

Development of Suture Pad from Silk-Reinforced Polydimethylsiloxane Composite



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2018

Copyright of Chulalongkorn University

การพัฒนาแผ่นฝึกเขียนผลจากคอมพิวเตอร์ของพอลิไคเมทิลไซลอกเซนเสริมแรงด้วยเส้นใยไหม



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2561

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

Thesis Title Development of Suture Pad from Silk-Reinforced
Polydimethylsiloxane Composite
By Mr. Radhitya Banuaji Prastowo
Field of Study Chemical Engineering
Thesis Advisor Professor SARAWUT RIMDUSIT, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial
Fulfillment of the Requirement for the Master of Engineering

..... Dean of the Faculty of Engineering
(Professor SUPOT TEACHAVORASINSKUN, D.Eng.)

THESIS COMMITTEE

..... Chairman
(Associate Professor THARATHON MONGKHONSI, Ph.D.)

..... Thesis Advisor
(Professor SARAWUT RIMDUSIT, Ph.D.)

..... Examiner
(Dr. PARAVEE VAS-UMNUAY, Ph.D.)

..... External Examiner
(Associate Professor Chanchira Jubslip, D.Eng.)

ราติยา บานัวจิ ปรัสโตโว : การพัฒนาแผ่นฝักเย็บแผลจากคอมพอสิตของพอลิไดเมทิลซิล
 ลอกเซนเสริมแรงด้วยเส้นใยไหม. (Development of Suture Pad from Silk-
 Reinforced Polydimethylsiloxane Composite) อ.ที่ปรึกษาหลัก : ศ. ดร.ศราวุธ
 ริมดุสิต

ในงานวิจัยนี้มุ่งเน้นที่จะศึกษาสมบัติทางกลของพอลิซิลลอกเซนที่เสริมแรงด้วยเส้นใยไหม
 ชนิดเส้นใยสั้นสำหรับการใช้งานเป็นแผ่นฝักเย็บแผล โดยศึกษาผลของอัตราส่วนความยาวต่อ
 เส้นผ่าศูนย์กลางของเส้นใยและปริมาณของเส้นใยต่อสมบัติต่างๆของพอลิซิลลอกเซนที่เสริมแรง
 ด้วยเส้นใยไหม จากผลการทดลองค่ามอดูลัสและความสามารถในการทนต่อแรงดึงของพอลิซิลลอก
 เซนที่เสริมแรงด้วยเส้นใยไหมมีค่าเพิ่มสูงขึ้นตามอัตราส่วนความยาวต่อเส้นผ่าศูนย์กลางของเส้นใย
 และปริมาณการเติมเส้นใยไหมที่เพิ่มขึ้นด้วย รวมถึงความสามารถในการทนต่อแรงฉีกหลังจากการ
 ฝักเย็บชิ้นงานก็เพิ่มสูงขึ้นตามปริมาณการเติมเส้นใยไหมที่เพิ่มขึ้นเช่นกัน นอกจากนี้ความแข็งแรง
 ของพอลิซิลลอกเซนได้ถูกพัฒนาให้มีค่าเพิ่มสูงขึ้นด้วยการเสริมแรงด้วยเส้นใยไหม และมีค่า
 ใกล้เคียงกับความแข็งแรงของผิวหนังของคนที่มีค่าประมาณ 40 HA ซึ่งจากการทดลองแสดงให้เห็น
 เห็นว่าพอลิซิลลอกเซนที่เสริมแรงด้วยเส้นใยไหมชนิดเส้นใยสั้นเหมาะสำหรับการนำมาประยุกต์ใช้
 งานเป็นแผ่นฝักเย็บแผลนั่นเอง

จุฬาลงกรณ์มหาวิทยาลัย
 CHULALONGKORN UNIVERSITY

สาขาวิชา วิศวกรรมเคมี
 ปีการศึกษา 2561

ลายมือชื่อนิสิต

ลายมือชื่อ อ.ที่ปรึกษาหลัก

6070289221 : MAJOR CHEMICAL ENGINEERING

KEYWORD: Silk, Polydimethylsiloxane, Suture Pad

Radhitya Banuaji Prastowo : Development of Suture Pad from Silk-Reinforced Polydimethylsiloxane Composite. Advisor: Prof. SARAWUT RIMDUSIT, Ph.D.

The aim of this research is to investigate the mechanical properties of polydimethylsiloxane reinforced with short silk fibers for suture pad application. The effect of aspect ratio and fibers content of the polydimethylsiloxane reinforced with silk fibers on the properties was evaluated. From the results, tensile modulus and tensile strength of polydimethylsiloxane reinforced with different aspect ratio were increased with increasing aspect ratio and fibers content. The composite with the addition of silk fiber produces higher tear resistance with suture thread compared with pure polydimethylsiloxane. Furthermore, the hardness of polydimethylsiloxane reinforced with short silk fibers was improved with the addition of silk fiber content. The hardness of polydimethylsiloxane composite was found to be close to that of human skin (ca. 40 HA). The results indicated that the short silk fiber reinforced polydimethylsiloxane composite has the potential to be applied as a suture pad.

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

Field of Study: Chemical Engineering

Student's Signature

Academic Year: 2018

Advisor's Signature

ACKNOWLEDGEMENTS

This work would not have been completed without the help and support of many individuals. Firstly, I would like to express my sincerest gratitude to my thesis advisor, Prof Dr. Sarawut Rimdusit for giving me advice, guidance, insight, and support during this research. I also would like to thank my thesis committee members, namely Associate Professor Dr. Tharathon Mongkhonsi, Dr. Paravee Vas-Umnuay, and Associate Professor Dr. Chanchira Jubsilp, for their comments and guidance. Furthermore, I would like to express my deepest gratitude to my parents and my siblings for their unconditional love, profound support, and encouragement. Sincere thanks also conveyed to all lecturers and program officer of the Chemical Engineering Department for their continuous assistance. Also, thank goes to my classmate from Chemical Engineering and Polymer Laboratorium 2017, seniors, and juniors. Then, thanks also raise to ASEAN Scholarship of Chulalongkorn University for providing me a fully funded scholarship during my study. Importantly, I would like to deliver my special thanks to all of my Indonesian colleagues in Thailand for their support and time during study master in Chulalongkorn University. Finally, I thank Assoc. Prof. Dr. Ruangsak Lertkhajonsuk from Obstetrics and Gynaecology King Chulalongkorn Memorial Hospital Assoc. Prof. Dr. Tipaporn Wonghongkul from Faculty of Nursing, Chiang Mai University for their kind suggestion on this project. My gratitude delivers to National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand, through its Research Network NANOTEC (RNN) program and PARA Rubber Research Program (Grant no. RDF62T0014) under the Thailand Research Fund (TRF) for the funding for this research.

Radhitya Banuaji Prastowo

TABLE OF CONTENTS

	Page
ABSTRACT (THAI).....	iv
ABSTRACT (ENGLISH).....	v
ACKNOWLEDGEMENTS	vi
TABLE OF CONTENTS	vii
LIST OF TABLES.....	ix
LIST OF FIGURES	x
CHAPTER I INTRODUCTION.....	1
1.1 Overview.....	1
1.2 Objectives.....	6
1.3 Scopes of Study	6
1.4 Procedure of Study	7
CHAPTER II THEORY	9
2.1 Structure and Properties of Skin.....	9
2.2 Composite	13
2.3 Aspect ratio	14
2.4 Composite Interfaces	15
2.5 Polydimethylsiloxane.....	18
2.6 Structure and Properties of Silk.....	19
CHAPTER III LITERATURE REVIEWS	22
CHAPTER IV EXPERIMENTAL.....	32
4.1 Materials	32

4.2 Specimen Preparation.....	32
4.2.1 Density Measurement.....	33
4.2.2 Tensile Test Measurement.....	33
4.2.3 Hardness Test.....	34
4.2.4 Suture Thread Resistance Test.....	34
4.2.5 Suture Pad Fabrication.....	34
CHAPTER V RESULTS & DISCUSSION.....	36
5.1 Density Analysis of Silk Fiber Reinforced Polydimethylsiloxane.....	36
5.2 Mechanical Properties of Silk Fiber Reinforced Polydimethylsiloxane.....	40
5.2.1 Effect of Aspect Ratio on Mechanical Properties of Silk Fiber Reinforced Polydimethylsiloxane.....	40
5.2.2 Effect of Fiber Concentration on Mechanical Properties of Silk Fiber Reinforced Polydimethylsiloxane.....	44
5.3 Hardness and Tear Resistance Silk Fiber Reinforced Polydimethylsiloxane.....	48
5.3.1 Hardness Test.....	48
5.3.2 Tear Resistance Test.....	50
5.3.3 Suture Pad Physical Evaluation.....	52
5.3.4 Suture Pad Economical Evaluation.....	54
CHAPTER VI CONCLUSIONS.....	56
REFERENCES.....	58
APPENDIX.....	62
VITA.....	64

LIST OF TABLES

	Page
Table 2.1. Various human skin mechanical properties.	12
Table 3.1. Tensile properties of SiO ₂ /PP reinforced PDMS with different content.....	25
Table 3.2. Mechanical properties of the PDMS/CF/SCP composites.....	27
Table 3.3. The amino acid composition of various B. Mori silk fibroin.	30
Table 5.1. The effect of various fiber aspect ratio and content on the hardness of short silk reinforced polydimethylsiloxane composite.....	49
Table 5.2. The material cost of silk reinforced polydimethylsiloxane suture pad.....	54
Table 5.3. The price list of commercially available suture pads	55



LIST OF FIGURES

	Page
Figure 1.1. Three main layers of human body skin.	2
Figure 1.2. Surgical suturing process on a suture pad model.	3
Figure 2.1. Langer’s line of human body flesh.....	10
Figure 2.2. Composite Interface Structure.	15
Figure 2.3. Water contact angle.....	17
Figure 2.4. Structure of polydimethylsiloxane.....	18
Figure 2.5. Silkworm physical structure (left), SEM image of silk fiber (right).	20
Figure 3.1. Normalized IR spectrums for different kinds of fumed silica.	23
Figure 3.2. Stress-strain curve for network filled with a) variant surface treated fumed silica b) variant concentration of R106.....	24
Figure 3.3. Stress-strain curve polydimethylsiloxane reinforced cellulose fiber.....	28
Figure 4.1. Silk reinforced polydimethylsiloxane suture pad layer thickness.	35
Figure 5.1. The effect of fiber content on the density of short silk reinforced polydimethylsiloxane	38
Figure 5.2. Tensile stress of the short silk reinforced polydimethylsiloxane at the different aspect ratio	40
Figure 5.3. The effect of aspect ratio variation on the tensile modulus of the short silk reinforced polydimethylsiloxane.....	41
Figure 5.4. The relation between elongation at break and fiber aspect ratio of short silk reinforced polydimethylsiloxane.....	43
Figure 5.5. The tensile stress of short silk reinforced polydimethylsiloxane at various content of silk fibers	44
Figure 5.6. The effect of fiber content on the tensile modulus of short silk reinforced polydimethylsiloxane	46

Figure 5.7. Elongation at break at different fiber content of short silk reinforced polydimethylsiloxane 47

Figure 5.8. Suture thread resistance at a) commercial suture pad, b) 1 phr, c) 2 phr, and d) 3 phr of silk fiber reinforcement on the polydimethylsiloxane composites. ... 51

Figure 5.9 Suture equipment evaluation of the unfilled network and filled network of polydimethylsiloxane. 52



CHAPTER I

INTRODUCTION

1.1 Overview

Surgical care operation has been an essential part of health care worldwide for over a decade. As the incidences of traumatic injuries, cancers and cardiovascular disease continue to rise, the impact of surgical intervention on public health systems will continue to grow. While surgical procedures are intended to save lives, unsafe surgical care can cause substantial harm. The demand for a better surgeon in the future leads to a better learning device which can improve the performance of the medical student while reducing the cost of learning as efficient as possible. Therefore, the suture pad device is commonly used to practice suturing in a learning environment rather than a real human body. In the development of a suture pad, the mechanical properties of skin are a crucial property to make the studies more practical in the future.

