properties are seemingly decreased. Unexpectedly, the sauna cured treatment has noticeably higher the strengths. At the given test temperature, it is seen that strengths of the PLA blends are superior than neat PLA but much lower than LDPE.

Unbreakable with the assigned impact energy of LDPE is observed at room temperature test condition.

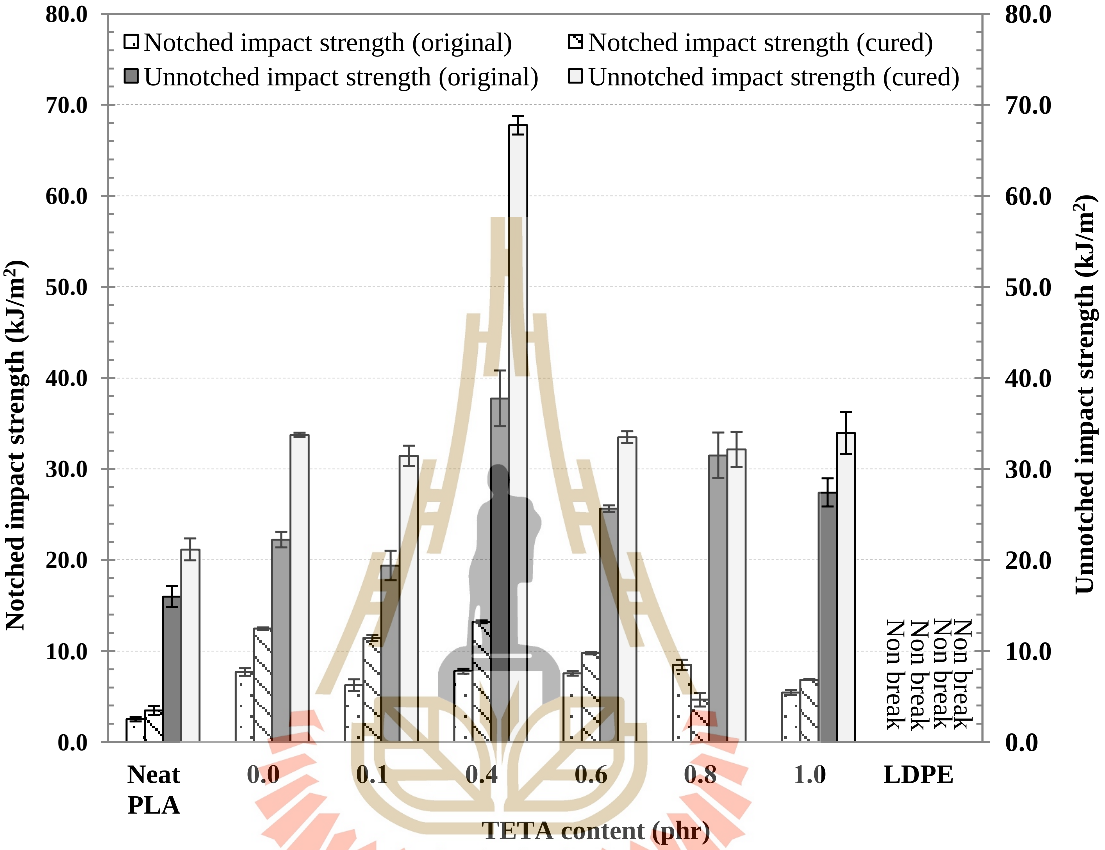


Figure 4.43 Impact properties of TETA cured PLA/silicone compounds.

Figure 4.44 illustrates the plot of notched and unnotched impact strengths at sub zero temperature, at approx. -98^{o}C, of PLA/silicone blends against the TETA contents. The similar trend to those tested performed at room temperature is found. The maximum impact strengths for both notched and unnotched are found at 0.4 phr of TETA addition. Beyond this concentration, the toughness of the compound is decreased. It is also noticed that the notched strength of the blends is not only higher than the number obtained from virgin PLA but also higher than the test value derived from the film grade LDPE. However, for the unnotched test, the strength of LDPE is still much higher than the PLA blends as it is unbroken with the given impact energy, 5.4 joule.

The relationship between the impact strengths, both at room and low temperatures testing, and the amount of TETA added into PLA/silicone blend is found that increasing the TETA from 0.0 to 0.4 phr has increased the strengths beyond this concentration the toughness is decreased. The results could reinforce the earlier statement that the excess of TETA using as silicone curing agent would react with the PLA chain and causing the depolymerization process. As the result, the compound would become inferior in the ductility and fracture toughness.

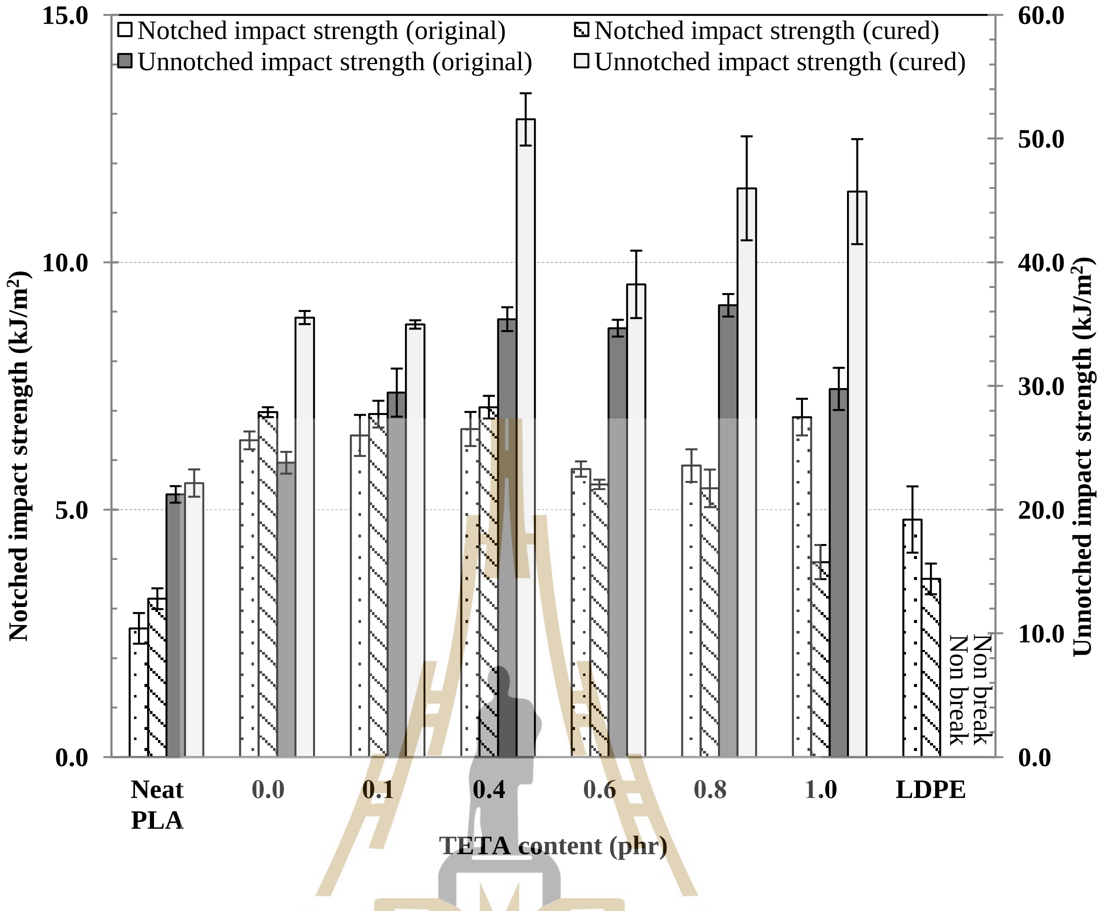
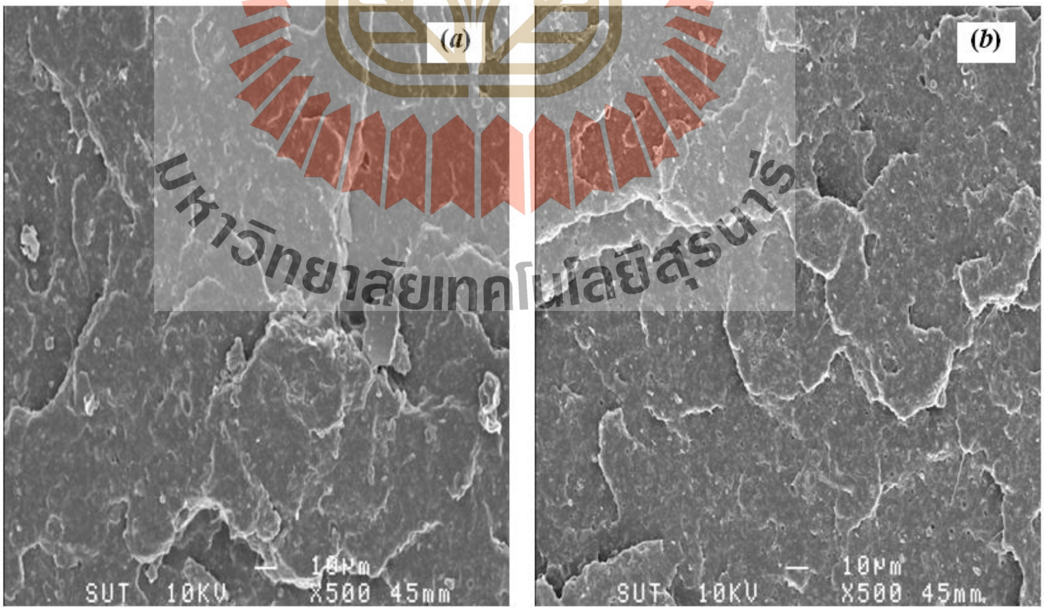


Figure 4.44 Impact properties at low temperature of TETA cured PLA/silicone compounds.

4.3.6 Scanning electron microscopy (SEM)

The miscibility between added silicone rubber and PLA is important not only the mechanical properties point of view but appearance, especially clarity of film product, of the compound is also concerned. Clear or at least translucent packaging is prime desirable for food packaging. General observation, it is observed that the injected specimen from the compound is heavily translucent. The clarity or light transmit ability was evidenced that it was inversed with the silicone content. Therefore, the discussion of the miscibility between PLA and silicone rubber was verified by the phase homogeneity through the SEM technique. Figure 4.45 (*a*) to 4.45 (*d*) are the SEM photographs obtained from fractured surface of the notched specimens of the compound having the TETA contents of 0.0 and 0.4 phr, respectively. When compare between sample without and with 0.4 phr TETA, it is seen that there is no obvious different in term of size of the dispersed phase. However, with compare between sample with sauna and no sauna treatment at the same TETA content, it is seen that the dispersed phase is more distinctive. It size become obviously seen smooth. By the point of fracture toughness, slightly smoother trace surfaces of 0.4 phr TETA added PLA/silicone compounded than the sample without TETA addition. It indicates that adding TETA curing agent into the two pack silicone system can improve the fracture toughness of the compound as indicated by the impact strength in Table 4.30.



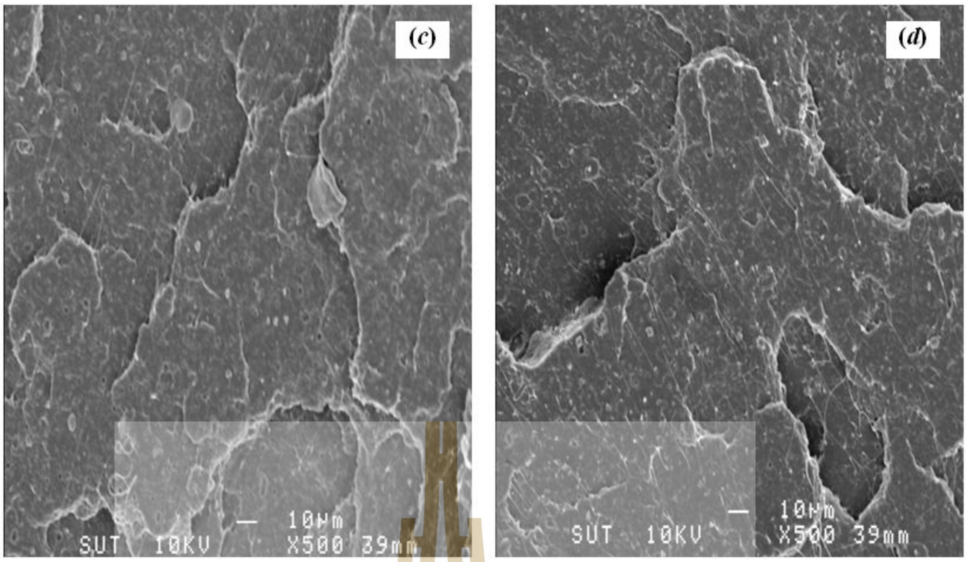


Figure 4.45 SEM micrograph of the TETA cured PLA/silicone compounds; (***a***) 0.0 phr (original), (***b***) 0.0 phr (cured), (***c***) 0.4 phr (original) and (***d***) 0.4 phr (cured) , respectively.

4.3.7 Elementary biodegradability observation

One of the most important properties for conduction biodegradable polymers research is the biodegradability of the material. Also, the main purpose of this study is to obtain the biopolymer applied for frozen food packaging which has good service properties and it must be biodegraded under the landfill condition. Therefore biodegradability testing is necessarily. The test was conducted by using the simulated landfill chamber at 60^{o}C under aerobic atmosphere as previously described in the experimental section. Figure 4.46 shows the plot between sample weigh lost against the buried times of the PLA/silicone compound and pure PLA specimen. The result indicates that neat PLA sample is slightly degraded within four weeks of buried time. After that the biodegradation rate is visibly increased. Within ten weeks of the composted time, the sample was disintegrated into small pieces where the weight loss measurement cannot be performed. Similarly, the PLA/silicone compounded at 8.0 phr of silicone, 1.0 phr of silane, 1.0 phr of polyol and 0.4 phr of TETA, both original and cured, manifest that the degradation process is initially observed after four weeks of burying. After that, the degradation rate is sharply increased. Within ten weeks of the composting time, samples were completely disintegrated into small pieces where the weight loss measurement was not being able to perform. According to the weight loss measurement found in Figure 4.46, it is seen that the degradability of PLA/silicone compound samples are faster than the neat PLA. It is well known and well recognized that PLA is biodegradable polymer. It can be completely composted within 24 weeks. Taken the biodegradability testing in this work and elementary compare with the PLA material, it can be pronounced that the PLA/silicone compound derived from this research work can be completely biodegraded. It seems that the material can be degraded faster than the PLA.

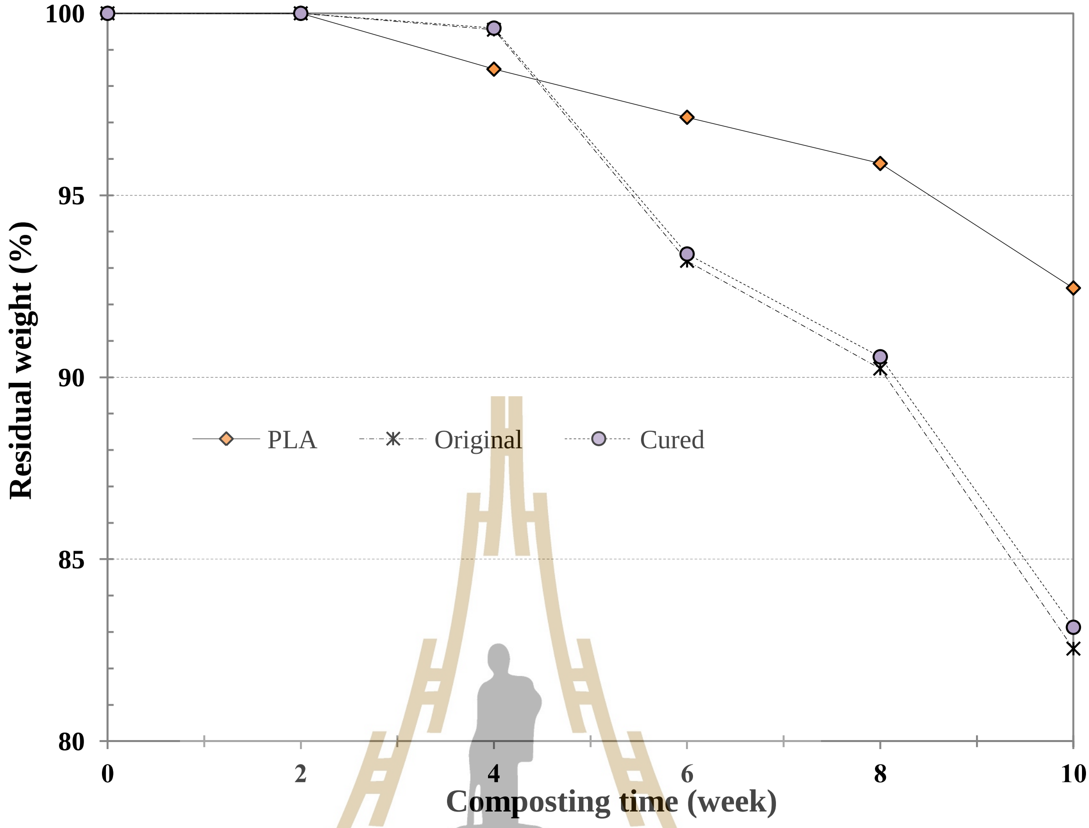


Figure 4.46 Biodegradability of neat PLA and 0.4 phr TETA cured PLA/silicone compound.

4.4 Single component silicone and PLA compound

In this experimental section, the PLA and moisture cured silicone, or single component, is used in place of two component silicone system. The blend formula concluded from the previous experiment; 1.0 phr of silane, 1.0 phr of polyol and 1.0 phr of processing stabilizer, were adopted. The single component silicone was varied from 0 to 12 phr. The designed formula for the experiment is summarized in Table 4.31. The injection molded of the compound specimen was tested and the results are reported in Table 4.32 and 4.33.

Table 4.31 The blend of PLA and single component silicone rubber.

Run No.	PLA (g)	Silicone (g) (phr)	Silane (g) (phr)	Polyol (g) (phr)	Stabilizer (g) (phr)
1	700	0.0 (0.0)	7 (1.0)	7 (1.0)	7 (1.0)
2	700	28.0 (4.0)	7 (1.0)	7 (1.0)	7 (1.0)
3	700	56.0 (8.0)	7 (1.0)	7 (1.0)	7 (1.0)
4	700	84.0 (12.0)	7 (1.0)	7 (1.0)	7 (1.0)

Table 4.32 Rheological and tensile properties of PLA/single component silicone rubber.

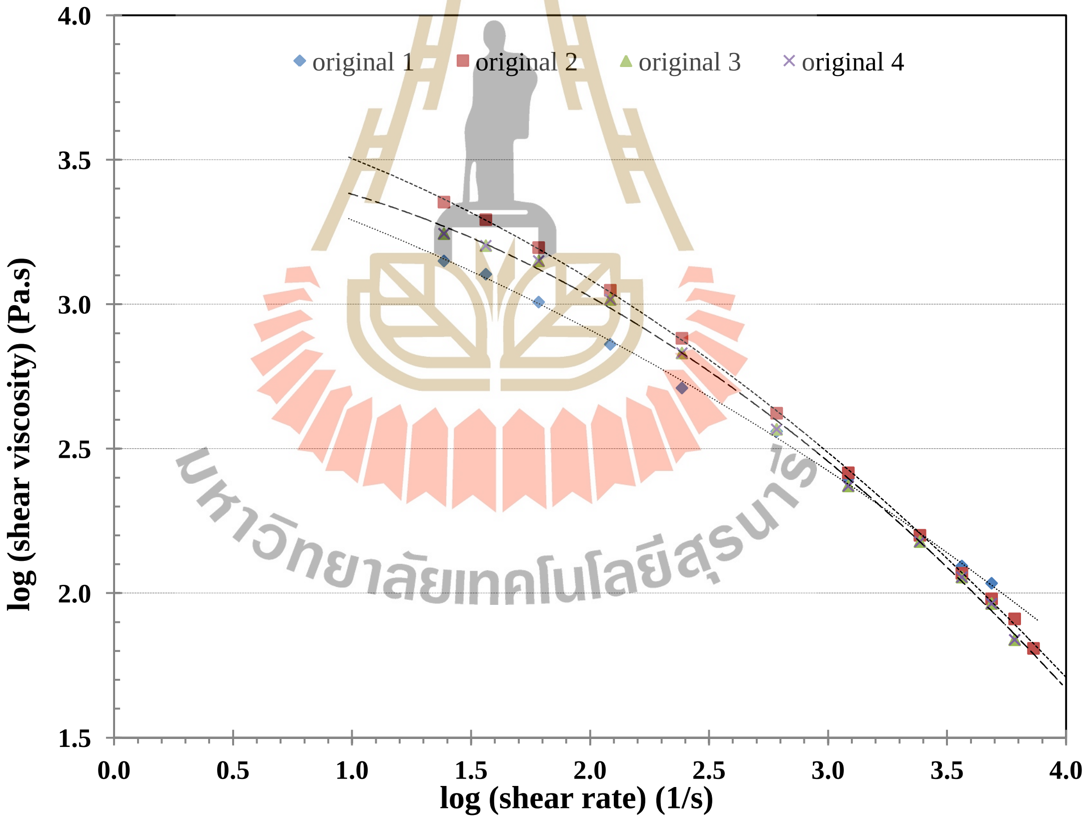
Silicone content (phr)	η_o viscosity (Pa.s)		MFI (g/10min)		Tensile strength (MPa)		Elongation at break (%)		Young's modulus (GPa)	
	Original	Cured	Original	Cured	Original	Cured	Original	Cured	Original	Cured
LDPE	3698.28	3630.78	2.86±0.07	2.84±0.05	8.16±0.43	8.43±1.12	91.93±2.26	91.28±3.12	0.15±1.22	0.14±1.31
PLA	4655.47	4320.23	1.41±0.04	1.77±0.02	52.38±0.93	59.48±1.57	4.33±0.26	4.94±0.42	2.58±1.07	2.67±0.96
0.0	4570.88	4686.38	1.80±0.07	1.61±0.05	65.75±1.45	63.75±1.45	3.82±0.11	3.82±0.11	2.29±0.12	2.29±0.12
4.0	3548.13	3630.78	2.48±0.11	2.32±0.05	20.02±9.46	36.71±1.29	11.74±5.61	11.93±3.51	1.97±0.64	1.96±0.74
8.0	2814.56	3375.69	3.01±0.11	2.54±0.11	14.82±7.43	28.97±2.88	19.32±9.38	15.16±7.47	1.85±0.67	1.29±1.32
12.0	2286.25	2824.34	3.15±0.09	2.96±0.21	17.51±5.26	27.98±1.18	17.47±5.97	14.47±3.49	1.79±0.81	1.70±0.71

Table 4.33 Impact and thermal properties of PLA/single component silicone rubber.

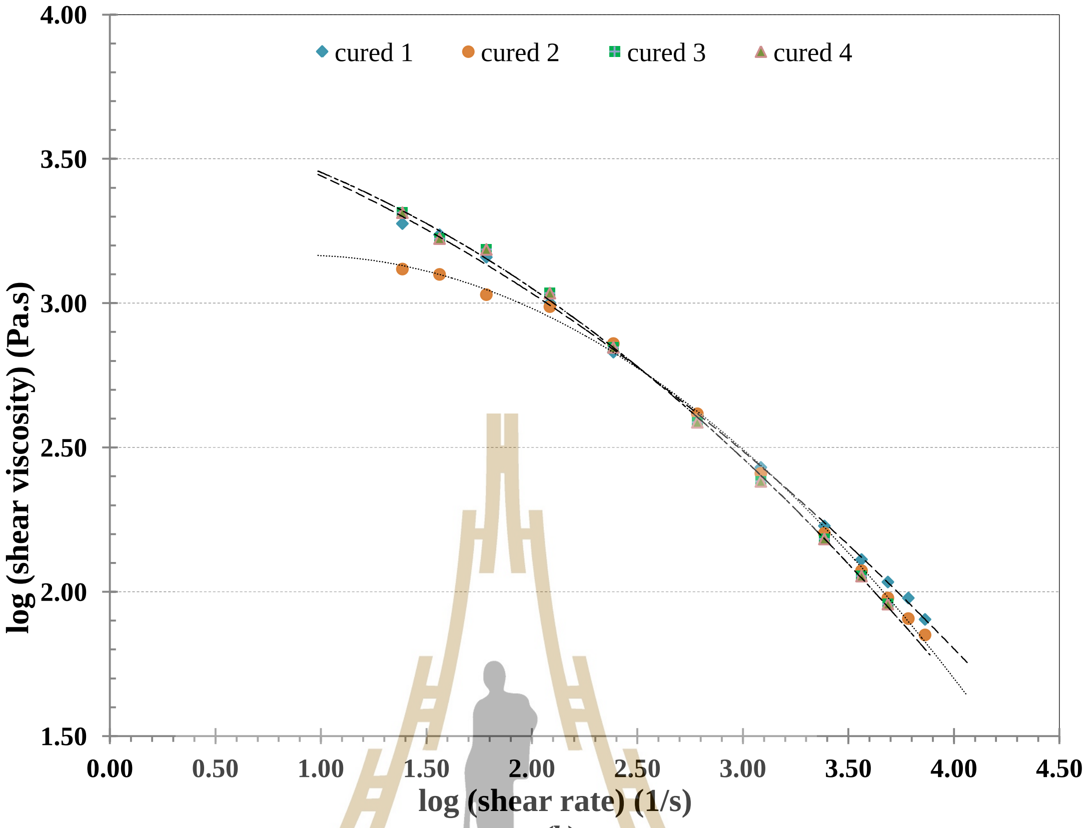
Silicone content (phr)	**Unnotched impact (kJ/m^2)**		**Notched impact (kJ/m^2)**		**Low temperature unnotched impact (kJ/m^2)**		**Low temperature notched impact (kJ/m^2)**		**HDT (^oC)**	
	Original	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**
LDPE	No break	No break	No break	No break	No break	No break	4.80±1.34	3.60±0.62	36.60±2.00	39.60±1.59
PLA	15.97±2.35	21.15±2.41	2.49±0.48	3.45±0.98	21.23±1.34	22.15±2.21	2.60±0.62	3.20±0.42	51.67±0.58	52.40±0.72
0.0	17.95±4.35	18.94±2.70	3.22±0.48	3.86±0.20	24.27±0.71	27.36±1.67	3.76±0.56	4.46±0.61	43.67±1.53	56.00±3.00
4.0	28.91±7.02	29.91±9.75	6.35±0.69	9.71±0.54	32.92±2.66	41.04±3.34	6.53±1.36	7.92±1.80	46.67±3.51	55.00±1.73
8.0	40.34±5.74	54.62±6.16	8.35±0.38	11.50±0.96	34.64±3.35	50.12±4.83	6.78±0.40	8.32±0.56	45.67±4.04	53.67±1.53
12.0	29.87±5.10	33.03±4.28	9.53±0.83	9.33±0.49	32.59±1.22	37.01±1.18	7.29±0.29	7.93±0.34	45.33±3.21	53.67±0.58

4.4.1 Zero shear viscosity of PLA/silicone single component compound

The appearance shear viscosity and shear rate performed at 180°C of the blends at the given silicone contents are given the Figure 4.46 (***a***) and 4.46 (***b***), for the original and cured sample, respectively. From the plots and by using the power law model the zero shear viscosity ($\boldsymbol{\eta_o}$) was obtained and summarized in Table 4.32. It is seen that the $\boldsymbol{\eta_o}$ of the PLA/silicone blends are graduate decreased with increasing the silicone used. It is also observed that the zero shear viscosity was noticeably higher after the sauna curing process.



(a)



(b)

Figure 4.47 Shear viscosity plot of the PLA/silicone compounds; (*a*) original and (*b*) after sauna treatment, respectively.

4.4.2 MFI of PLA/silicone single component compound

The melt flow index, MFI, of the PLA/silicone blends were measured and given in Table 4.32. The plot as function between silicone content and MFI is also presented in Figure 4.48. Typically, it indicates that MFI of the compounds almost linearly increased with increasing the silicone content, except at 12 phr of silicone. This result is in agreement with the melt viscosity outcome. Sauna curing gives rise to the lower in the melt flow rate, higher in viscosity and the similar trend, with respect to silicone addition, is found for the cured samples. The decreasing in the

MFI of the blends via the sauna curing is probably explained by the fact that the single pack silicone system used in this experiment is normally cured with moisture. Combination between crosslinking of silicone added and intermolecular chain connection through the silane/moisture condensation would increase the melt viscosity of the blends.

4.4.3 HDT of PLA/silicone single component compound

Figure 4.48 also the HDT plot of PLA/silicone blends against silicone contents. It is seen that HDT of PLA blends before sauna cured is seemingly lowered by the amount of silicone addition. When compare with pure PLA, the HDT of PLA compounds are approx. 6^{o}C lower. Nevertheless, the sauna curing treatment has increased the HDT of the compound. The HDT is increase by roughly 10^{o}C through the treatment. However, the service temperature of cured specimen is independence of the silicone used. The test figures are similar to that pure PLA. The increasing in HDT via sauna treatment can be hypothesized by two folds; silicone curing via water molecule and intermolecular bridging through the silane reaction. The increasing in HDT of cured sample may be advantage over the LDPE. It is seen that the HDT of LDPE is much lower, 39^{o}C, than the blends. If other properties of the blends are adequate to the LDPE, it means that higher temperature applications than the olefin can be possible.