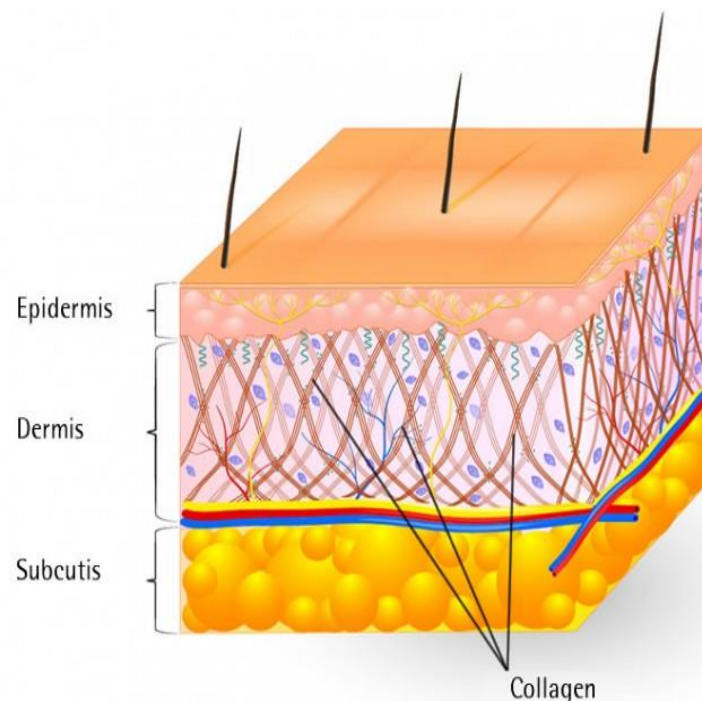


Figure 1.1. Three main layers of human body skin.
(Matrix)

Skin is the outer layer of our body which purpose as a barrier from an inhospitable environment. The skin has three general layer consist of the epidermis (the outer layer), dermis (the middle layer) and subcutis (the layer that mostly consists of fat). The epidermis and fat layer is soft; the dermis section, however, is harder because it consists of collagen that provides tensile strength and elasticity to the skin through an extracellular matrix composed of collagen fibrils, microfibrils, and elastic fibers (Marks & Miller, 2017). The dermis section of skin is the thickest part between the three-layer which mostly determine the mechanical properties of the whole skin. According to its structural shape, the dermis is a natural fiber composite. Therefore, this research

proposed to fabricate an engineering composite which could mimic skin structure consists of fiber and matrix.

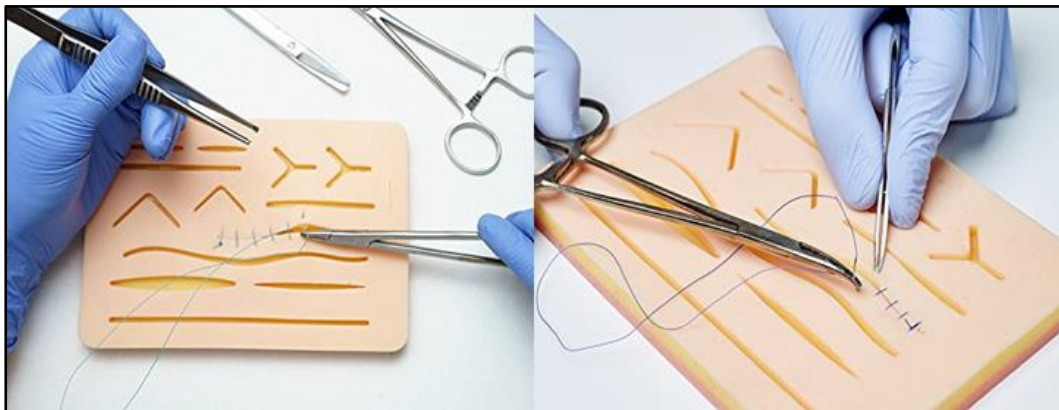


Figure 1.2. Surgical suturing process on a suture pad model.
(Kenley, 2018)

Commercially available suture pad use polydimethylsiloxane as material because of its high flexibility and low toxicity (R. C. M. P. Aquino, 2003). Polydimethylsiloxane is widely used in medical devices because of its flexibility to mimic human body parts (Lassila, Keulemans, Sailynoja, Vallittu, & Garoushi, 2018). However, polydimethylsiloxane has poor mechanical properties which limit its performance. Furthermore, fumed silica is a common reinforcing material for polydimethylsiloxane because of its high processability. Yue *et al.* (2013) investigated the effect of surface treatment on fumed silica on mechanical properties of polydimethylsiloxane composite. The result indicates better interface bonding between

polydimethylsiloxane and fumed silica after surface treatment by lowering the suspension viscosity.

Fiber reinforced composites are used commonly in engineering appliance because of its superior properties. The fibers in a composite usually form bundles or filaments. Therefore, even if several fibers break, the load force is redistributed to the other fibers, which lessen the chance of failure (Liu, 1998). Short fiber has gained importance than that of long fiber because of its advantages in processing. There are many factors to improve short fiber reinforced composite mechanical properties such as aspect ratio, critical fiber length, fiber loading, and fiber orientation (Lassila et al., 2018). Aspect ratio is the fiber length by fiber diameter ratio. Song-Ryeoul *et al.* (2001) investigate the effect of aspect ratio of short nylon fiber in the range of 0-500, the result shows increase tensile property until aspect ratio at 400 when it starts to decrease. This trend implies an optimum aspect ratio for short fiber composite.

Composites based on reinforced natural fiber have gained increasing interest because of their eco-friendly kinds of property (Cheung, Lau, Tao, & Hui, 2008; Koh et al., 2015; Prakash et al., 2016; Valentini, Bittolo Bon, Mussolin, & Pugno, 2018). Researches have been done to investigate the natural fiber reinforced composites. These natural fibers including jute, silk, coir, and sisal which not only it is abundant renewable material they also have similar properties with the synthetic ones or even superior (Prakash et

al., 2016; R. C. M. P. Aquino, 2003; Valentini et al., 2018). Natural, biodegradable plant-based fibers have been studied to improve the mechanical properties of polydimethylsiloxane as well (Silva, Goncalves, & Yoshida, 2006; Zahid, Heredia-Guerrero, Athanassiou, & Bayer, 2017; Zhang, Tingaut, Rentsch, Zimmermann, & Sebe, 2015). However, their naturally highly hydrophilic surface has low interfacial bonding with polydimethylsiloxane thus further surface treatments were conducted to improve their compatibility (Silva et al., 2006; Zahid et al., 2017; Zhang et al., 2015).

On the other hand, Kaewpravit *et al.* investigated amino acid composition within silk fiber incorporation with its hydrophilicity and hydrophobicity. The report shows a high percentage of hydrophobicity in three different silk fibers, thus implies better compatibility with polydimethylsiloxane. Also, silkworm silk fiber has unique mechanical properties, biocompatibility, and adaptability as well. It also commonly used in bioengineering structures in which they serve as a model of light-weight and inert fiber for composites (Cheung et al., 2008; Koh et al., 2015; Valentini et al., 2018).

Cheung, H. Y. *et al.* (Cheung et al., 2008) reported the effect of length and fiber content towards mechanical properties of short fiber composite with silk fiber. The result shows an increase of hardness in linear with fiber content but decreases as fiber length longer than 5 mm. The hardness of the composite used to indicate the mechanical properties

of the sample. Therefore, the effect of aspect ratio and content of short silk fiber as polydimethylsiloxane filler determination are essential factors in composite materials

In the present study, the authors propose to develop suture pad made from composites of short silk fibers. In this study, polydimethylsiloxane resin was chosen as the matrix for these composites. The effect of fiber composition of fiber on the mechanical properties has been studied for these composites. The main aim of the authors is to make environmental friendly composites for a medical device suture pad.

1.2 Objectives

To study the effect of short silk fiber on physical and mechanical properties improvement of short silk fiber-reinforced polydimethylsiloxane for suture pad.

1.3 Scopes of Study

1. Investigation of the effect of curing agent concentration in the range of 1.0 - 2.0 phr on the process ability of silk and polydimethylsiloxane suspension.
2. Preparation of silk-reinforced polydimethylsiloxane composite sample with 5 mm long ranging at 1 phr, 3 phr, and 5 phr, content of silk fibers.
3. Preparation of silk-reinforced polydimethylsiloxane composite sample with 5 mm long ranging at 1 phr, 3 phr, and 5 phr, content of silk fibers.

4. Preparation of silk-reinforced polydimethylsiloxane composite sample with different aspect ratio at 500, 1000, 1500 of silk fibers.
5. Investigation of the interfacial bonding and dispersion of silk fiber within polydimethylsiloxane by
 - Scanning Electron Microscope
 - Optical Microscope
6. Investigation of polydimethylsiloxane composites with suture equipment.
7. Investigation of thermal and mechanical properties of short silk-fiber reinforced polydimethylsiloxane by
 - Universal Testing Machine
 - Thermal Gravimetric Analyzer

1.4 Procedure of Study

1. Reviewing related literature.
2. Preparation of chemicals and equipment that needed for this research.
3. Fabrication of silk-reinforced polydimethylsiloxane composite.
4. Characterization of tensile strength, dispersion properties of silk-reinforced polydimethylsiloxane composite as follows:
 - Scanning Electron Microscope
 - Optical Microscope

- Universal Testing Machine
 - Thermal Gravimetric Analyzer
5. Analysis of the experimental result.
 6. Preparation of the final report



CHAPTER II

THEORY

2.1 Structure and Properties of Skin

The skin is the largest organ of the human body with several functions. The primary function of the skin is to protect against external influences. The skin is an organized structure which consists of three main layers as follows: epidermis, dermis, and hypodermis (Marks & Miller, 2017). The epidermis is mostly consisting of the keratinocytes, largely moving cells which formed in the epidermis layer. The layer below epidermis is the dermis layer which is a tissue layer-like composite composed of many collagen fibers, elastin fibers, and some ground substances; this structure forms a major mass of whole skin. The third layer, the subcutaneous fat layer which mainly consists of fat tissue and the thickness varies in any parts of human skin.

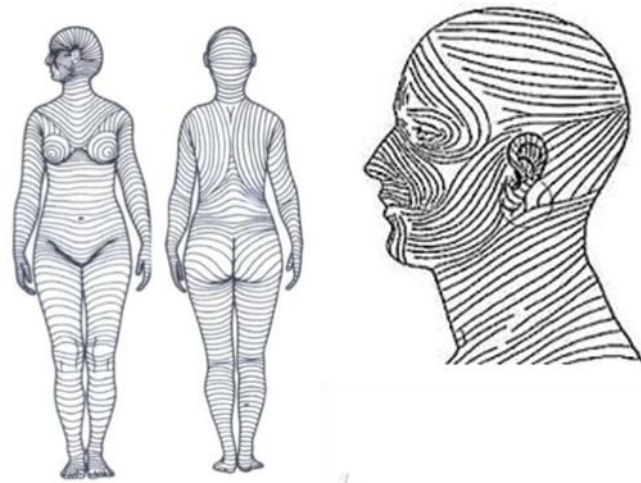


Figure 2.1. Langer's line of human body flesh.
(Langer, 1861)

The report on skin mechanical properties is dependent on many factors such as age, body parts, skin orientation (Langer's line), and tested sample structure. Age is one of the main factor reported by Vogel et al. (Vogel, 1987) from various parts of a human cadaver from a young age to elderly. The human child has the mean modulus 21 MPa where human elderly have less mean modulus of 17 MPa. Silver et al. (Silver, 2001) also reported skin mechanical properties on the human abdomen with a mean thickness of sample 2 mm resulted in mean modulus of 18.8 MPa. This value was gained from fresh skin from a human cadaver, but from preserved skin, it gave a different value of 17.6 MPa. Also, Glogowska et al. (Gasior-Glogowska et al., 2013) reported ultimate tensile stress of human skin thigh with 1.5 mm thickness sample has 30 MPa when tested along the Langer's line while 1.2 MPa when measured

perpendicular to the langer's line. Ottenio et al. (Ottenio, Tran, Ni Annaidh, Gilchrist, & Bruyere, 2015) also reported on the ultimate tensile strength of human back skin with a mean thickness of sample 2.3 mm perpendicular and parallel with langer's line has a value of 15.6 MPa and 28 MPa respectively. It can be inferred that the tensile strength of the skin is between 1.2 MPa to 30 MPa depend on its location and orientation.



Table 2.1. Various human skin mechanical properties.

(Gasior-Glogowska et al., 2013; Ni Annaidh, Bruyere, Destrade, Gilchrist, & Ottenio, 2012; Ottenio et al., 2015; Silver, 2001)

References	Skin Source	Thickness	E (MPa)	UTS (MPa)	Langer's Line
Silver et al. (2001)	Human Abdomen (47-86)	2	18.8		
	Acellular Dermis	2	18.4		
	Processed Human Dermis	2	17.6		
Glogowska et al. (2012)	Human Thighs (53)	1.5	12	30	Parallel
	Human Thighs (53)	1.5	2	1.2	Perpendicular
Annaidh et al. (2012)	Human back bottom (79)	2.6		17.6 ± 4.8	Parallel
	Human back bottom (79)	2.6		10.5 ± 8.4	Perpendicular
Ottenio et al. (2015)	Abdomen (90)	2.3		28.0 ± 5.7	Parallel
	Abdomen (90)	2.3		15.6 ± 5.2	Perpendicular

Skin anisotropic was recognized as far back as the 19th century by Langer (1861), who mapped the natural lines of tension which occur within the skin (Langer, 1861). These lines are identified by puncturing the skin with a circular device. The wounds then

assume an elliptical shape, and by joining the principal axes of the ellipses, a system of lines can be drawn as shown in Fig. 1. The lines shown in the human body is known as the Langer's lines. The Langer's line orientation is affected by the collagen fiber orientation in the skin dermis layer.

2.2 Composite

Composite is a unique material which is made from a combined of two or more different materials with a recognizable interface between them that result in more superior properties than any of its former or parental materials either it increased its strength, toughness or can also be used to decrease its weight and cost [6, 7]. The composite material has the properties of conventional materials in general from the manufacturing process through non-homogeneous mixing between the reinforcing material and the matrix. The reinforcing material can be either particulate, fiber or fabric where the matrix plays a role as a binder.

There are many factors which affect the properties of the composite such as aspect ratio, interfacial bonding, surface area, and chemical bonding between both reinforcing material and the matrix. A good composite is where the applied stress on the matrix can be transmitted to the reinforcing material. Thus the composite has stronger properties than its parental materials.

2.3 Aspect ratio

Aspect ratio is important parameters in short fiber reinforced composite (SFRC) that affect the mechanical behavior such as tensile strength, strain, flexural stress, and fiber efficiency. Aspect ratio is the fiber length value to the fiber diameter ratio (Lassila et al., 2018).

$$\text{Aspect ratio} = \frac{l_f}{d}$$

Length fibers are mostly being varied to find the optimum values and mechanical behavior inside the matrix. Normally, the matrix strains more than the fiber because it has a lower modulus than the fiber. Difference strain occurs along the length of the fiber. The fiber limits the strain of the matrix which adhere to the fiber. Thus, for a composite under tension, shear stress appears in the matrix that pulls from the fiber. The pull is uniform over the area of the fiber. This makes the force on the fiber be minimum at the ends and maximum in the middle.

$$l_c = \frac{\sigma_f(UTS) \cdot d}{\tau_m}$$

Composites containing chopped short fibers can be as strong as those containing continuous fibers as long as the fibers exceed a critical length. Fibers that is shorter than the critical length will much likely to no be able to reach their maximum load,

and thus the fiber reinforcement will not be efficient. If the average length is above the critical length, the fibers will carry an increasing fraction of the applied load and may fracture before the matrix especially if the matrix material has some ductility. Therefore, it is necessary to determine the critical fiber length. Critical length (l_c) is defined as the minimum length of fiber when the center of the fiber reaches the ultimate tensile strength (σ_f) as the matrix used achieves the maximum shear strength (τ_m).

2.4 Composite Interfaces

The important dimension of a composite is the interface. The interface is the area between different materials in a composite. An excellent and applicable composite is to form a strong enough interface towards its maximum compatibility between materials.

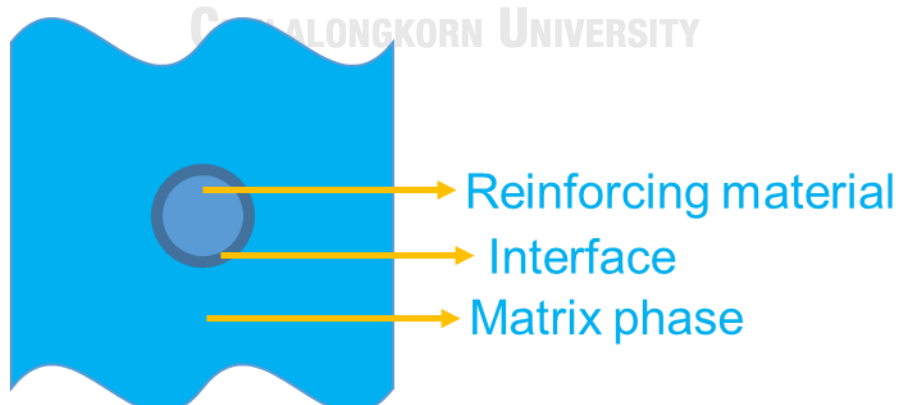


Figure 2.2. Composite Interface Structure.

A strong interface gradient is crucial for material to survive under stress. Stresses applied to the matrix can be optimally transferred to the fiber across the interface. Thus, the size of this gradient and chemical interaction present in the composite material will affect the strength and characteristic of the composite. The same concept can be applied to blends as well. The interface between materials has to reach a certain level of interaction in which prevent each component to separate from each other.



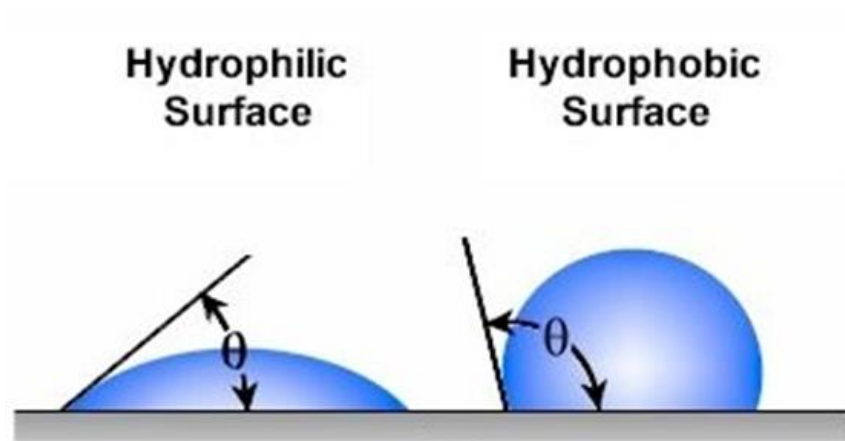


Figure 2.3. Water contact angle.

(Chaplin, 2003)

During the manufacturing process, the wettability of the materials plays a vital role in which whether the reinforcement will be able to adhere to the matrix or not. A good wettability means that the liquid form of the matrix will easily flow covering every surface of the reinforcing material and displace air. Thus the matrix viscosity has to be controlled in order for it to flow in between the reinforcing material. Wettability factor will increase interfacial bonding as well by minimizing air void in between matrix and reinforcing the material. Wettability of the material can be measured by water contact angle as shown in Figure 4. The water contact angle or θ between 0° to 90° indicates the hydrophilic surface of the material whereas θ higher than 90° indicates hydrophobic surface.

There are many studies reported to increase interface bonding for better compatibility between reinforcing material with the matrix by modifying the surface of the reinforcing material by chemical bonding with appropriate coupling agents as well (Sang-Ryeoul Ryu, 2001; Wu & Wang, 2018; Wu & Zuo, 2018).

2.5 Polydimethylsiloxane

Polydimethylsiloxane (PDMS) belongs to a polymeric group of organosilicon compounds. The compact methyl groups substituent associated with low London dispersion forces on the main intermolecular interactions between chains combined with long, highly flexible siloxane chains, it produces an elastomer with a very low glass transition temperature.

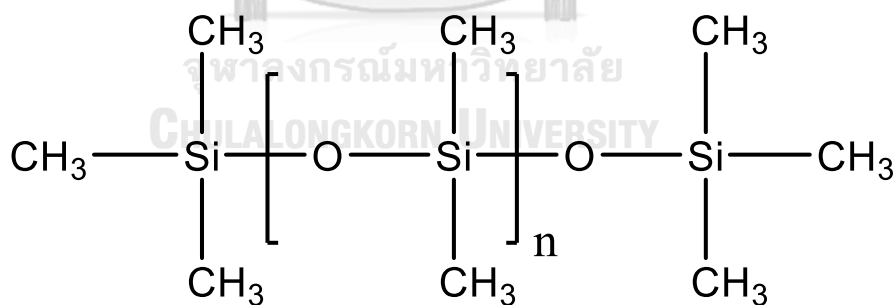


Figure 2.4. Structure of polydimethylsiloxane.