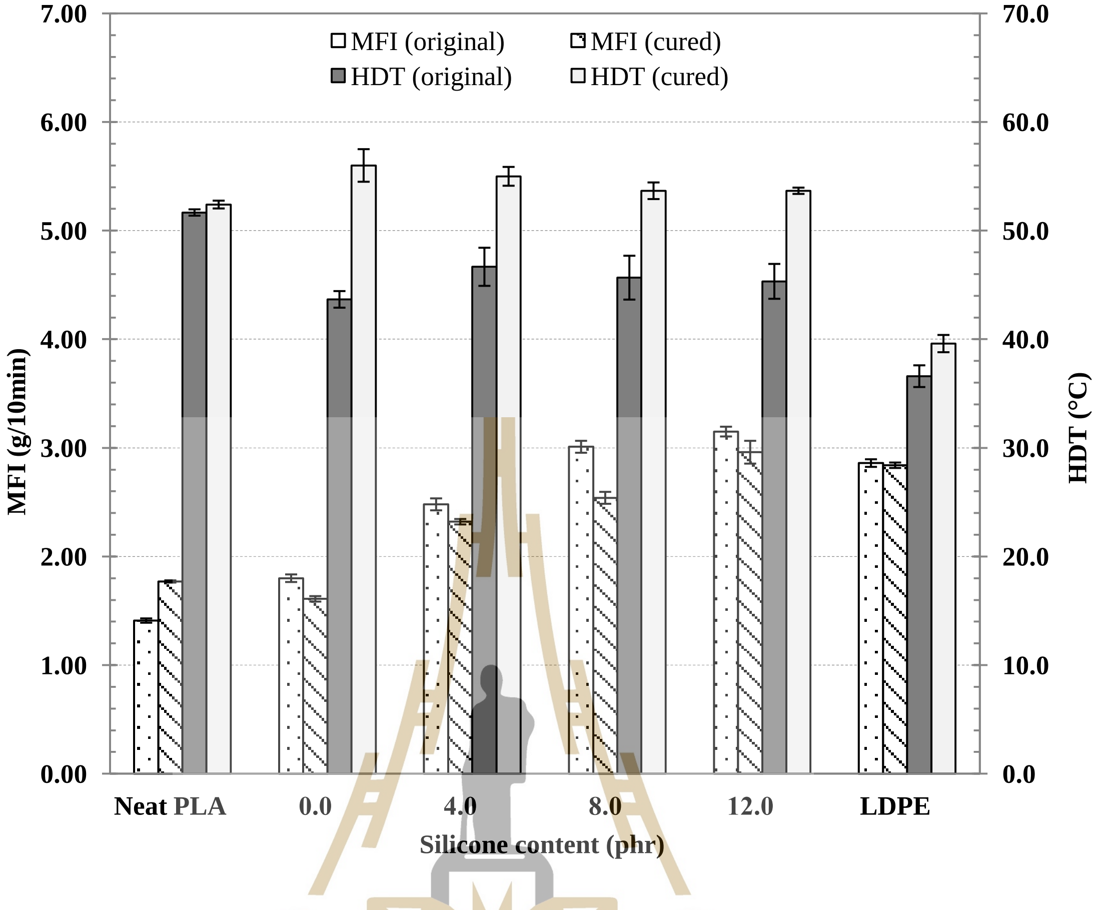


Figure 4.48 HDT and MFI of PLA/silicone compound as function of silicone contents.

4.4.4 Tensile properties of PLA/silicone single component compound

The plot of tensile strength and modulus of the PLA blended with one component silicone rubber plotted in corresponding with the rubber content is presented in Figure 4.49. It is observed that tensile strength and modulus are gradually lowered when higher the silicone content for both original and cured conditions. When compare the blend with and without silicone, it is seen that the strength of the cured sample with silicone blending obviously higher than the original one. On the other hand, the modulus is inversed direction. It is quite common to see the decreasing in the strength of the blends with increasing the rubber content. According to the rule of mixture, the low tensile properties of the rubber added would have the negative effect to the tensile characteristic of the PLA blends. Also Figure 4.50 illustrates % elongation at break of the blend against the silicone content. It is seen that the elongation is increased from 0 to 8.0 phr of the rubber added. After that the value is slightly dropped and it is observed that the sauna cured sample has lower % elongation than the original. Again, it is generally observed the increasing in the tensile deformation when adding more of the rubber into the blend.

Taken from the tensile testing results, when the samples were sauna cured, the strength and elongation are vastly increased but modulus is fractionally decreased. It demonstrates that the ductility of material likely to be increased with increase the amount of silicone. However, the superiority in term of tensile properties is bounded by the amount of the rubber as well. From the tensile results, it reveals that as the silicone content is increased, the elastomeric behavior; low strength and modulus, and high elongation at break, of the compound is noticed. Vice versa, network forming via the silane/moisture and silicone/moisture reactions, probably in the rubber phase, causing the compound behave slightly less rubbery.

When compare the tensile properties between neat PLA and LDPE with the PLA/silicone blends obtained in the experiment, it is generally seen that the blends have better ductility than neat PLA but less than LDPE especially in term of elasticity of material.

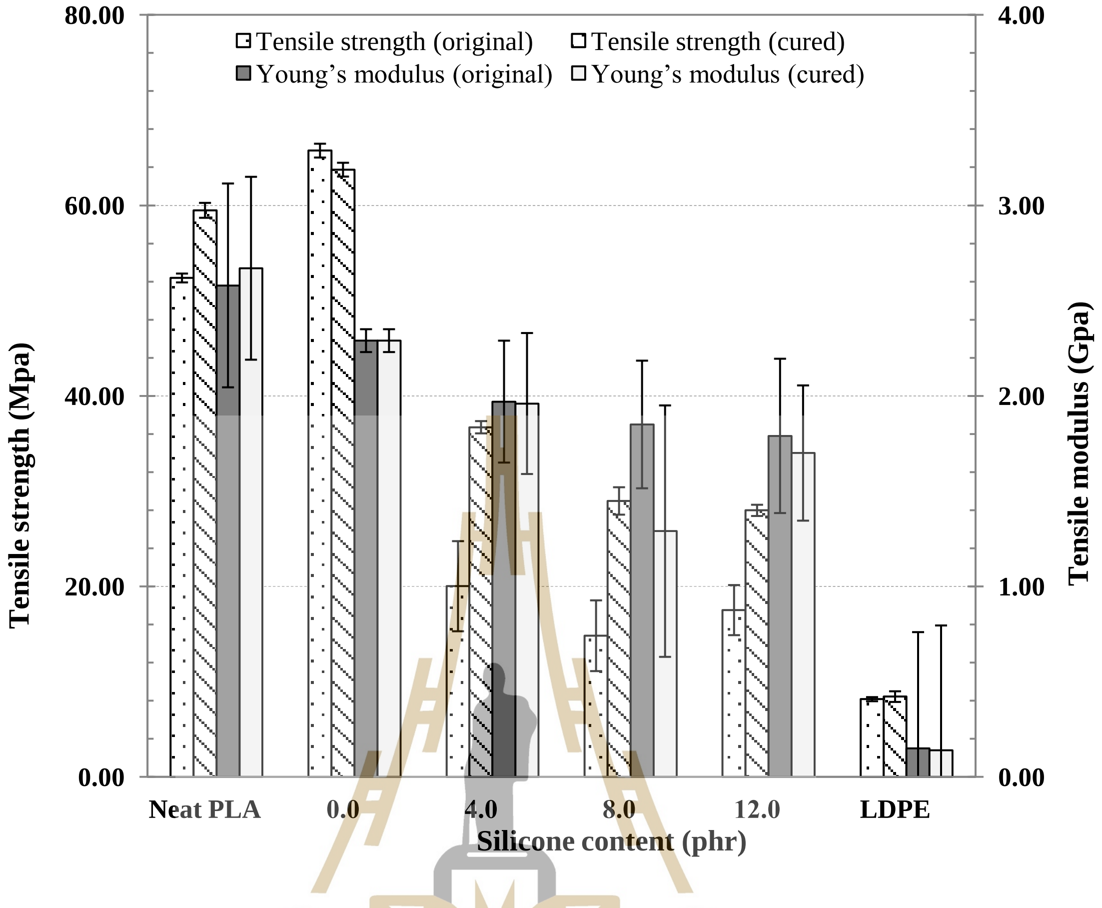


Figure 4.49 Tensile strength and tensile modulus of PLA/silicone compound as function of silicone contents.

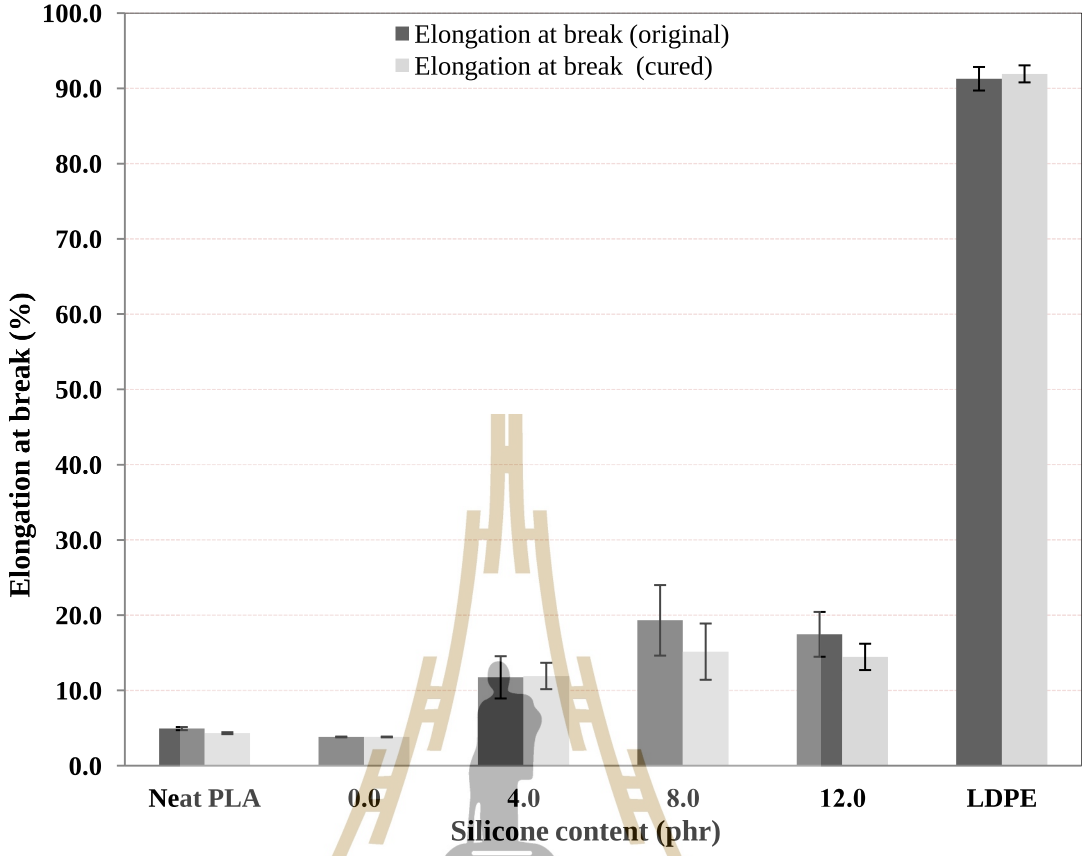


Figure 4.50 Elongation of PLA/silicone compound as function of silicone contents.

4.4.5 Impact strength of PLA/ silicone single component compound

The notched and unnotched impacts of the PLA/silicone blends performed at room temperature were plotted against silicone content is presented in Figure 4.51. It is seen that the notched impact strengths both original and sauna cured samples are increased with increasing the silicone rubber addition except for the sauna cured with 12.0 phr of silicone where the test value is noticeably lower than at 8.0 phr. The similar trend is also found for the unnotched mode of test in which the strengths are increased from 0.0 phr to 8.0 phr of silicone content. The value is sharply lowered when further increase the rubber to 12.0 phr. In comparison between original and sauna cured samples for both test modes, it is generally observed that the strength of cured sample is higher than the original one. Within this experiment boundary, adding 8.0 phr of the single component silicone rubber into the PLA shows the maximum impact strengths. Beyond this adding figure, the strengths are decreased. It indicates that the silicone rubber is acted as the impact modifier, or impact energy absorber, for the PLA compound. At the optimal rubber content, the strength of PLA/silicone blend is superior than neat PLA but inferior when compare with LDPE.

The impact tests conducted at low temperature, at approx. -98^{o}C, of the blends are graphically shown against the silicone added in Figure 4.52. The identical trend to those tested at room temperature is observed. The impact strengths both notched and unnotched are increased with increasing the silicone contents. However, with the assisting of silane/moisture condensation reaction during sauna cured, the strength of the sample is significantly higher than the original and it is dramatically increased with adding silicone rubber at 8.0 phr. Again, further increase the silicone content to 12.0 phr, it is found that the strengths are dropped. The highest impact values are found at 8 phr of silicone. The notched test figure is not only higher than the value obtained from virgin PLA but also higher that the test value derived from the film grade LDPE. So, from the result found it can preliminary confirmed than the PLA blended with single component silicone rubber at 8.0 phr can be used in place of LDPE in low temperature packaging applications.

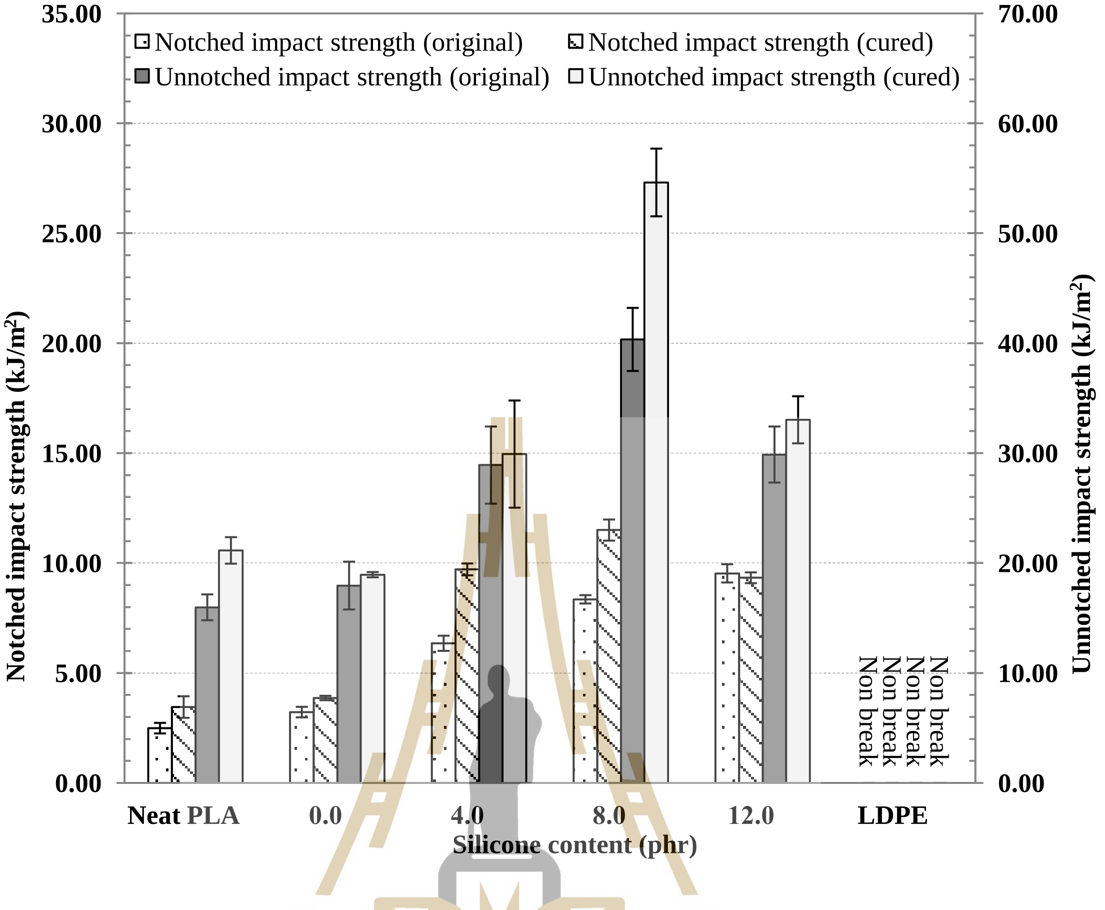


Figure 4.51 Impact strengths at room temperature of PLA/silicone compound as function of silicone contents.

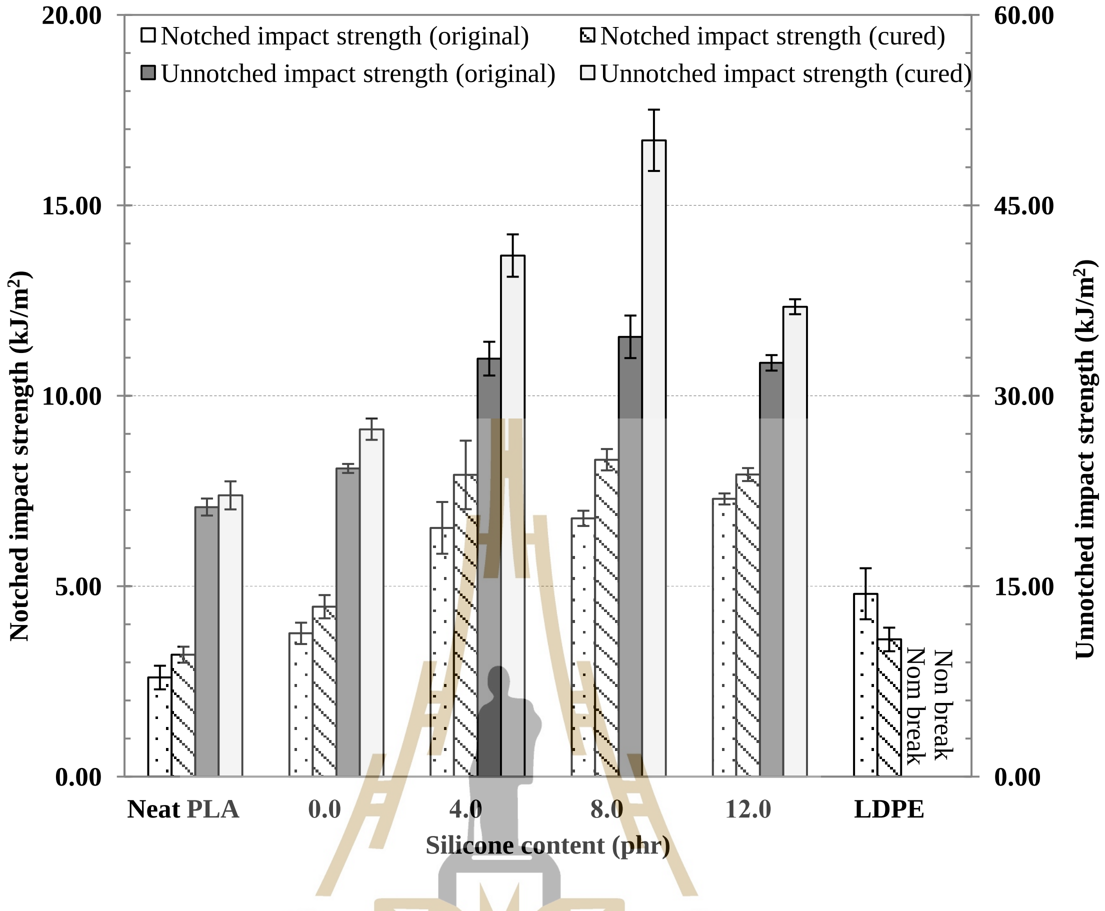
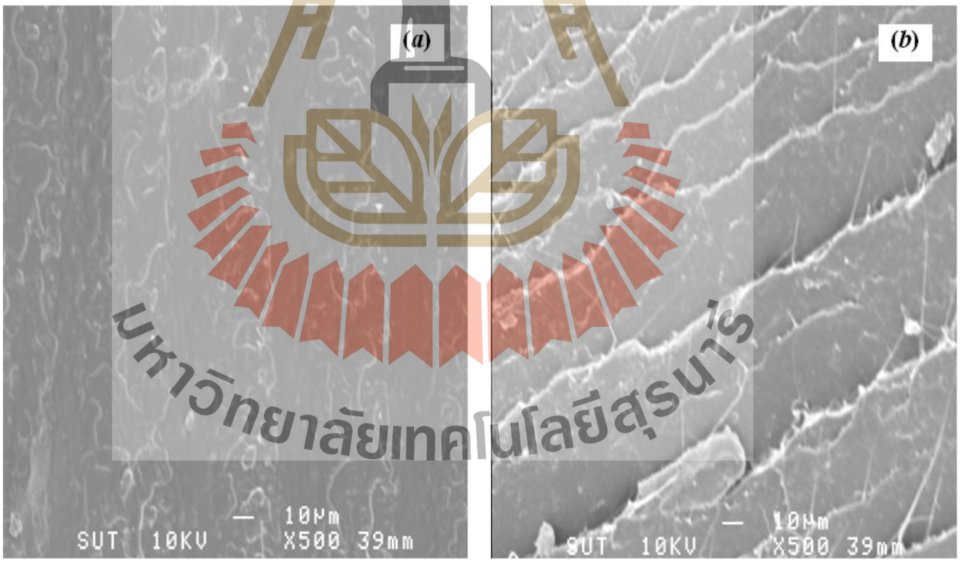


Figure 4.52 Impact strengths at low temperature of PLA/silicone compound as function of silicone contents.

4.4.6 Scanning electron microscopy (SEM)

General observation, it is evidenced that the injected specimen from the compound is translucent. The clarity or light transmit ability is inversed with the silicone contents. From the mechanical investigation, it is also found that adding the moisture cured silicone system into PLA at 8.0 phr the properties of the blend can be completed with LDPE and superior in the impact strength at low temperature. Further increase in the silicone content beyond the optimal amount found that the properties are ruined. The rubber phase separation would be one of the reasons for the decreasing of the properties. Figure 4.53 (*a*) to 4.53 (*d*) are the SEM traces obtained from the fractured surface of the broken notched impact specimens without and with 8 phr of silicone for the original and sauna cured, respectively. It is seen that there is no obvious phase separation from the SEM photograph of the blend without silicone added. However, the rubber phase separation, tiny drops of particle, is clearly seen on the fractured surfaces of 8 phr silicone/PLA blend. It is believed that the rubber droplets would become larger at 12.0 phr of silicone/PLA blend. This observation indicates that adding silicone rubber into PLA matrix beyond 8.0 phr, the rubber phase separation would become dominate. Hence, the properties especially fracture toughness would be weakness.



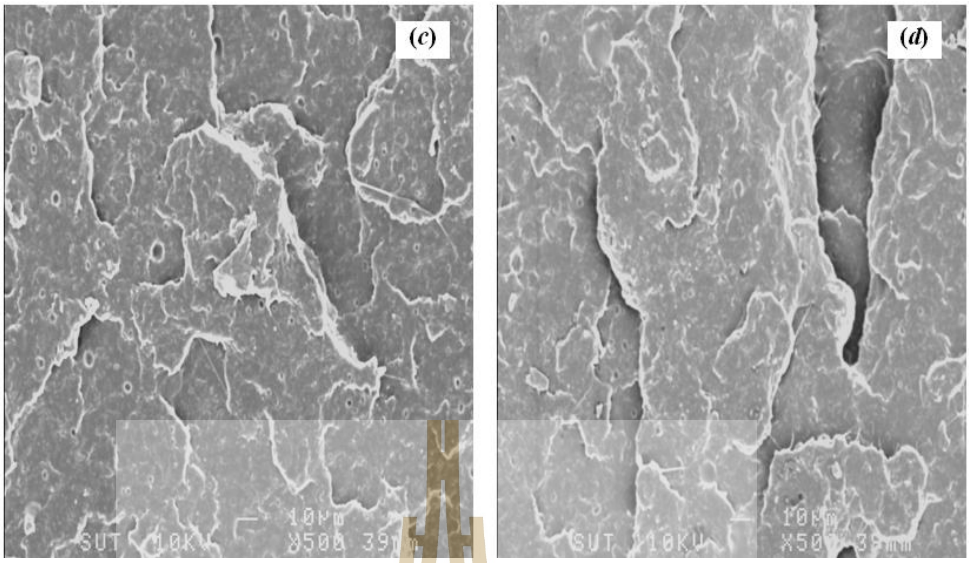


Figure 4.53 SEM micrograph of PLA/single component silicone rubber at; (***a***) 0 phr (original), (***b***) 0 phr (cured), (***c***) 8 phr (original) and (***d***) 8 phr (cured), of silicone, respectively.

Within the limitation of this experimental and according to the accepted standard deviation error of the test results, it can be pronounced that the PLA/silicone compounds at silicone content of 8.0 phr show the promising properties especially impact strength at sub zero temperature to complete with the LDPE material for the frozen food packaging applications. The properties of the blends, except the elongation at break and impact strength at room temperature, are relatively better than the LDPE. Further improvement not only of the disadvantage properties but also the process ability of the blend by adding the talc filler will be discussed.

4.5 Effect of talc filler on the PLA/silicone compound

From the previous experimental section, the PLA and moisture cured silicone, or single component silicone system, blended at 8.0 phr showed the outstanding properties especially the toughness and tensile elongation. The suggested blend formula were blended at 8.0 phr of single pack silicone, 1.0 phr of silane, 1.0 phr of polyester polyol and 1.0 phr of processing stabilizer, respectively. There is no difficult to fabricate this compound formula by injection molding. In the preliminary attempt to produce film product by blown film process was found that the processing method was impossible by using conventional blown film processor. It was because the very low melt strength of the compound. The film bubble was exploded as soon as it exits from the die. It was also observed that the molten PLA/silicone compound was shear rate sensitive. One of the compounding techniques that can be used to increase the melt strength or melt viscosity of polymer is filler addition. In this experiment, addition of talc as filler to increase the viscosity and also cost reduction was performed. The talc in the formula was varied from 0 to 50 phr with respect to the PLA matrix. The experimental formula is given in Table 4.34. The compound and the injection molded specimen were routinely tested and the results are summarized in Table 4.35 and 4.36.

Table 4.34 The blend formula of the talc filled PLA/silicone compounds.

Run No.	**PLA (g)**	**Silicone (g) (phr)**	**Silane (g) (phr)**	**Polyol (g) (phr)**	**Talc (g) (phr)**	**Stabilizer (g) (phr)**
1	700	56.0 (8.0)	7 (1.0)	7 (1.0)	0 (0.0)	7 (1.0)
2	700	56.0 (8.0)	7 (1.0)	7 (1.0)	140 (20.0)	7 (1.0)
3	700	56.0 (8.0)	7 (1.0)	7 (1.0)	210 (30.0)	7 (1.0)
4	700	56.0 (8.0)	7 (1.0)	7 (1.0)	280 (40.0)	7 (1.0)
5	700	56.0 (8.0)	7 (1.0)	7 (1.0)	350 (50.0)	7 (1.0)

Table 4.35 Rheological and tensile properties of talc filled PLA/silicone compounds.

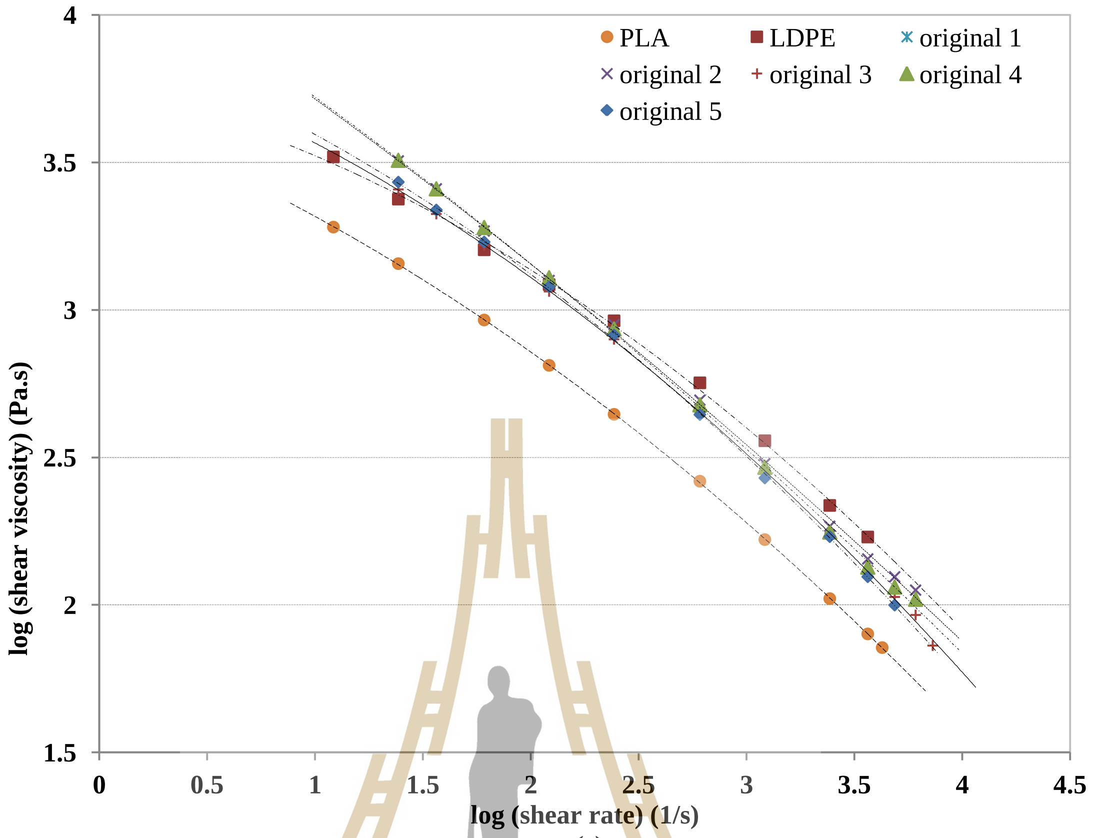
Talc content (phr)	**η_o viscosity (Pa.s)**		**MFI (g/10min)**		**Tensile strength (MPa)**		**Elongation at break (%)**		**Young's modulus (GPa)**	
	Original	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**
LDPE	5322	5428	2.86±0.07	2.84±0.05	8.16±0.43	8.43±1.12	91.93±2.26	91.28±3.12	0.15±1.22	0.14±1.31
PLA	4655	4320	1.41±0.04	1.77±0.02	52.38±0.93	59.48±1.57	4.33±0.26	4.94±0.42	2.58±1.07	2.67±0.96
00.0	2814	3375	3.01±0.11	2.54±0.11	14.82±7.43	28.97±2.88	19.32±9.38	15.16±7.47	1.85±0.67	1.29±1.32
20.0	5794	4784	0.92±0.02	1.27±0.05	16.44±7.05	32.88±0.70	11.58±4.61	9.10±1.33	3.20±0.29	2.93±0.11
30.0	7379	5445	0.74±0.12	0.98±0.10	32.85±1.78	38.57±1.13	5.79±1.35	4.46±0.68	3.72±0.16	3.96±0.13
40.0	9120	6275	0.63±0.12	0.82±0.20	39.95±0.89	46.77±1.58	3.52±0.37	2.76±4.49	4.22±0.09	4.03±0.15
50.0	9977	7531	0.48±0.10	0.57±0.20	46.91±1.08	51.31±1.81	2.69±1.10	2.43±2.49	4.60±0.13	4.37±0.10

Table 4.36 Impact and thermal properties of talc filled PLA/silicone compounds.