PDMS is generally inert, biocompatible, non-toxic, and non-flammable.

Polydimethylsiloxane (PDMS) displays a various combination of properties such as

good electrical properties, low glass transition temperatures, high thermal stability, hydrophobicity, high gas permeability, and physiological inertness or biocompatibility. These attractive properties explain why PDMS is used in a large number of applications such as heat resistant tiles, lubricants, and medical devices. Its thermal and chemical resistivity was useful as an insulator in the electrical field, its hydrophobicity surface has led to its use in aerospace and its inert properties together with its biocompatibility has led to its usage as a biomaterial in medical applications, devices and healthcare (Sang-Ryeoul Ryu, 2001).

However, PDMS has a low glass transition temperature and feeble intermolecular forces between polymer chains which led to poor mechanical properties. In order to reach reasonable mechanical properties, PDMS must be cross-linked and filled with reinforcing fillers (Mi, Jing, Huang, & Turg, 2018; Valentini et al., 2018; Wu & Wang, 2018; Ziraki, Zebarjad, & Hadianfard, 2016).

2.6 Structure and Properties of Silk

Silk is natural fiber produced by a certain insect to form a cocoon or nest such as silkworm, spider, and bees. The one common silk is biosynthesized by *Bombyx mori* silkworm which then widely be cultivated as clothing material. Silkworm silk constructed by two types of protein that is fibroin and sericin (Kaewprasit, Promboon,

Kanokpanont, & Damrongsakkul, 2014; Rusa, Bridges, Ha, & Tonelli, 2005). Fibroin is a core protein filament mainly composed of the amino acids such as glycine, alanine, and serine while sericin is a glue-like protein that sticks multiple single fibroin filaments together.

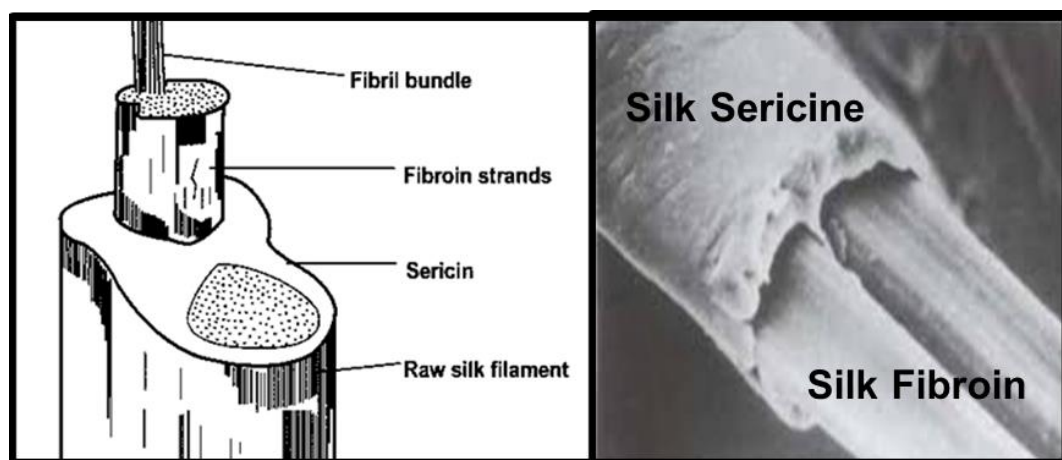


Figure 2.5. Silkworm physical structure (left), SEM image of silk fiber (right).

(Kaewprasit et al., 2014)

CHULALONGKORN UNIVERSITY

Silk fibroin has biocompatibility which is quite useful for many biomedical applications while its exceptional mechanical properties can be utilized as reinforcing material (Rusa et al., 2005). Kaewprasit et al. (Kaewprasit et al., 2014) investigated amino acids components from Thai-silk fibroin namely Nangnoi-Sisaket and classified them into two groups; hydrophilic and hydrophobic group. The hydrophilic group contained acidic,

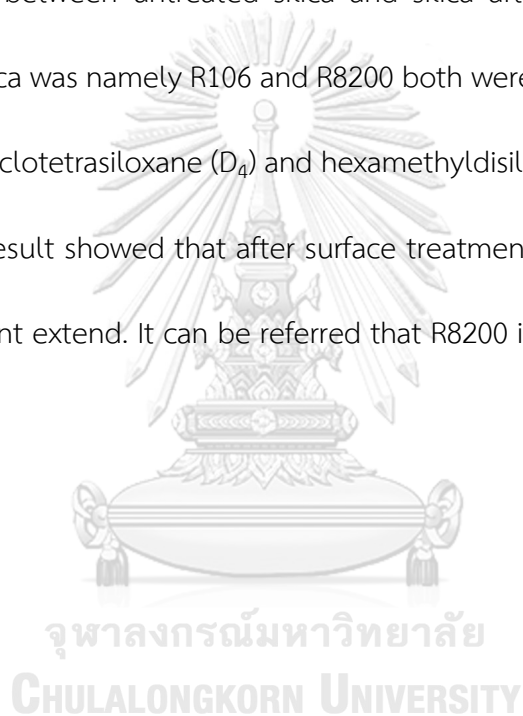
basic, and polar amino acids while the hydrophobic group consisting of aromatic and non-polar amino acids.



CHAPTER III

LITERATURE REVIEWS

Fumed silica was Polydimethylsiloxane Yue *et al.* (Yue et al., 2013) investigated the thermal and mechanical properties of fumed silica filled polydimethylsiloxane. The author compared between untreated silica and silica after surface treatment. The surface treated silica was namely R106 and R8200 both were A300 fumed silica treated with octamethylcyclotetrasiloxane (D_4) and hexamethyldisilazane (HDMS) respectively. The IR spectrum result showed that after surface treatment the peak for Si-OH group decreased to variant extend. It can be referred that R8200 is more fully modified than R106 as well.



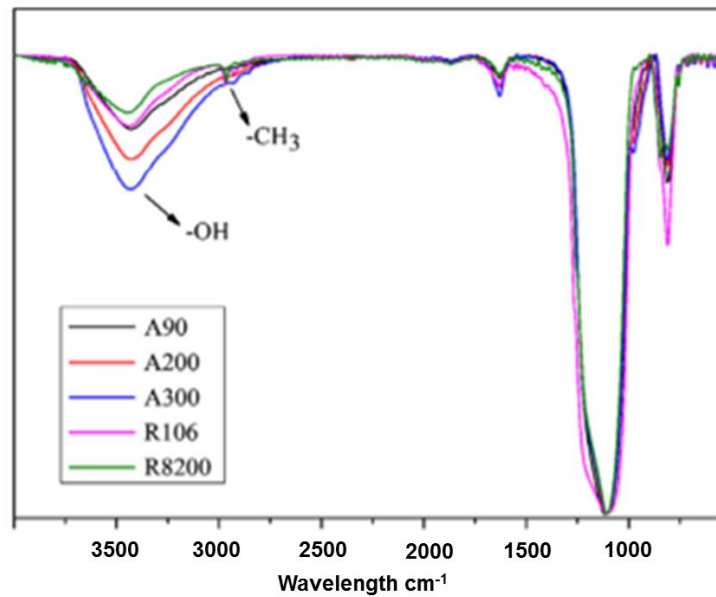


Figure 3.1. Normalized IR spectrums for different kinds of fumed silica.
(Yue et al., 2013)

The tensile test result showed surface treated silica with HDMS has higher modulus but slightly lower tensile stress from the untreated silica while silica treated with D_4 exhibit lower tensile stress. This phenomenon can be explained by Si-OH group on the silica surface. The untreated silica has an excessive amount of Si-OH that made the suspension behaves more like solid and formed many agglomerates. After solution curing, a certain amount of occluded rubber forms within huge agglomerates. This kind of network structure can affect the properties of the composite. On the contrary, the surface modification led to improved dispersion, and the amount of occluded rubber within agglomerates decreased which theoretically improve tensile strength. The author reported that the result on moderate surface modification lies in reducing the

viscosity of filled suspension and improving dispersion without highly damaging the mechanical properties of the composites.

Effect of concentration on the tensile properties of the filled network was also investigated. The author varies the filler content between 1 phr to 10 phr. Indeed, the mechanical properties increased with filler concentration as shown in Figure 10a.

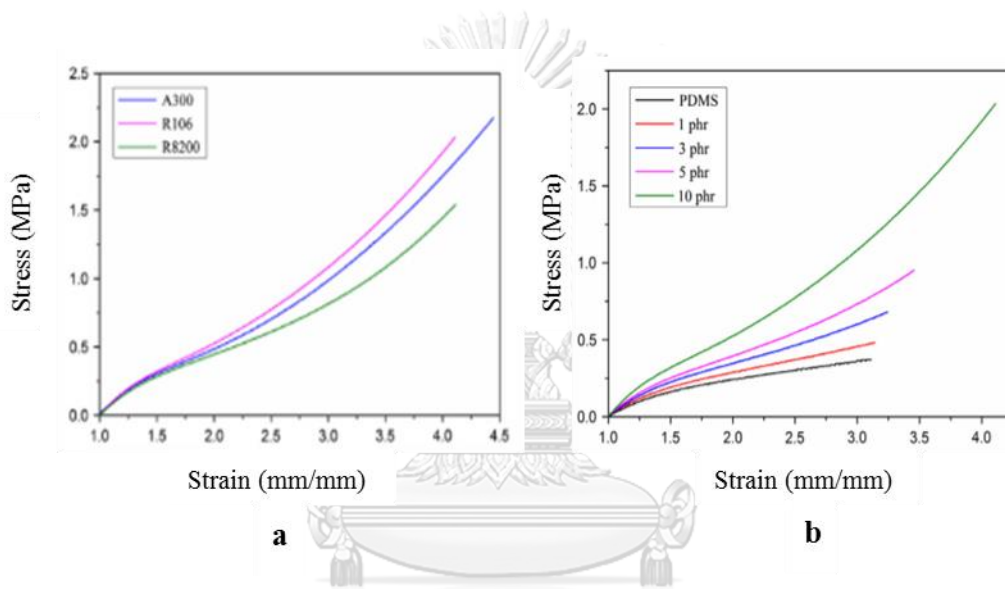


Figure 3.2. Stress-strain curve for network filled with a) variant surface treated fumed silica b) variant concentration of R106.

(Yue et al., 2013)

Recent study about hybrid fiber reinforced polydimethylsiloxane was also reported. Ziraki *et al.* Ziraki et al. (2016) investigated tensile properties of short polypropylene fiber and silica as reinforcing additives on the polydimethylsiloxane. The author reported that the addition of silica and polypropylene fiber causes an increase in tensile strength. The fumed silica particle size was 25 nm, and PP fiber diameter was

30 μm with a length between 10-15 mm with an aspect ratio between 300-500. The initial tensile strength of silicone used was 3.9 MPa, and with the addition of polypropylene fiber and silica, it was increased to 6.9 MPa and 5.6 MPa at 2% weight respectively. The result indicates that the increase in tensile properties was in parallel with filler

The result reported that the fiber pulling out during the tensile test consumes part of the applied load in which increase the strength and toughness. In theory, the pull out energy required can be increased by using fiber which longer than the critical length. The critical length (l_c) of fiber was 3 mm, and the fiber length used was higher than l_c .