Talc content (phr)	Unnotched impact (kJ/m^2)		Notched impact (kJ/m^2)		Low temperature unnotched impact (kJ/m^2)		Low temperature notched impact (kJ/m^2)		HDT (^oC)	
	Original	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**	**Original**	**Cured**
LDPE	No break	No break	No break	No break	No break	No break	4.80±1.34	3.60±0.62	36.60±2.00	39.60±1.59
PLA	15.97±2.35	21.15±2.41	2.49±0.48	3.45±0.98	21.23±1.34	22.15±2.21	2.60±0.62	3.20±0.42	51.67±0.58	52.40±0.72
00.0	40.34±5.74	54.62±6.16	8.35±0.38	11.50±0.96	34.64±3.35	50.12±4.83	6.78±0.40	8.32±0.56	45.67±4.04	53.67±1.53
20.0	39.12±1.40	37.48±5.84	7.97±0.27	8.60±0.34	32.12±1.11	33.93±0.48	5.61±0.32	4.90±0.60	45.47±0.5	67.00±5.20
30.0	31.45±4.44	30.38±2.40	7.84±0.40	8.26±0.27	27.35±1.89	26.76±0.51	4.21±0.39	3.51±0.32	48.00±2.00	75.67±6.03
40.0	26.93±2.27	26.67±1.55	4.91±0.30	5.26±0.31	25.07±1.87	24.27±1.76	2.84±0.32	3.26±0.24	49.00±3.61	92.67±2.52
50.0	23.21±2.60	22.05±1.31	3.59±0.23	3.91±0.26	22.41±3.84	22.15±1.66	1.65±0.23	2.09±0.26	50.00±3.61	95.00±2.00

4.5.1 Zero shear viscosity versus talc content on PLA compounds

The plot of appearance shear viscosity and shear rate performed at 180°C of the blends and at the given talc contents are presented in Figure 4.54 (***a***) and 4.54 (***b***), for the original and sauna cured sample, respectively. When comparing with LDPE and neat PLA, the shear viscosities of the PLA compounds are line in between PLA and LDPE. From the plots, by applying the power law model the zero shear viscosity ($\boldsymbol{\eta_o}$) was resolved and reported in Table 4.35. As normally expected, it is seen that the $\boldsymbol{\eta_o}$ of the PLA/silicone blends are gradually increased with increasing the talc used. It is also observed that the zero shear viscosity was noticeably lowered after the sauna curing process. The decreasing in the viscosity through the sauna treatment might be due to the moisture residual in the compound that would cause the chain degradation via the hydrolysis during the polymer melting.


PLA
LDPE
original 1
original 2
original 3
original 4
original 5
4
3.5
3
2.5
2
1.5
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
log (shear viscosity) (Pa.s)
log (shear rate) (1/s)

(a)

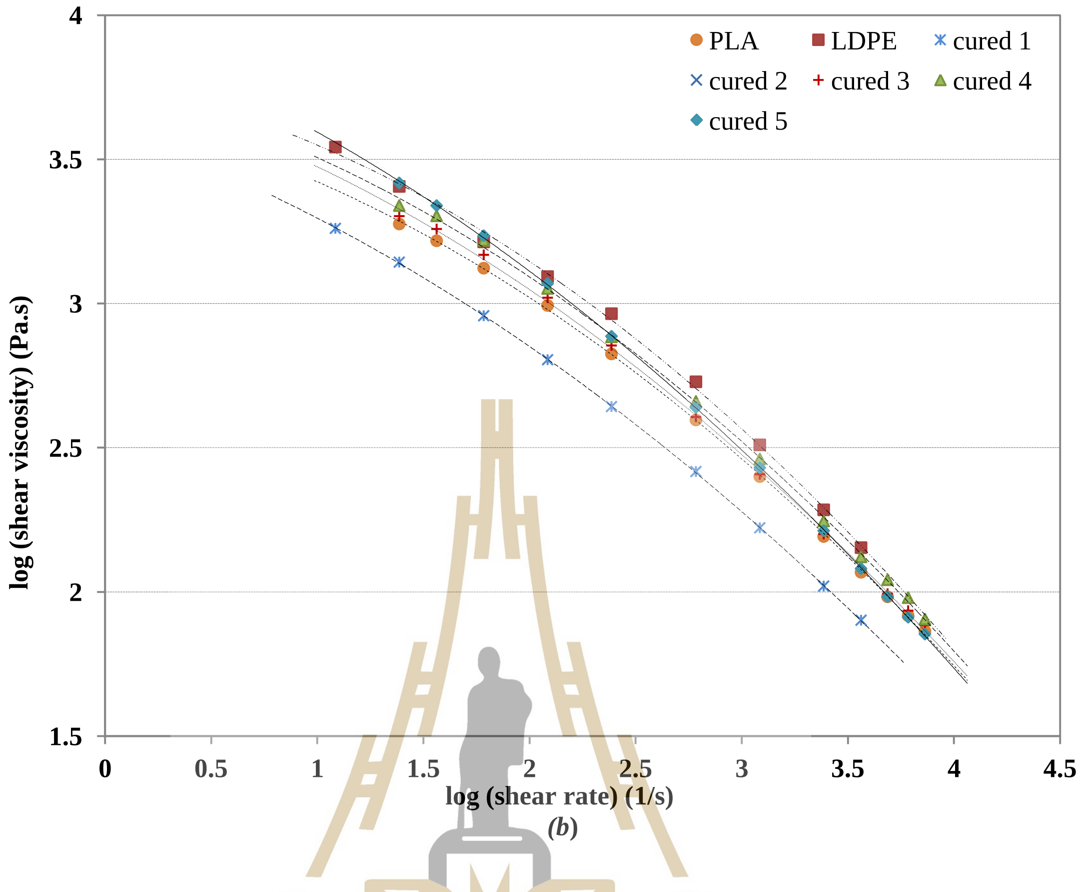


Figure 4.54 Shear viscosity plot of the talc filled PLA/silicone compounds for; (*a*) original and (*b*) after sauna treatment, respectively.

4.5.2 MFI of the PLA/silicone compound and effect of talc contents

The melt flow index, MFI, of the PLA/silicone blends were also tested and reported in Table 4.35 and they are plotted as function talc content in Figure 4.55. There is no surprise on the test result because MFI of the compounds are almost linearly decreased, difficult to flow, with increasing the talc content. This result is in agreement with the melt viscosity as discussed in section 4.5.1. At the given talc content, it is noticed that sauna curing gives rise to the higher in MFI, lower in viscosity, as also found in the viscosity. The hydrolysis of chain via the moisture residual would be the suspected cause.

4.5.3 HDT of PLA/silicone compound and effect of talc contents

Figure 4.55 is the HDT plot of PLA/silicone blends against talc contents. It is seen that HDT of PLA blends before and after sauna cured are increased by increasing the amount of filler addition, especially the sauna cured PLA blends where the increasing in the service temperature is very obvious and shows almost the linear trend. The increasing in the HDT with addition of filler and also fiber reinforcement is commonly found for the polymer compound industries. But, the increasing in HDT via sauna treatment can be hypothesized by intermolecular bridging through the silane grafting reaction between polymer chain and filler particle. The HDT increasing of cured sample may be advantage over the LDPE because it might be used for both low and high temperature applications from the single compound. If other properties of the blends are equated with the LDPE, it means that higher temperature applications, than the olefin polymer, can be possible.

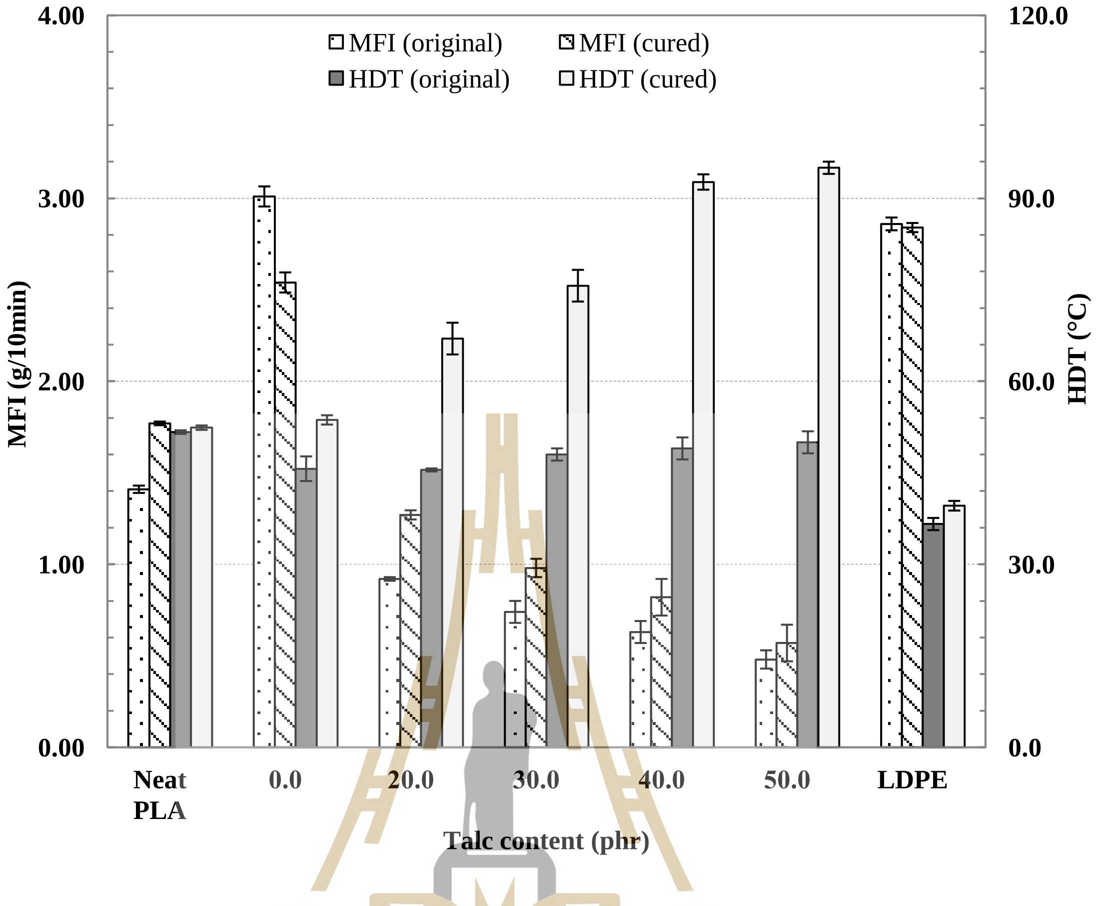


Figure 4.55 HDT and MFI of the talc filled PLA/silicone compounds as a function of talc content.

4.5.4 Tensile properties of PLA/silicone compound and talc contents

The plot of tensile strength and modulus of the PLA blended with single component silicone rubber are plotted in accordance of talc contents and presented in Figure 4.56. It is seen that tensile strength and modulus are linearly increased when increasing the talc content for both original and cured samples. It is also observed that the strength of the sauna cured sample is obviously much higher than the sample without treatment. In contrast with the strength, the modulus of cured sample is generally lower than the original sample. It is quite common to see the increasing in the tensile strength of the polymer compound with increasing the talc content. In contrast, adding more particulate solid filler into the compound would decrease the ductility or toughness of the material. It means that modulus is normally increased with decreasing the tensile elongation at break as seen in Figure 4.57. The tensile characteristic of the PLA/silicone compound filled with talc is in good agreement with the given statement. Because the strength and modulus of the material is increased but the % elongation at break is decreased when increasing the talc content, especially after the sauna incubation.

Taken only the tensile testing results, it is demonstrated that the flexibility of material likely to be decreased with increasing the amount of talc filler. In comparison with the tensile properties among neat PLA, LDPE and PLA/silicone blends obtained in this experiment, it is generally commented that the blends have better ductility than neat PLA but less than LDPE, especially in term of tensile elasticity.