Table 3.1. Tensile properties of SiO₂/PP reinforced PDMS with different content. (Ziraki et al., 2016)

Samples	Pure Silicone	1% SiO ₂	2% SiO ₂	1% PP	2% PP
Tensile Strength (MPa)	3.9	4.6	5.6	5.5	6.9
Elongation at break (%)	1114	1047	955	1044	910
Toughness modulus (MJ/m ³)	19.1	20.5	21.9	27.5	29.2

The author also investigates PP and silica reinforced PDMS hybrid composite at 1% weight respectively compared to both non-hybrid composites. The result of the hybrid composite was found to be according to the rule of mixture. PP fibers have a lower

density than fumed SiO_2 which in constant content the volume fraction of PP fibers is higher than fumed SiO_2 . The effect of reinforcing additives content and higher aspect ratio were proven to significantly improve the mechanical properties of polydimethylsiloxane.

There was also previous research about short carbon fiber reinforced polydimethylsiloxane since carbon fiber has high modulus, tear strength and high aspect ratio which is good composite filler material.



Table 3.2. Mechanical properties of the PDMS/CF/SCP composites.

(Soo Kim, 2011)

Sample	Max Stress (MPa)	Elongation at break (%)	Tear strength (N/m)	Shore A
PDMS	8.2	1100	13.6	72.1
PDMS/CF3.5	7.9	608	18.8	86.5
PDMS/CF3.5/SCP2	7.8	597	19.5	90.5
PDMS/CF3.5/SCP5	7.7	610	16.4	92.5
PDMS/CF3.5/SCP10	7.4	787	13.7	89.0
PDMS/SCP5	6.9	906	12.5	79.8
PDMS/SCP5/CF0.5	7.5	800	13.9	81.2
PDMS/SCP5/CF1.5	7.5	704	16.2	86.8
PDMS/SCP5/CF3.5	7.7	610	16.4	92.5

Kim *et al.* (Soo Kim, 2011) have investigated the mechanical properties of naked short carbon fiber and silicon carbide powder (SCP) hybrid reinforced polydimethylsiloxane. The carbon fiber used was chopped into 5-6 mm in length. The result from Table 3 shows an increase in tear strength compared to pristine polydimethylsiloxane at the highest value by 43% with 3.5 % weight carbon fiber and 2 % weight of silicon carbide powder but the tensile stress and elongation decrease by adding the filler. Shore A hardness of PDMS/CF composites was increased in parallel with the addition of CF content. Moreover, the composites filled with carbon fiber lose transparency when combined.

Although carbon fiber and polypropylene was proved as a good polydimethylsiloxane composite filler, composites based on reinforced natural filler have gained more interest because of their eco-friendly kinds of property. Recently, Zhang *et al.* (Zhang *et al.*, 2015) reported the use of natural filler to reinforce polydimethylsiloxane. The author uses cellulose fiber as reinforcing filler. Since cellulose is highly hydrophilic, it is unlikely to have good interfacial bonding with polydimethylsiloxane. In this research, cellulose fiber was treated with methyltrimethoxysilane oligomer to overcome the problem.

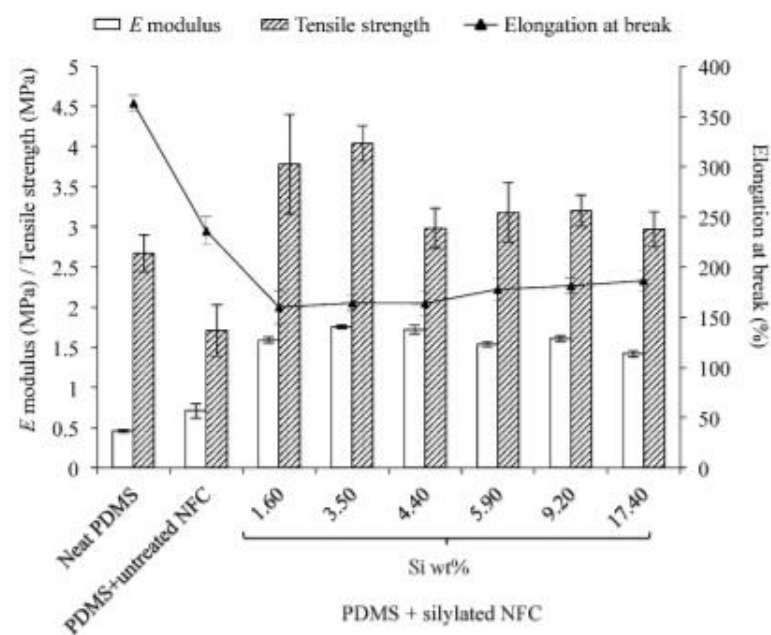


Figure 3.3. Stress-strain curve polydimethylsiloxane reinforced cellulose fiber.
(Zhang *et al.*, 2015)

The result in shows decreases in tensile stress for polydimethylsiloxane reinforced with the unmodified cellulose fiber which can be explained by the poor compatibility between the hydrophilic cellulose fiber and the hydrophobic polydimethylsiloxane as shown in Figure 10. The decrease in the strain at break can be assigned to the presence of a rigid particle within the matrix. On the contrary, modified cellulose fiber reinforced polydimethylsiloxane demonstrated significant increase with 1.6 wt% to 3.5 wt% loaded filler.



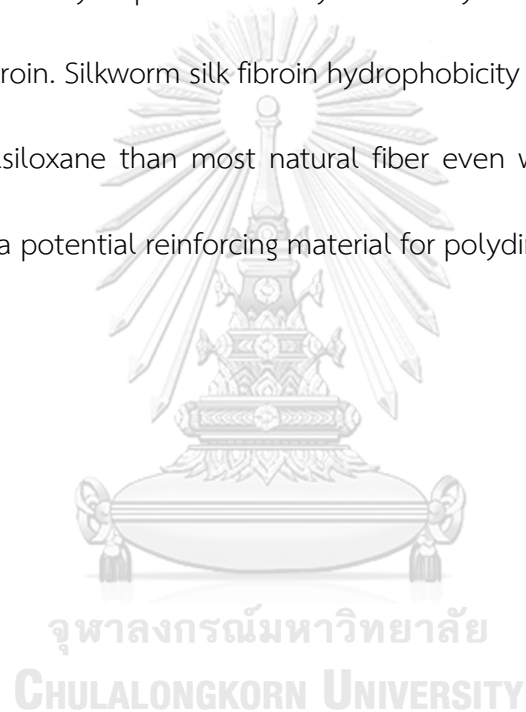
Table 3.3. The amino acid composition of various *B. Mori* silk fibroin.

(Kaewprasit et al., 2014)

	Thai Native (%mole)	Japanese Hybrid (%mole)	Chinese Hybrid (%mole)
Hydrophilic Group			
Aspartic acid	1.63	2.08	2.18
Glutamic acid	1.15	1.52	1.51
Arginine	0.30	0.31	0.44
Lysine	0.20	0.26	0.30
Histidine	0.83	0.81	1.02
Serine	13.42	16.87	16.30
Threonine	0.80	1.08	1.08
Cysteine	0.00	0.00	0.00
Total	18.33	22.93	22.83
Hydrophobic Group			
Glycine	38.32	33.00	35.76
Alanine	34.29	31.26	29.39
Proline	0.42	0.64	0.64
Valine	1.15	1.67	1.53
Leucine	0.30	0.38	0.43
Isoleucine	0.20	0.31	0.32
Methionine	0.08	0.13	0.10
Aromatic	6.94	9.68	9.00
Total	81.67	77.07	77.17

Most natural fiber has a hydrophilic surface which will result in low interfacial bonding with polydimethylsiloxane. Thus further surface treatments were conducted to

improve their compatibility (Silva et al., 2006; Zahid et al., 2017; Zhang et al., 2015). Contrarily, Kaewprasit *et al.* (Kaewprasit et al., 2014) investigated silkworm silk fibroin hydrophilicity and hydrophobicity incorporation to an amino acid percentage. The result shown in Table 2. indicates high hydrophobicity of silkworm silk fibroin. The hydrophobic nature of silk fibroin can be assigned to the presence of glycine and alanine at most while hydrophilic is mostly caused by the presence of serine in the structure of silk fibroin. Silkworm silk fibroin hydrophobicity shows better compatibility with polydimethylsiloxane than most natural fiber even without surface treatment. Thus, indicates as a potential reinforcing material for polydimethylsiloxane composite.



CHAPTER IV

EXPERIMENTAL

4.1 Materials

The materials in this research are polydimethylsiloxane resin, silicone oil, and degummed silk fiber. Polydimethylsiloxane resin is condensation cured room temperature vulcanized (RTV) silicone. Polydimethylsiloxane resin was supplied by Mat Wealth Co., Ltd from Taiwan under the product name of RTV 2-230 MW. Silicone oil was obtained from Resin Rungart Co., Ltd. The silk fiber is a degummed Thai silk purchased from Chul Thai Silk Co., Ltd. Silk fiber has a density of 1.230 g/cm^3 and diameter of $11.724 \text{ }\mu\text{m}$.

4.2 Specimen Preparation

Silk reinforced polydimethylsiloxane composite sample was prepared with different aspect ratio and content. Silk fiber was chopped into three different lengths of 0.5 cm, 1 cm, and 1.5 cm at fixed content of 1 phr of silk fiber. The content of fiber reinforcement was varied at 1 phr, 2 phr, 3 phr, 4 phr, and 5 phr at fixed length of 1 cm. Silicone resin was mixed with 20 phr silicone oil and then stirred to achieve uniform dispersion.

Curing agent was added to the mixture by 1 phr and have to be immediately stirred to avoid agglomeration. Then, the silk was added to the mixture and carefully stirred. The uncured composite was poured into the aluminum molder with a dimension of 15 cm x 15 cm x 1 cm. Then, the mixture was put inside a vacuum oven at room temperature. After 30 minutes, the mixture surface was closed with aluminum molder and then left it for two days to be fully cured before characterization.

4.2.1 Density Measurement

The composites were cut into small samples with dimension of 3 cm x 3 cm. The overall weight in the air from 4-5 gram. The density was measured by calculating the difference between theoretical density and actual density. The theoretical density was calculated with mixing rule principal. The actual density was measured using a hydrometer under room temperature.

4.2.2 Tensile Test Measurement

The sample was cut into a sample shape according to ASTM D 412 Type C. Tensile test was determined with Instron Universal Testing Machine with a load of 1 kN and testing speed of 500 mm/min. Three samples for each variable were tested. The maximum stress, young modulus, and strain at break were then examined.

4.2.3 Hardness Test

The samples were tested with shore A durometer according to ASTM D2240. The samples were tested five times for each variable at different content of fiber reinforcement at 1 phr, 2 phr, 3 phr, 4 phr, and 5 phr.

4.2.4 Suture Thread Resistance Test

The samples were cut into two rectangular shapes with specimen dimension of 3 cm x 3 cm. The two specimens were then sutured with suture equipment. The suture equipment uses a sharp suture needle with nylon thread of monofilament nylon NC 242 2-0 purchased from Nutri Plus Intertrade Co., Ltd. The sutured samples were pulled at 0.5 cm extension. The samples resistance towards suture thread were observed.

4.2.5 Suture Pad Fabrication

The suture pad was prepared with 2 layers. The first layer was silk reinforced polydimethylsiloxane composite formulation with thickness ~2 mm. The second layer was polydimethylsiloxane and silicone oil with a composition of 50 : 50 with a thickness ~8 mm as shown in Figure 4.1.

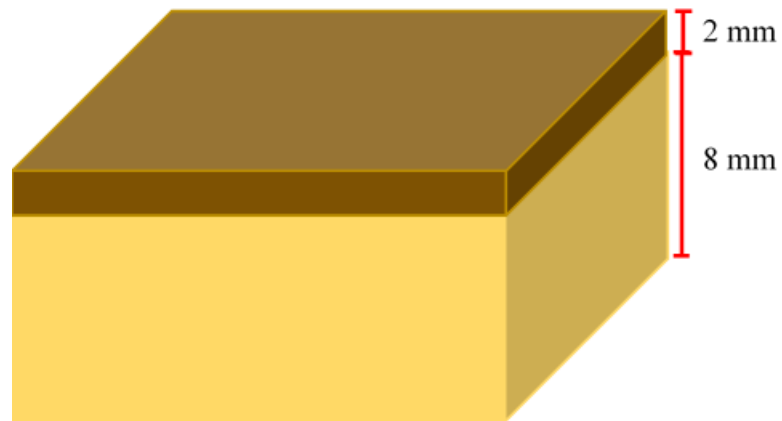


Figure 4.1. Silk reinforced polydimethylsiloxane suture pad layer thickness.



CHAPTER V

RESULTS & DISCUSSION

5.1 Density Analysis of Silk Fiber Reinforced Polydimethylsiloxane

The density measurement purpose is to analyze the dispersion of the silk fiber with the polydimethylsiloxane. The absence of air voids inside the composite sample can act as a sign of a fine dispersion of mixture between silk and polydimethylsiloxane. The voids fraction can be measured from the difference between the theoretical density of the silk polydimethylsiloxane composite and its actual density. The theoretical density of a composite is the maximum density it achieves without voids under theoretical states. Minimum difference between theoretical density and actual density of the composite will result in low air voids, thus imply well-fabricated samples. The theoretical density values are calculated according to the mixing rule. The theoretical equation of silk-polydimethylsiloxane composite uses the density of polydimethylsiloxane and silk fiber to calculate the density of composite without a void by the weight fraction of the mixture. From the weight fraction and density of each component of silk reinforced polydimethylsiloxane, the theoretical composite densities (ρ_f , ρ_m) were calculated as well.

$$\rho_{theoretical} = \frac{1}{\frac{\omega_f}{\rho_f} + \frac{\omega_m}{\rho_m}}$$

where,

ω_f is the weight fraction of silk fiber

ω_m is the weight fraction of polydimethylsiloxane

ρ_f is the density of silk fiber (1230 g/cm³)

ρ_m is the density of polydimethylsiloxane (1128 g/cm³)

The measurement of the actual composite density uses a hydrometer at room temperature. The density of the composite can be calculated in accordance with the Archimedes principle. The Archimedes principle stated that the weight of water displaced is equal to the difference between the weight of the solid in the air and the water. The ratio of the weight of water displaced and the density of water has the same proportion with the ratio of the weight of the sample and the sample density.

Therefore, the equation is as follow:

$$\rho_{actual} = \frac{A}{A - B} \cdot \rho_o$$

where,

A is the weight of composite in the air

B is the weight of composite in the water

ρ_0 is the density of water (1000 g/cm^3)

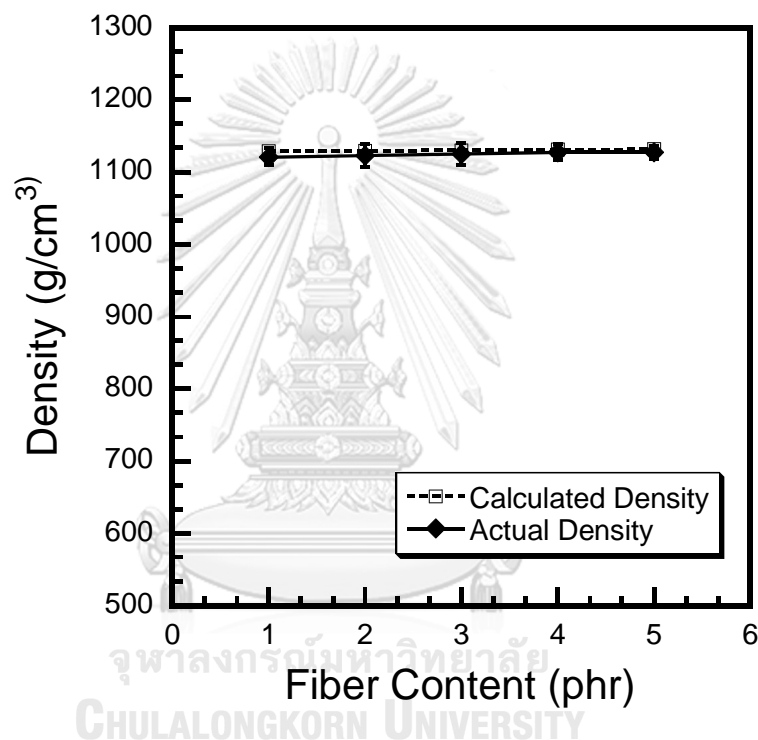
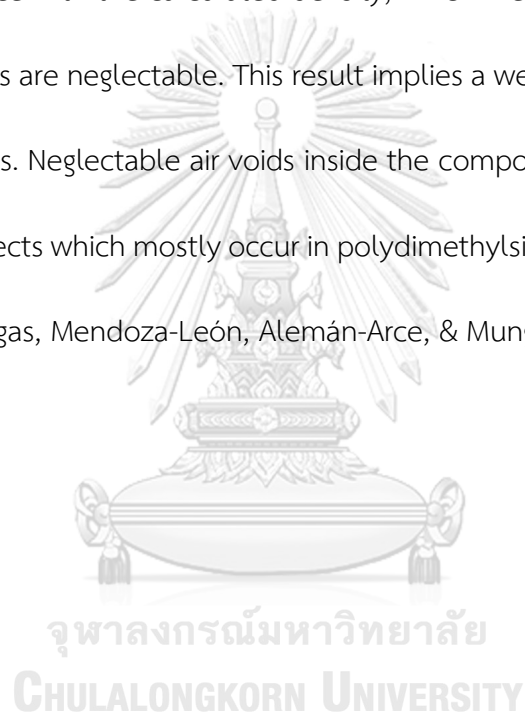


Figure 5.1. The effect of fiber content on the density of short silk reinforced polydimethylsiloxane

The result of the calculated values of the theoretical and actual density of silk reinforced polydimethylsiloxane is presented in Figure 5.1. It can be noted that with an increase in short silk fiber concentration, there is an increase in composite density which was due to using more silk fiber. The trend of composite density escalation with

an increase in silk fiber content is almost linear. In general, the composite density is influenced by the fiber content.

The difference values between the calculated theoretical density and actual density from the instrument were measured to be very low. The actual density has no significant difference with the calculated density, which means the air voids inside the composite samples are neglectable. This result implies a well-dispersed mixture of the composite samples. Neglectable air voids inside the composite mean that the sample has almost no defects which mostly occur in polydimethylsiloxane samples (Mendoza-Acevedo, Villa-Vargas, Mendoza-León, Alemán-Arce, & Munguía-Cervantes, 2017).



5.2 Mechanical Properties of Silk Fiber Reinforced Polydimethylsiloxane

5.2.1 Effect of Aspect Ratio on Mechanical Properties of Silk Fiber Reinforced Polydimethylsiloxane

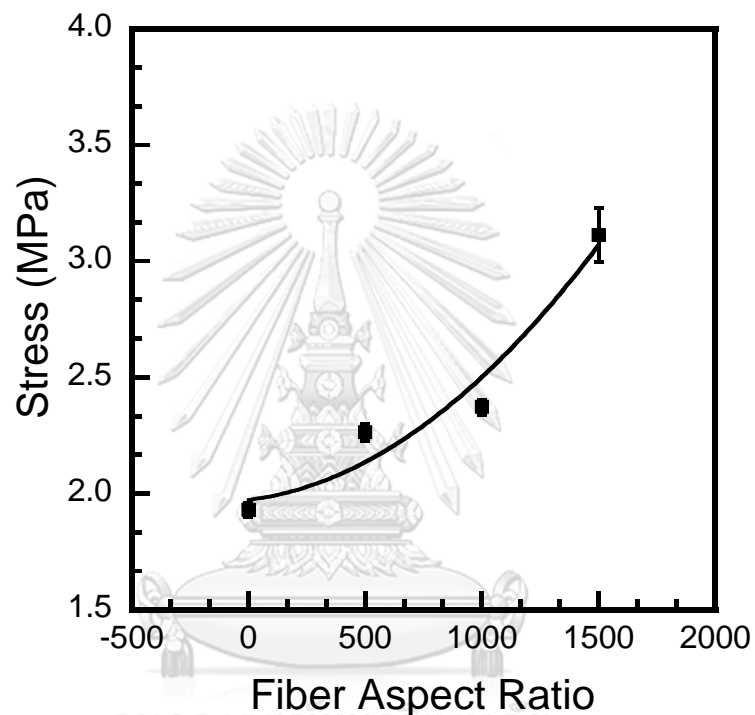


Figure 5.2. Tensile stress of the short silk reinforced polydimethylsiloxane at the different aspect ratio

The tensile stress of short silk fiber reinforced polydimethylsiloxane filled with 1 phr of silk fiber at a different aspect ratio of 500, 1000, and 1500 were measured with Universal Testing Machine at 1 kN load and 500 mm/min of testing speed shown in Figure 5.2.

From the figure, the result shows higher tensile stress with the increasing value of aspect ratio. This result is expected as the fibers which adhere to the fiber limit the strain of the matrix. Thus, a longer fiber will be able to hold the matrix from a tension load. The tensile stress was 2.26, 2.37, and 3,11 MPa for three different aspect ratio of 500, 1000, and 1500 respectively. As the aspect ratio of the fiber increased from 500 to 1000 the tensile stress increase by 4% and at the aspect ratio of 1500 the tensile stress increased by 37%. The average diameter of the silk fiber is $11.724 \mu\text{m}$ so the difference between the varied length of silk fibers were 5, 10, and 15 mm. Valentini *et al.* reported a similar result where the tensile modulus substantially increase in conjunction with the fiber length (Valentini *et al.*, 2018).