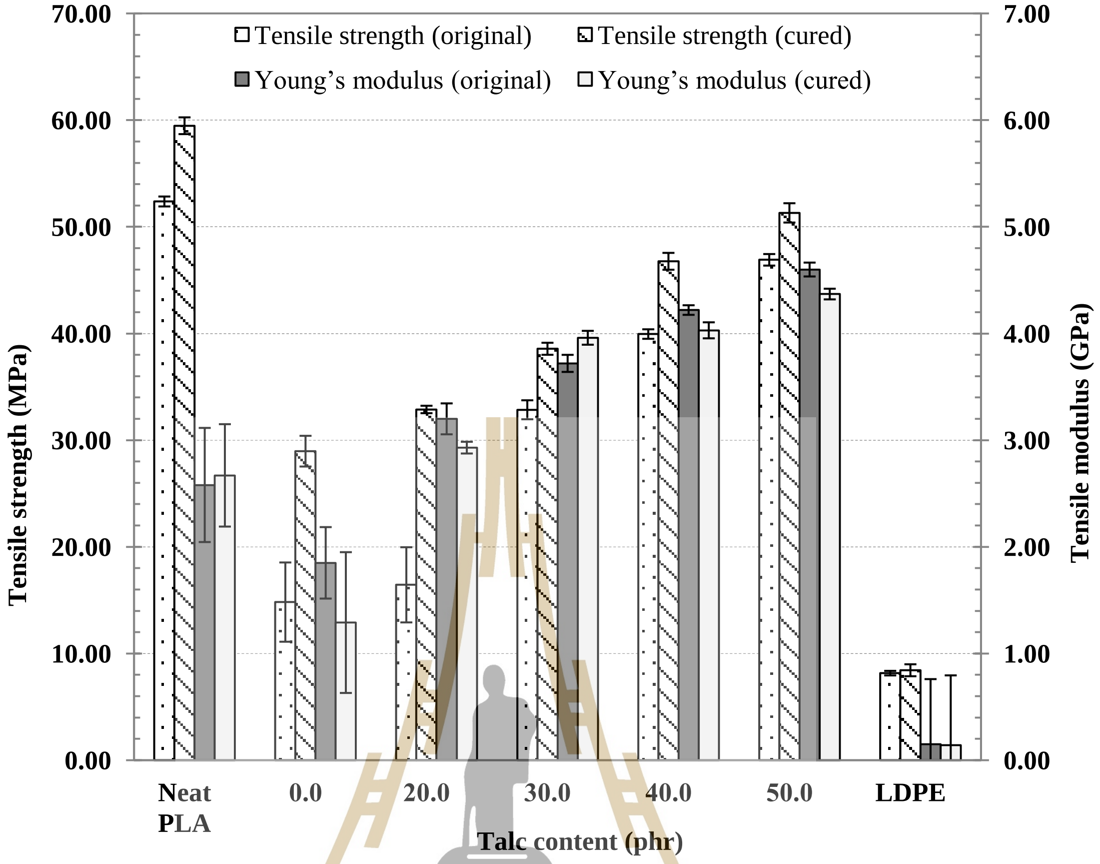


Figure 4.56 Tensile strength and tensile modulus of the talc filled PLA/silicone compounds as a function of talc content.

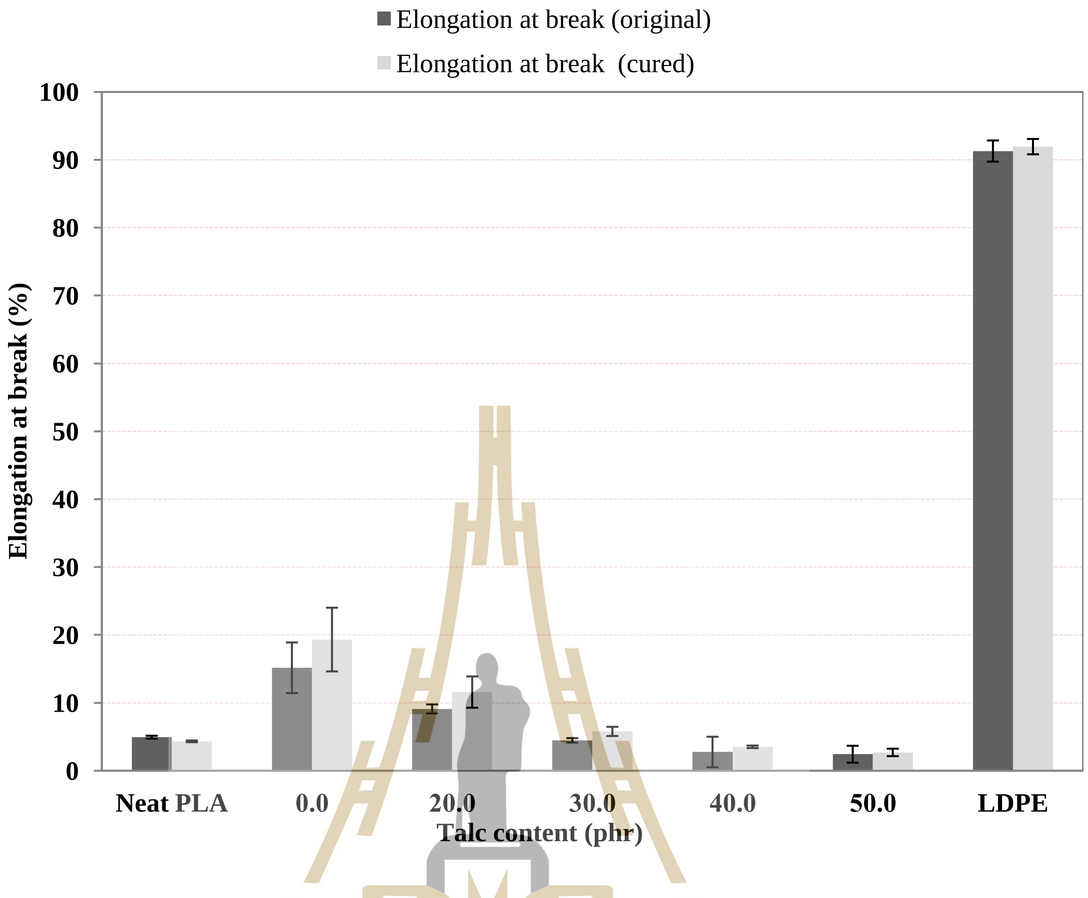


Figure 4.57 Elongation of the talc filled PLA/silicone compounds as a function of talc content.

4.5.5 Impact strengths of PLA/silicone compound and effect of talc contents

The notched and unnotched impacts of the PLA/silicone blends performed at room temperature are plotted against talc content and illustrated in Figure 4.58. It is seen that both notched and unnotched impact strengths for original and cured samples are sharply decreased with increasing the talc addition. In comparison between original and sauna incubated cured samples, it is generally observed that the strength of cured sample is fractionally higher than the original for notched testing. But for the unnotched, the strength of cured sample is slightly lower than the original one. Within this experiment constrain, PLA/silicone without talc shows the maximum impact strengths. When adding talc, the strengths are dramatically decreased. It indicates that the talc as solid filler and has negative effect for impact strengths on the PLA compound. There are two hypothesizes to explain this phenomenon. First, the solid filler particle acts as energy distributor in the matrix phase. It magnifies the absorbed impact energy and then transfers into nearby matrix phase. As the result, the crack propagation would be accelerated and brittle material would be evidenced. The inferior in the interfacial adhesion between filler and polymer matrix would be another drawback point of discussion. Weaker adhesion means lower in fracture toughness of material.

The impact tests conducted at sub zero temperature, >-98°C, of the blends are graphically demonstrated as A function of talc loading in Figure 4.59. From the plot, the trend of test values are exactly the same as conducted at room temperature. The impact strengths, notched and unnotched, are rapidly decreased with increasing the talc loading. The highest impact values are seen from the blends without talc addition. Sauna incubation does not entirely exhibit the superiority of the strengths of talc filled sample at the given loading. Some do and some do not.

When compare the impact strengths between PLA, LDPE and talc filled PLA/silicone materials it is seen that the strengths of PLA/silicone compound are much higher than the strength of pure PLA. At ambient temperature the fracture toughness properties of LDPE is much superior than the others. However, at lower temperature, in this study at lower than -98°C, the notched impact strength of

PLA/silicone loaded with talc less than 20 phr shows the higher test values than LDPE.

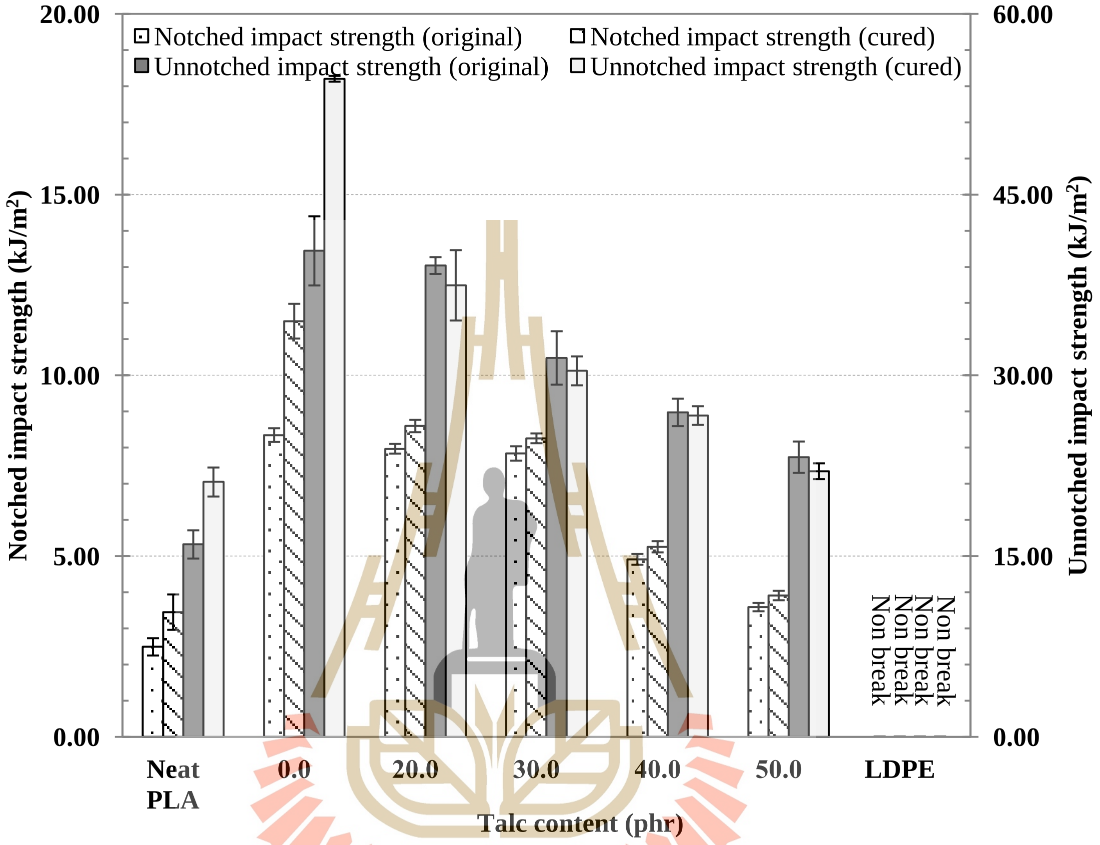


Figure 4.58 Impact strengths at room temperature of the talc filled PLA/silicone compounds as a function of talc content.

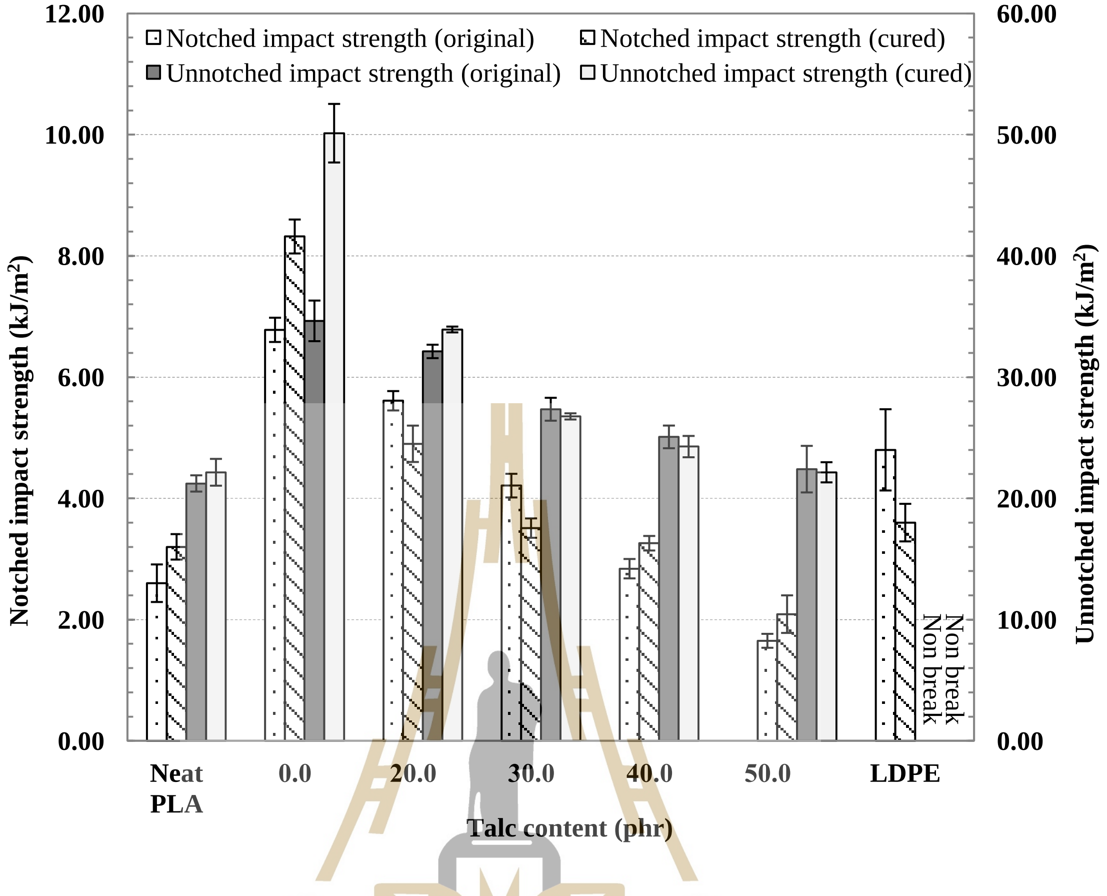
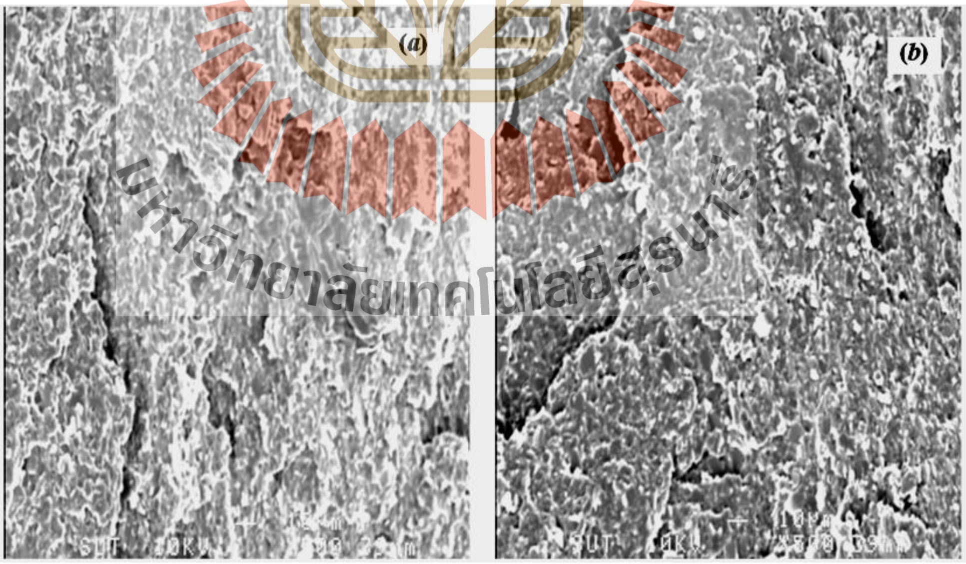


Figure 4.59 Impact strengths at low temperature of the talc filled PLA/silicone compounds as a function of talc content.

From the results found, it can preliminary confined that the impact properties of PLA/silicone compounded with talc filler are lowered by adding the solid particulate filler for both tested at ambient and sub zero temperatures.

4.5.6 Scanning electron microscopy (SEM)

The phase miscibility between PLA/silicone blend and talc is important not only the mechanical point of views but the film processing ability is also importance. The opaque film having the uneven immiscible filler phases is undesirable. Therefore, the investigation of the homogeneity between PLA/silicone and talc was verified by the fractured surface image through the SEM technique. Figure 4.60 (*a*) to 4.60 (*d*) are the SEM photographs of the notched fractured surface for 40 phr talc loaded PLA/silicone specimen tested at room and low temperature, respectively. Observation between the original and sauna cured samples, it is seen that there is no obvious different in term of crack traces for both fractured at room and sub zero temperatures. It is difficult to differentiate the phase morphology between the sample with and without sauna treatment by the SEM method. Even thought the toughness properties of those two samples were changed by the treatment. Moreover, the filler particle is too small to see the matrix/dispersed particle interfacial adhesion at the given magnification. Increasing the image magnification was attempted but the degradation of the surface of the sample was experienced because of the higher electron indent energy.



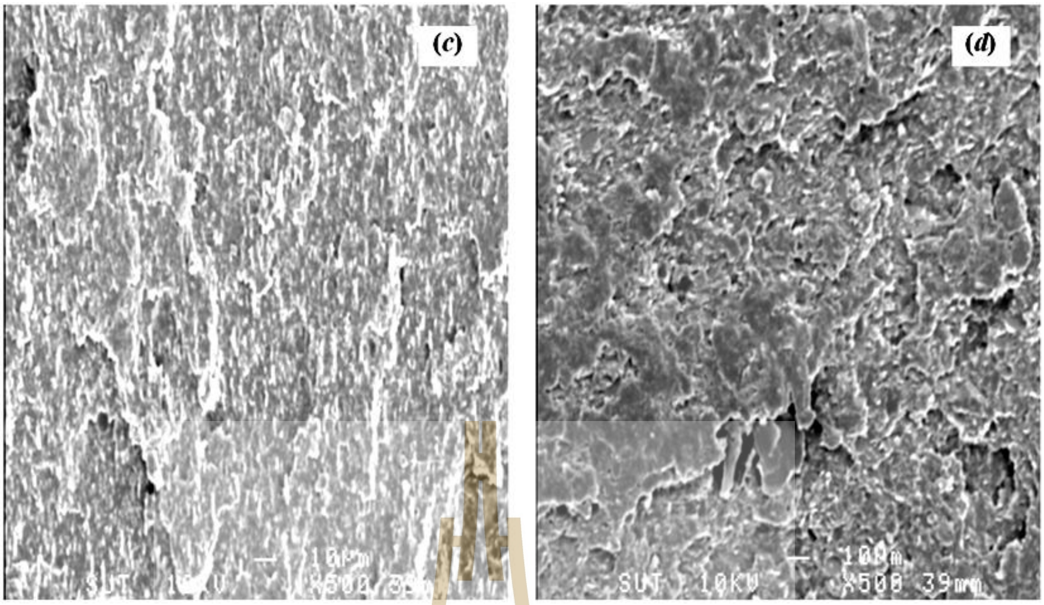


Figure 4.60 SEM micrograph of the 40 phr talc filled PLA/silicone compounds; (***a***) original, (***b***) cured fractured at room temperature and (***c***) original, (***d***) cured samples fractured at low temperature, respectively

4.5.7 Blown film processing ability investigation of PLA/silicone compound

Blow film process is widely used for manufacturing the flexible packaging. Shear thinning viscosity at low shear rate phenomena during the blowing of extrudate immerged from the die is very importance material characteristic. Material in which melt strength is easily lowered by shearing must be avoided. In this research experiment, the LDPE blown film extruder was used to manufacture the polymer films. According to the plot of appearance shear viscosity and shear rate performed at 180^{o}C presented in Figure 4.61, it seen that the viscosity profile of PLA/silicone blends filled with 40 phr of talc is similar to the blown film grade LDPE. Especially at the plateau region, low shear rate, the shear induced viscosity relationship of the compound is similar to the LDPE. It means that it is less shear thinning when comparing with PLA. From the rheological point of view the PLA/silicone with 40 phr of talc was selected to perform the blown film manufacturing. During the processing, it was observed that the film bubble was easily exploded as soon as it exits from the die. With carefully adjust the flow rate, pressure of the blowing air and melting temperature profile, the relatively thick film, comparing with LDPE film obtained from the same machine, was successfully blown with great difficulty. The properties of the blown film obtained from the given PLA/silicone compound is given in the appendix A. Further improvement in the properties of the PLA compound regarded to the blown film fabrication is needed. However, from this research work it provides that the blown film of PLA/silicone compound has high possibility to produce by using the conventional blown film extruder that is designed for manufacturing the LDPE film.

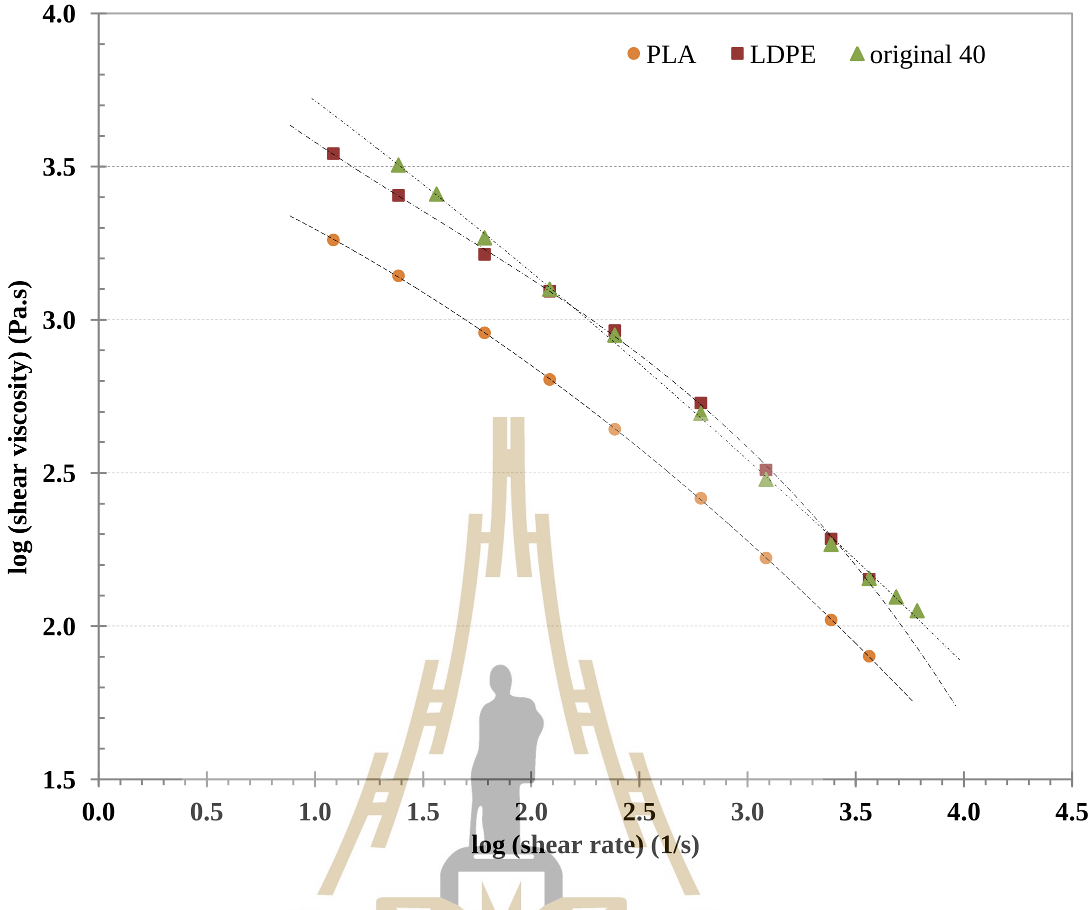


Figure 4.61 Shear viscosity plots of the the 40 phr talc filled PLA/silicone compound and LDPE

CHAPTER V

CONCLUSIONS

The main study of this research was to produce PLA/silicone compounds for low temperature food packaging applications especially as film products. Statistical study, by mean of 2^K factorial DOE, of the compound between PLA and two components silicone rubber having silane as coupling agent and polyester polyols as plasticizer found that silicone rubber at high level of content had significantly improved the toughness of the blends both at room and sub zero temperature, lowered the tensile strength become and enhanced in the elongation at break. Sauna treatment had fractionally and negatively influenced on the toughness by mean of the impact strengths. Further studied indicated that at 8.0 phr of silicone the compound manifested the overall properties. Adding TETA as the common amine based silicone curing agent enhanced the tensile properties of the PLA/silicone blend. It was found that the optimal property of the blend was at less than 0.4 phr of TETA. The initial observation manifested that the blend can be biologically degraded within four weeks of the soil composting.

The blend between PLA and single component silicone rubber having 8.0 phr of the rubber showed the adequate properties, especially impact strength at sub zero temperature, to the LDPE. Further exploration by adding the talc filler into the blend found that the ductility of the compound was decreased with increasing the filler contents. From the rheological point of view the PLA and single component silicone rubber blend having 40 phr of talc was selected to perform the blown film process. It was observed that blown film of the blends was produced with great difficulty to control the stability of the film bubble.

In conclusion, there are two blending formula resolved from this research work. They are PLA blended with two component silicon rubber and PLA with single component silicone rubber, respectively. These two blending ingredient are summarized in Table 5.1. The properties of the blended materials derived from these ingredients are adequate to those obtained from blown film grade LDPE, especially at sub zero temperature applications. The materials could be used in placed of LDPE and more environmental friendliness.

Table 5.1 The optimal formulation ingredient of PLA/silicone compounds.

Formula ingredients	**Silicone type**	
	2 component (g)	**1 component (g)**
PLA	100	100
Silicone (phr)	8.0 (8.0)	8.0 (8.0)
Silane (phr)	1 (1.0)	1 (1.0)
Polyol (phr)	1 (1.0)	1 (1.0)
TETA (phr of silicone)	0.032 (0.4)	-
Stabilizer (phr)	1 (1.0)	1 (1.0)

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APPENDIX A

FILMS PROPERTIES

Test.	PLA (g)	Silicone (g) (phr)	Silane (g) (phr)	Polyol (g) (phr)	Talc (g) (phr)	Stabilizer (g) (phr)
PLA/silicone	700	56.0 (8.0)	7 (1.0)	7 (1.0)	280 (40.0)	7 (1.0)

Type	Thickness (μm)	MD			TD		
		Tensile strength (Mpa)	Elongation at break (%)	Modulus (MPa)	Tensile strength (Mpa)	Elongation at break (%)	Modulus (MPa)
LDPE	53	2.34	127.48	18.91	2.81	244.25	12.64
PLA	30	5.23	3.14	34.21	4.56	3.05	27.34
PLA/silicone	31	1.24	14.73	16.37	1.06	8.41	10.75

APPENDIX B

PUBLICATIONS

Publication

Khiansanoi, A., and Meekum, U. (2011). Design of experiment: Poly(lactic acid)/ silicone compound. In **Proceeding of 2nd Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and The 17th PPC Symposium on Petroleum, Petrochemicals, and Polymers**. Bangkok, Thailand.

DESIGN OF EXPERIMENT: POLY(LACTIC ACID)/SILICONE COMPOUND

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ABSTRACT

PLA/silicone rubbers blend for low temperature toughness improvement was investigated. The design of experiment was used to optimize and quantify the amount of PLA/silicone blend ingredient. The 2^k factorial design of experiment was engaged. In this study, three parameter; which k = 3, consisted of silicone(A), silane(B) and polyester polyols(C) as chain extender were allocated. Each parameters was divided into two levels; high(+) and low(-). Eight PLA/silicone formulas were compounded into pellets by co-rotation twin screw extruder at 190°C and the test specimens were prepared by injection molding. The testing conditions were classified into two conditions; original and sauna cured. The original were allowed the samples to anneal at room temperature for a day. The sauna cured was achieved by incubation in moisture saturated oven at 65°C for 12 hrs. The tensile properties, HDT and impact strength both at room and at sub zero temperatures were obtained and utilized as the statistical respond effects. The ANOVA testing showed that silicone and polyol had positive effect on the impact properties both room and sub zero temperatures. Moreover, the mechanical properties were improved via sauna treatment. Scanning electron microscopy(SEM) was characterized to support the evidences of crosslink reaction and hence the measured mechanical properties accordingly. Improvement of ductility by blending of PLA with silicones and hence possibly low temperature applications was promisingly achieved.

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INTRODUCTION

Poly(lactic acid)(PLA) is a biodegradable plastic and renewable from natural materials. It has an incompetency due to its brittleness in nature. Therefore, it has not been commercially and wildly used as packaging applications especially at low temperature. Nevertheless, the flexibility of PLA can be improved by modifying its properties through several approaches including copolymerization and blending or compounding[1, 2]. Blending/compounding with other polymers or filler normally offer a cost effective way to enhance the hardness and ductility of PLA. In this studied, PLA/silicone rubbers blend were explored. Silicone is broader thermal stability and retain it toughness at low temperatures. The mechanical properties by mean of tensile and impact strength both at room and sub zero temperatures was investigated. Also, the effect of silicone on morphology, melt rheology, and thermal properties of PLA/silicone blend will be discussed. The statistical approach by mean of design of experimental(DOE) on the parameters that effect the properties of PLA/silicone was the prime interests. The experimental design on PLA/silicone blends used 2^k factorial experimental design was obtained and verified the significant effect on the mechanical properties of PLA/silicone blends.