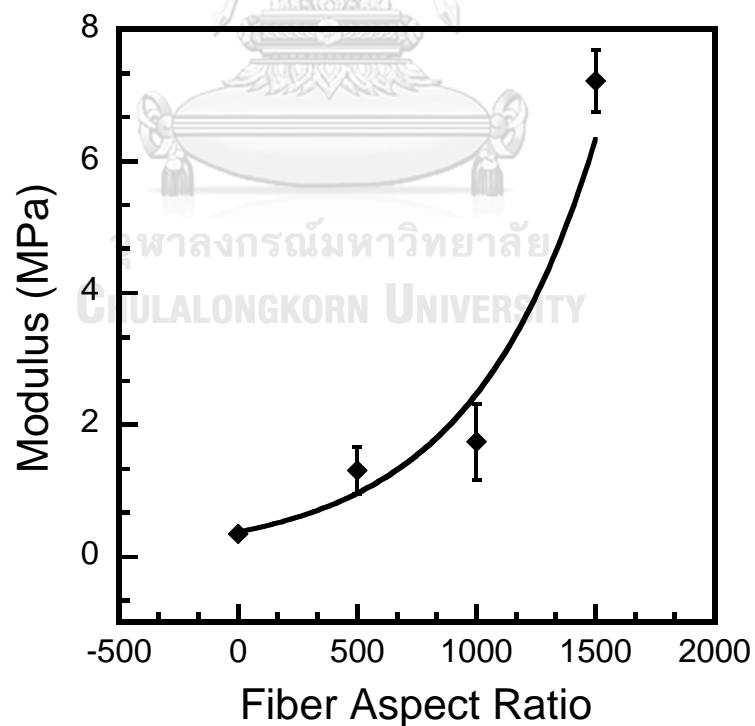


Figure 5.3. The effect of aspect ratio variation on the tensile modulus of the short silk reinforced polydimethylsiloxane.

Tensile modulus (Young's modulus) was calculated from the initial slope of the stress-strain curve. Tensile modulus increases from 0.3 MPa of the unfilled network to 1.3 MPa at 1 phr of silk fiber with 500 aspect ratio. The tensile modulus steadily increases as the aspect ratio varied to 1000 but have significant increase at 1500 aspect ratio with 6.9 MPa. This result suggests that the longer the fiber length will reduce the gap between fibers inside the composite network, thus rendering the ability of the composite sample to deform and make the composite has high stiffness. When the fiber length is too long, the mixing process produces an entanglement and the fiber tends to overlap with each other that create a high density of silk fiber. This fiber filler morphology corresponds with high stiffness of the composite network as well. According to Sang-Ryeoul Ryu *et al.*, fiber reinforcement with higher length exhibit lower tensile modulus than shorter fiber because the entanglement of the longer fiber makes an uneven distribution in the composite network and this defect led to lower tensile modulus (Sang-Ryeoul Ryu, 2001). Therefore, the decreasing value of tensile modulus depends on the distribution of the fibers within the network. The result from Figure 5.3 suggests a well distribute fibers within the composite networks.

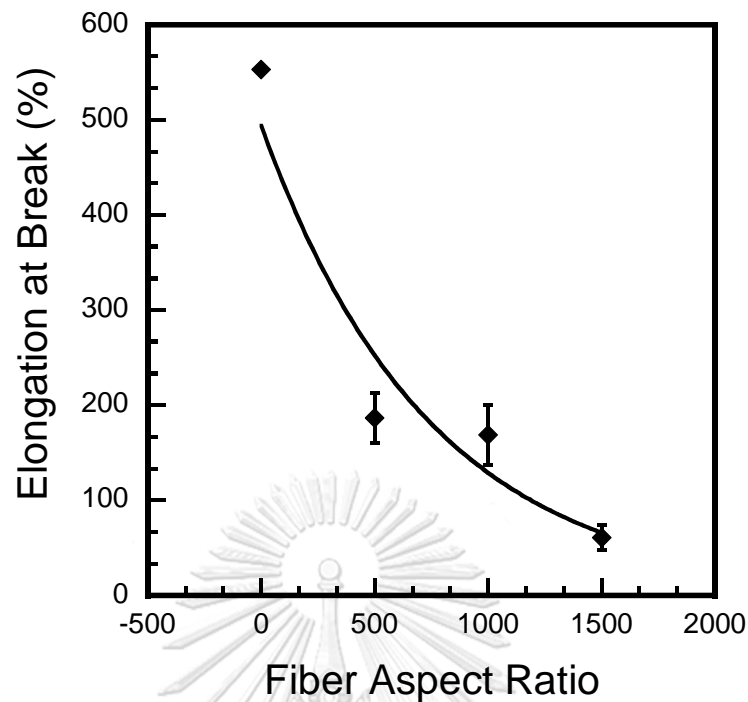


Figure 5.4. The relation between elongation at break and fiber aspect ratio of short silk reinforced polydimethylsiloxane

Silk reinforced polydimethylsiloxane decrease in elongation with increasing of fiber aspect ratio. From Figure 5.4, unfilled polydimethylsiloxane has a higher elongation at break at 554% than a filled network which continuously decreases to 176%, 175%, and 55% at a fiber aspect ratio of 500, 1000, and 1500 respectively.

In the study of the aspect ratio, the composite with an aspect ratio of 1000 is chosen. The optimum aspect ratio is chosen due to compatibility with the suturing process. The longer fibers have high entanglement when mixed randomly inside the network (Sang-Ryeoul Ryu, 2001). This fiber entanglement will make the suture thread hard to penetrate the suture pad although shorter fiber will reduce the probability of fiber

entanglement. In principle, shorter fiber filler increases the distance between each fiber as well. This occurrence causes the fiber to be less effective as a barrier to hold suture thread.

5.2.2 Effect of Fiber Concentration on Mechanical Properties of Silk Fiber

Reinforced Polydimethylsiloxane

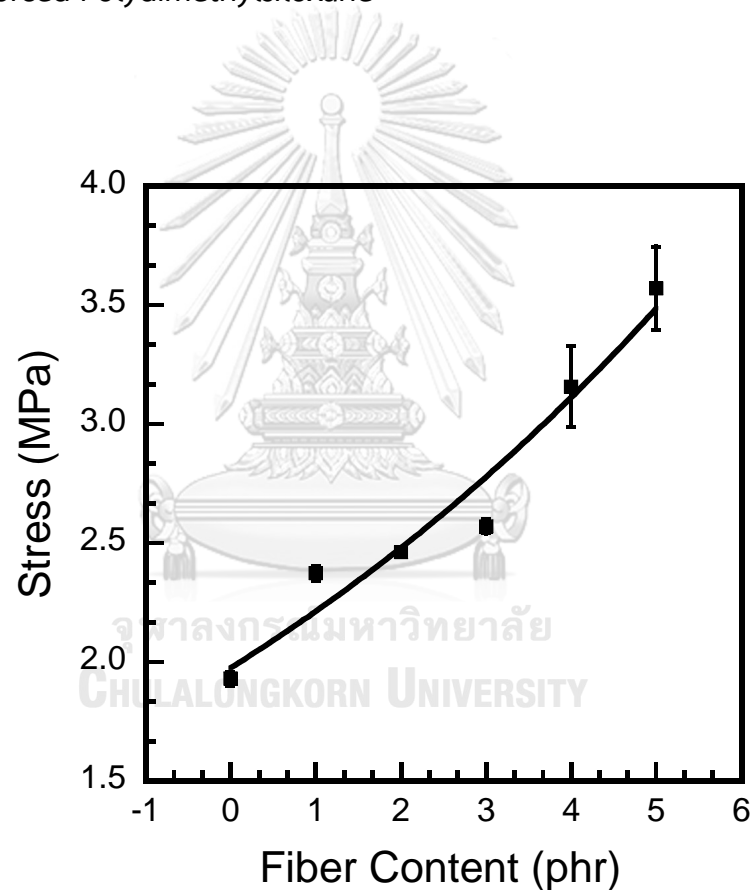
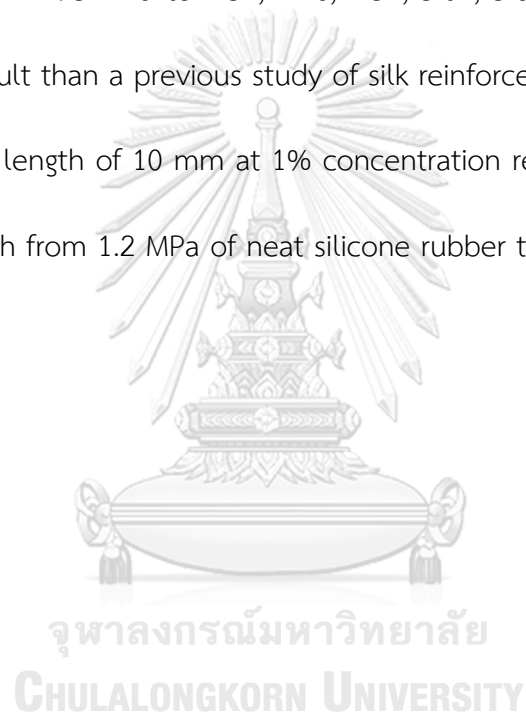


Figure 5.5. The tensile stress of short silk reinforced polydimethylsiloxane at various content of silk fibers

The test result from shows tensile stress measurement from varied silk fibers content from 0, 1, 2, 3, 4, 5 part per hundred of polydimethylsiloxane with 10 mm of fiber

length. The result from the figure at a higher fibers content, tensile stress became a fiber dominated property and enhanced as the fiber content increase. This result is in good correspond with the measured tensile stress of the silk fiber reinforced composite suggests that the interface from across the matrix efficiently transfer the load into the fiber. As the content of the fiber increase from unfilled network to 5 phr, the tensile stress increase from 1.93 MPa to 2.37, 2.46, 2.57, 3.02, 3.63 MPa as well. This result exhibits higher result than a previous study of silk reinforced polydimethylsiloxane of which at silk fiber length of 10 mm at 1% concentration resulting in the decrease of the tensile strength from 1.2 MPa of neat silicone rubber to 0.9 MPa (Valentini et al., 2018).