EXPERIMENTAL

A. Material

The polylactic acid(PLA), 2002D was purchased from Nature Works®. Two components type silicone, SILASTIC® 3483, was kindly provided from Dow Corning Corporation. The *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. The blended 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 and properties. Three parameters, k = 3, explicitly as silicone(A), silane(B) and polyols(C) contents were assigned. Each parameter was divided into two levels; high(+1) and low(-1), respectively. In each level, it was also subdivided into two levels as shown in table 1. For example, silicone content at 0.5 and 1.0 phr, corresponding to 100g of PLA, were assigned as low level, vice versa 2.0 and 3.0 phr were high level, respectively. All eight formula matrices 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 and levels of DOE

Parameters	Low level(-1)		High level(+1)	
Silicone(phr)	0.5	1.0	2.0	3.0
Silane (phr)	0.2	0.5	1.0	1.5
Polyol (phr)	1.0	2.0	4.0	5.0

Table 2. DOE matrix

Test	Silicone(A)	Silane(B)	Polyol(C)	Process-aids
1	0.5(-1)	0.5(-1)	2.0(-1)	1
2	1.0(-1)	0.2(-1)	5.0(+1)	1
3	1.0(-1)	1.5(+1)	1.0(-1)	1
4	0.5(-1)	1.0(+1)	4.0(+1)	1
5	2.0(+1)	0.2(-1)	1.0(-1)	1
6	3.0(+1)	0.5(-1)	5.0(+1)	1
7	3.0(+1)	1.0(+1)	2.0(-1)	1
8	2.0(+1)	1.5(+1)	4.0(+1)	1

C. Sample preparation

PLA pellets was underwent dehumidification in vacuum oven at 80°C for 2 hrs. The assigned amounts of silane and viscous polyester polyols were manually and vigorously premixed. The dried PLA pellet and silicone were mixed by mechanical stirrer. The coated silicone PLA was then blended with the mixed liquid. Finally, thermal/processing stabilizer solid powder was added and again vigorously stirred for a few minutes. 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 consists of three kneader zones. The mixing was achieved at 10 rpm screw speed and barrel temperature profile at 150, 160, 170, 180, 190°C from feed to die zones, respectively. The extruded strand was allowed to cool down under atmospheric condition and granulated. The dehumidified pellet was molded into test specimen by using Chuan Lih

Fa, model CLF-80T, 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 65°C in sealed and moisture saturated oven for 12 hrs. The former was called original and the later called sauna cured sample, respectively. For the sub zero temperature test condition, the sample was immersed in N_2(liquid)/methanol mixture for at least ten minutes. Then, the deep cooled sample was taken out and immediately tested within a fraction of second.

D. Properties measurement and testing

Melt flow index(MFI) of the blend was obtained using the Kayeness melt flow indexer, model 4004, at 180/2.16. Tensile testing of the compound was performed according to ASTM D638, using the Instron universal testing machine(UTM), model 5565. Notch and Unnotched Impact strength, method A, was tested in according to ASTM D256. Impact properties was tested both at room and sub zero temperatures. HDT of the sample was obtained in accordance with ASTM D648 at standard load of 0.455 MPa(66 psi) and heating rate of 2 ±0.2°C/min by using Atlas Machine, model HDV 1. Morphology of the fractured surface from was examined by SEM at 10 keV. The samples were ionize coated with gold prior to test.

RESULTS AND DISCUSSION

A. DOE analysis

Table 3 summarizes the MFI, tensile properties, impact strengths and HDT for both original and sauna cured samples. Only notched impact strength was obtained at both room and sub zero temperatures. Quick observation, the test values indicate that sauna incubation obviously enhance the mechanical and thermal properties of the blend. It is emphasised that crosslink reaction through silane/water condensation reaction had been taken place during the brewing process and hence superior in the properties. Comparison with film grade LDPE, most of the compound formulae manifests better tensile strength, modulus, and impact properties, except % elongation. Moreover, the PLA/Silicone blends also reveal the superior in toughness than neat PLA. As it is prime interest for this work, the notched impacts strength, obtained at room temperature, responds, , was statistically analysed using the Design Expert^{TM}. The normal probability against the standardized effects is plotted and seen in figure 1(a) and 1(b), for original and cured sample, respectively. Also, figure 2(a) and 2(b) are the statistically results of notched impact respond tested at sub zero temperature, respectively. For the ambient temperature respond, the plot shows that silicon has obvious positive effect(**A+**) for the impacts strength of the PLA/silicone both before and after sauna cured. According to ANOVA testing result at 95% of confidential (p-value < 0.05) confirms the model designed is significant and also the parameter A was the significant affects on the notched impacts strength of the blend. The rests of the parameters are lined on the linear trend indicated that there are no significantly effect to the impact of the sample. At sub ambient temperature test condition, impact responds/effect plot for the original sample is given in figure 2(a). The analysis reveals that all calculated effects of the parameters are approximately fitted into the trendy linear line. It indicates that the designed model has no significant or perhaps the level of parameters has no significant to the impact of uncured sample at low temperature. The statement is reinforced with the calculated ANOVA result as indicated on the figure. However, figure 2(b) demonstrates that, parameters A+, C- and BC- are probably and noticeably seen to be significant effects on the impact values of the sample underwent sauna curing. Again, the ANOVA testing conceal that the designed model is significant and those parameters are also significant effects to the notched impact strength of the PLA compound. Moreover, whenever the model is significant, the statistical approach can also be utilized to construct the regressed model for prediction the impact strength of the PLA/silicone compound as a function of the parameters content. The prediction model is listed in table 4. By applying the exact approach described above, the regressed models for the other responds are also summarized in table 4.

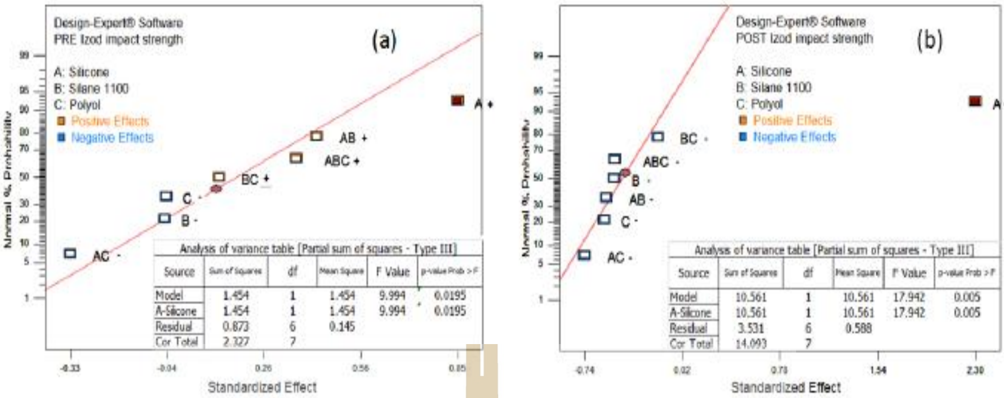
Table 3. Result data of original and cured samples

Run	MFI (g/10m)	Tensile strength (MPa)		Elongation @break (%)		Tensile modulus (GPa)		Notched impact (kJ/m^2)		Unnotched impact (kJ/m^2)		Notched impact @low temp (kJ/m^2)		HDT (°C)	
	original	original	cured	original	cured	original	cured	original	cured	original	cured	original	cured	original	cured
LDPE	2.86	8.38	8.38	83.0	82.2	0.17	0.17	Nb*	Nb*	Nb*	Nb*	3.92	4.43	32.1	41.2
PLA	1.41	52.3	59.4	4.9	4.3	2.67	2.58	2.49	3.45	15.9	21.1	2.60	5.73	52.0	52.4
1	2.07	43.9	47.6	4.4	6.5	2.49	2.33	2.54	3.23	20.3	22.2	5.40	5.36	49.2	59.3
2	2.43	38.2	41.0	4.3	8.7	2.48	2.21	3.07	3.05	21.5	24.2	3.16	4.99	48.0	57.8
3	2.64	38.9	45.2	6.0	9.3	2.52	2.43	2.31	2.96	22.0	23.2	5.40	6.70	49.3	57.6
4	2.43	37.4	43.1	6.9	8.1	2.50	2.23	2.37	3.45	26.0	28.7	4.75	3.86	47.9	60.0
5	2.45	34.2	40.9	7.5	16.8	2.52	2.48	3.66	6.34	29.7	32.7	6.05	6.40	48.5	57.9
6	3.22	29.5	38.6	9.1	12.4	2.45	2.31	2.81	5.69	26.0	36.2	6.45	6.60	47.3	58.0
7	3.28	31.6	39.8	12.9	12.8	2.53	2.39	3.56	5.93	25.3	28.8	5.24	7.38	48.5	60.3
8	2.48	34.4	42.2	5.1	9.9	2.39	2.38	3.67	3.93	20.6	26.1	6.16	5.67	47.8	58.6

* No-break

B. Scanning electron microscopy (SEM)

Visual observation of the molded compound, deep translucent piece of specimen was obtained. The SEM photographs of the fractured surface of the samples; neat PLA and Run#6 including original and cured, are presented in figure 3(a) -3(c), respectively. Figure 3(a) illustrates the surface of glassy clear neat PLA. The trace fracture surface is smooth similarly to those brittle glassy materials. However, the surfaces of PLA/silicone compounded at high silicone and polyols and low silane contents, Run#6, that outstandingly exhibit better impact strength both at room and deep cold temperatures, are illustrate on figure 3(b) and 3(c) for original and cured samples, respectively. They signify rougher fracture traces than the neat one. The ultra tiny separated particles are also observed. These dispersed droplets may be the silicone rubber. They would dissipate the impact energy and hence increase the impact resistance of the sample as evidence in the test results. The size of the dispersed phase is too tiny that still allow the light to pass through. Therefore, the compound is apparently translucent and when it is blown to form the thin film, it would become shaded transparent. Accordingly, it would possibly to be applied for frozen film application without limiting its clarity.



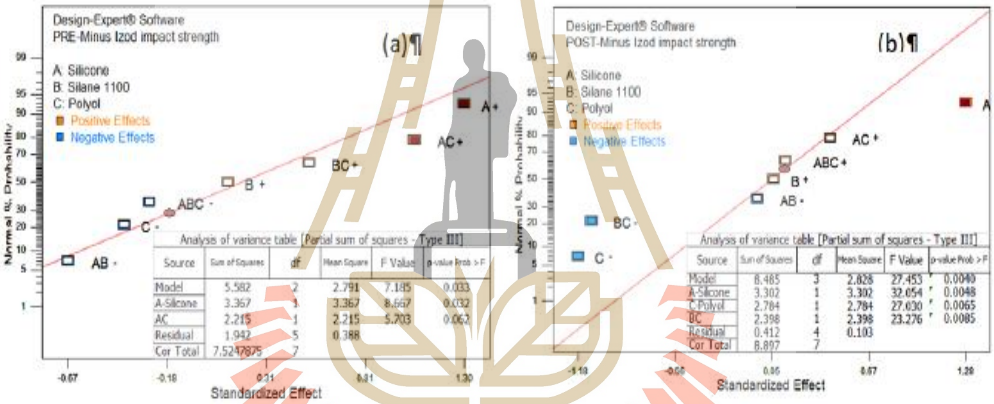
Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	1.454	1	1.454	9.994	0.0195
A-Silicone	1.454	1	1.454	9.994	0.0195
Residual	0.873	6	0.145		
Cor Total	2.327	7			

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	10.561	1	10.561	17.942	0.005
A-Silicone	10.561	1	10.561	17.942	0.005
Residual	3.531	6	0.588		
Cor Total	14.093	7			

Figure 1. Normal probability plots of notched impacts tested at room temperature for (*a*) original and (*b*) cured PLA/Silicone compound.



Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	5.582	2	2.791	7.185	0.033
A-Silicone	3.367	1	3.367	8.667	0.032
AC	2.215	1	2.215	5.703	0.062
Residual	1.942	5	0.388		
Cor Total	7.5247875	7			

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	8.485	3	2.828	27.453	0.0040
A-Silicone	3.302	1	3.302	32.054	0.0048
C-Polyol	2.784	1	2.784	27.030	0.0065
BC	2.398	1	2.398	23.276	0.0085
Residual	0.412	4	0.103		
Cor Total	8.897	7			

Figure 2. Normal probability plots of notched impacts tested at sub zero temperature for (*a*) original and (*b*) cured PLA/Silicone compound.

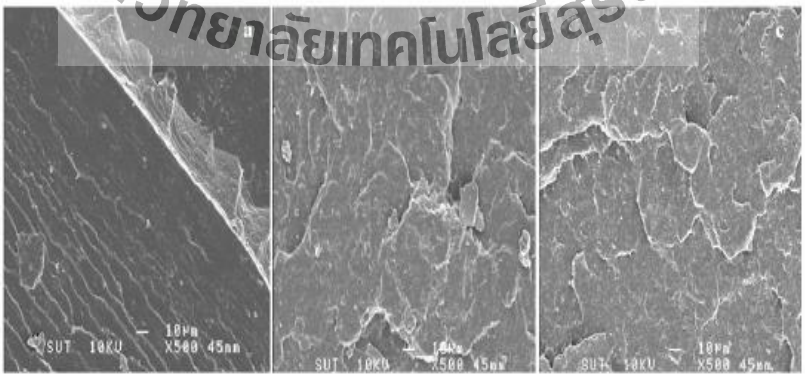


Figure 3. SEM micrograph of (a) neat PLA (b) Run#6(original) (c) Run#6(cured) at X500.

Table 4. The predicted regression model for properties of PLA/silicone derived from ANOVA testing

Properties	Regressed models
Room Temperature	
Original:	
Melt Flow Rate	No significant
Tensile strength	36.06-3.60(A)
Elongation@break	No significant
Tensile modulus	2490.12-30.69(C)-22.99(AC)
Notched impact	3+0.43(A)
Unnotched impact	No significant
HDT	48.35-0.30(A)-0.56(A)
Sauna Cured:	
Tensile strength	No significant
Elongation@break	10.62+2.41(A)
Tensile modulus	2350.69-63.82(C)
Notched impact	4.32+1.15(A)
Unnotched impact	No significant
HDT	No significant
Sub Zero Temperature	
Notched impact(original)	No significant
Notched impact(cured)	No significant

CONCLUSIONS

Compounding PLA with silicone rubber in the present of polyester polyols plasticizer and silane coupling/crosslink agent gave rise to the blend having better properties than conventional LDPE and virgin PLA. Translucent and flexible appearance of the compound obtained exhibit the tendency for using it in packaging applications both as container and films. The silane/water crosslink reaction through the sauna treatment also proved that enhancing in properties can be achieved. The statistical approach by mean of DOE concluded that the incorporated ingredient; silicone, polyester polios and silane, play the important role for construction the PLA/Silicone compound with the desired properties. The formula having silicone and polyester polyols content at high level and silane content at low level, Run#6, will be further exploring to assess the final formula and then processes selections. In overall, this formula exhibits comparably good properties.

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BIOGRAPHY

Mr. Apichart Khiansanoi was born on January 4, 1985 in Nakhon Ratchasima, Thailand. He graduated his Bechelor's Degree in Polymer Engineering from Rajamangala University of Technology Thanyaburi (RMUTT) in 2008. He then continued his Master's degree in Polymer Engineering at school of Polymer Engineering, Institute of Engineering Suranaree University of Technology. During his Master's degree study, he present a poster entitled of "**POLYLACTIC ACID COMPOUNDING FOR SUB ZERO TEMPERATURE APPLICATIONS**" in the Symposium on Petrochemical and Materials Technology and Symposium on Petroleum, Petrochemicals, and Polymer 2011(PETRO-MAT and PPC SYM 2011), Bangkok, Thailand.