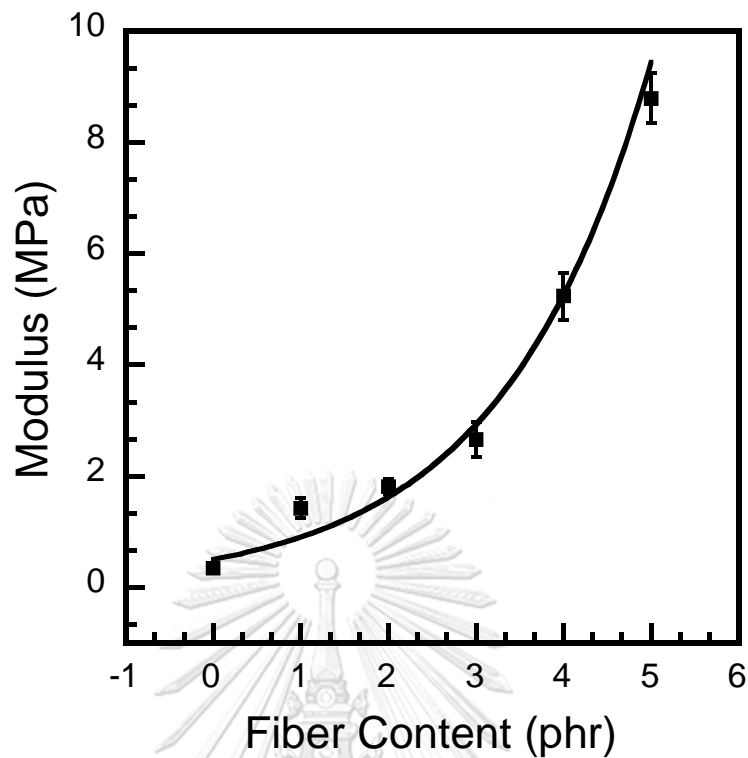


Figure 5.6. The effect of fiber content on the tensile modulus of short silk reinforced polydimethylsiloxane

Tensile modulus curve of polydimethylsiloxane reinforced with short silk fiber content ranging from 0, 1, 2, 3, 4, 5 phr is illustrated in Figure 5.6. From the figure, the tensile modulus of the composites has a tendency to increase in conjunction with the fibers content. The increasing value of tensile modulus implies good interaction between polydimethylsiloxane with silk fibers as filler reinforcement. Thus, an increase of silk fiber filler content produces a composite with higher stiffness. The modulus results in similarity with the modulus of real skin thigh between the range of 2-12 MPa (Gasiorn-Glogowska et al., 2013).

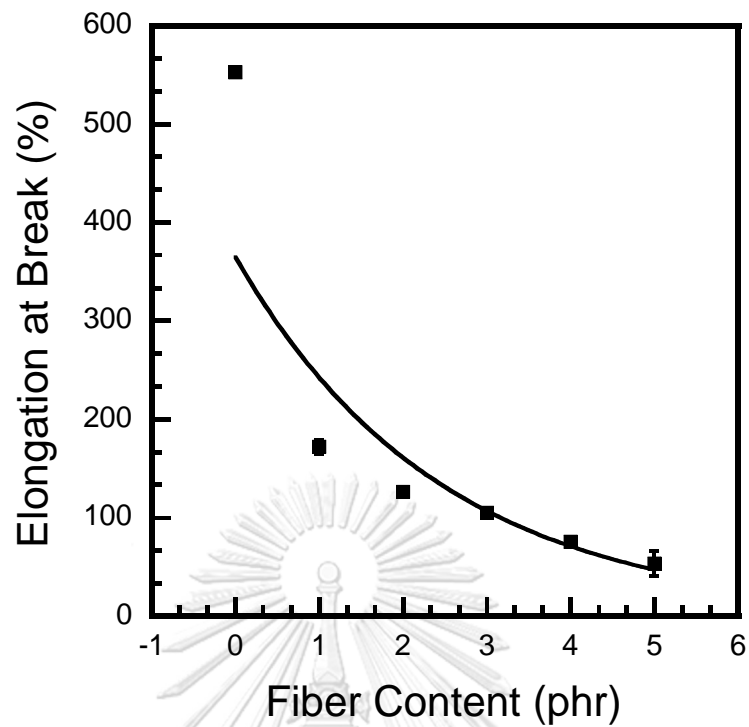


Figure 5.7. Elongation at break at different fiber content of short silk reinforced polydimethylsiloxane

The similar result occurs at composite with different fiber content ranging from 0, 1, 2, 3, 4, and 5 phr as well. The elongation at break tends to decrease at higher fiber content, as shown in Figure 5.7. This result is due to the semi-crystalline property of silk fiber with elongation at 4-26% (Koh et al., 2015). A similar result with short fiber reinforced rubber investigated by Sang-Ryeoul Ryu *et al.*, while the fiber aspect ratio as well as the content increase, the distance between rubber molecules decrease which causes the decrease in elongation at break relatively (Sang-Ryeoul Ryu, 2001).

The mechanical properties of the polydimethylsiloxane reinforced with short silk fiber have an average similarity with mechanical properties of real human skin. The tensile stress of human skin in Table 2.1 shows a wide range of value from 1.2 to 30 MPa. The value on tensile modulus or stiffness of the human skin shows in a wide range as well starting at 2 to 12 MPa. The mechanical properties of the human skin have a wide range because of many factors such as skin parts, age, and sample freshness (Gasiorglogowska et al., 2013; Ni Annaidh et al., 2012). Therefore, the real human skin mechanical properties standard cannot be defined in the exact value. In comparison, the polydimethylsiloxane reinforced short silk fibers has the closest value with the human thigh mechanical properties. This result suggests that the polydimethylsiloxane composite is still able to mimic real human skin.

5.3 Hardness and Tear Resistance Silk Fiber Reinforced Polydimethylsiloxane

5.3.1 Hardness Test

The hardness test was done by shore A durometer apparatus with composite samples at different content ranging from 0 to 5 phr of silk fibers. The hardness test result done in five times reading with a minimum thickness of 6.4 mm according to ASTM D2240 from Table 5.1 shows the expected result, which shows increasing hardness of the composite.

Table 5.1. The effect of various fiber aspect ratio and content on the hardness of short silk reinforced polydimethylsiloxane composite

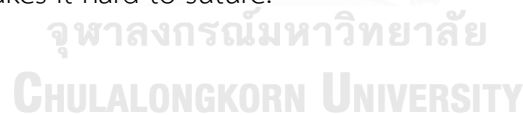
Silk (phr)	Aspect Ratio	Thickness (mm)	Shore A (HA)					Average Hardness (HA)
0	0	7.8	13.5	14.5	17	14	15.5	14.9
1	500	7.4	37.5	35.5	27.5	34	24.5	31.8
1	1000	7.2	35	34.5	34	41	30	34.9
1	1500	9.1	45.5	42.5	53.5	50.5	50	48.3
2	1000	7.7	38	39	35.5	40	50	41.8
3	1000	7.5	50	57.5	48.5	51	40.5	49.5
4	1000	8.8	54.5	59	59	51.5	54.5	55.7
5	1000	8.9	61.5	65.5	64.5	64.5	66	64.4

The aspect ratio difference on the hardness test shows an increasing tendency, although the difference is not very significant. The higher aspect ratio gives higher hardness as a result of the high entanglement of the fibers (Sang-Ryeoul Ryu, 2001). High entanglement can be seen as good properties since it gives higher strength of the material but it also makes the material has low elongation at break according to Figure 5.4. In the application of the suture pad, the hardness of the material plays an important role. The texture of the suture pad needs to be similar to the real human skin. The hardness test of the skin done by S. Derler et al. reported that average human skin hardness is approximately 40 HA (Derler, Schrade, & Gerhardt, 2007). The correlation of the result from Figure 5.3 and Figure 5.6 shows that the higher hardness shows high tensile modulus as well. This relation explained the poor suturing

experience process with high tensile modulus. This outcome will result in the difficulties of the needle and the suture thread to penetrate the composite because of the high fiber entanglement. Therefore, the silk fibers reinforced polydimethylsiloxane composite hardness with 2 phr of fiber content proved to have a similar result with real human skin.

5.3.2 Tear Resistance Test

The tear resistance test was done with a sutured sample with nylon suture thread to different fiber content for each sample. The silk fiber reinforced polydimethylsiloxane composite exhibits better suture thread resistance than the suture pad available commercially. However, the continuous addition of silk fiber towards polydimethylsiloxane increases the stiffness and hardness of the sample composite, which in return makes it hard to suture.



The suturing procedure was done to determine the appropriate hardness as well. The suturing process requires for the needle and the fiber to easily penetrate the suture pad while retaining the durability of the samples against the suture equipment. A composite sample at lower content of the filler reinforcement produces soft material, which accommodates easiness for the suture needle and the thread to penetrate

through the network. In return, soft material has low durability from the suture thread resistance test proven in Figure 5.8.

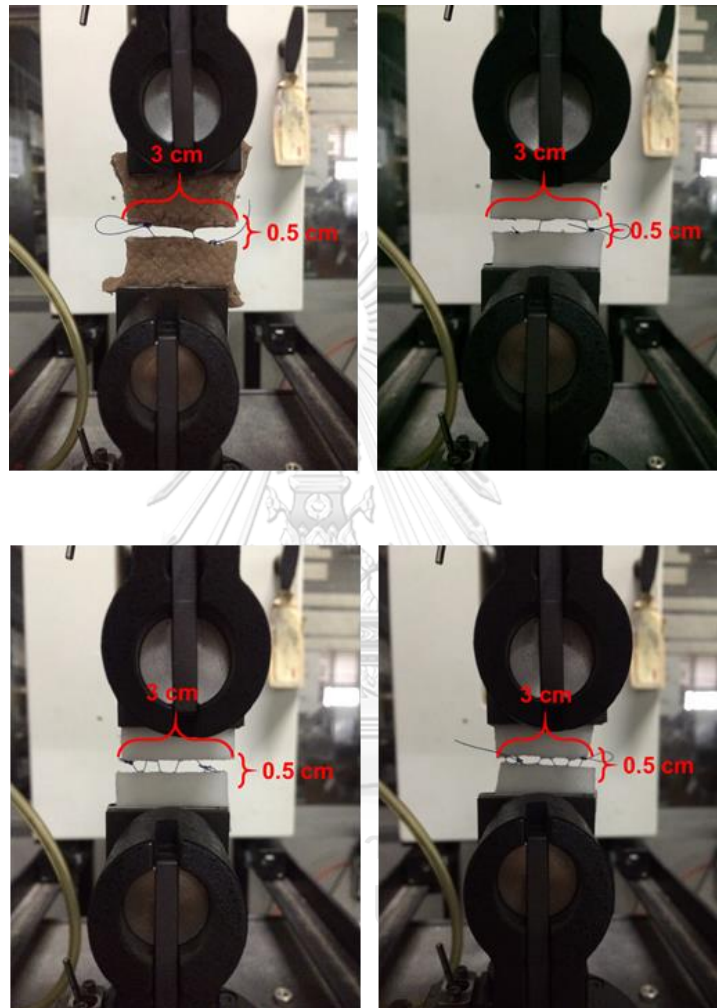


Figure 5.8. Suture thread resistance at a) commercial suture pad, b) 1 phr, c) 2 phr, and d) 3 phr of silk fiber reinforcement on the polydimethylsiloxane composites.

At higher concentration, the composite is hard to suture because the distance between the fiber is minimal and the entanglement of the fiber obstruct the suture thread from penetrating through the networks.

5.3.3 Suture Pad Physical Evaluation

The suture pad is fabricated with two different layers. The upper layer is polydimethylsiloxane reinforced with 2 phr of short silk fiber. The other layer is polydimethylsiloxane mixed with 50 phr of silicone oil. The color of the suture pad is adjustable, but this sample uses light brown for the upper layer and yellow for the lower layer. The texture of the upper layer is flexible but still be able to maintain its hardness. The flexibility of the suture pad lies in the lower layer since the upper layer is thin for about 2 mm. The suturing evaluation was done to the suture pad as well.

The suturing equipment uses a sharp needle with nylon thread.

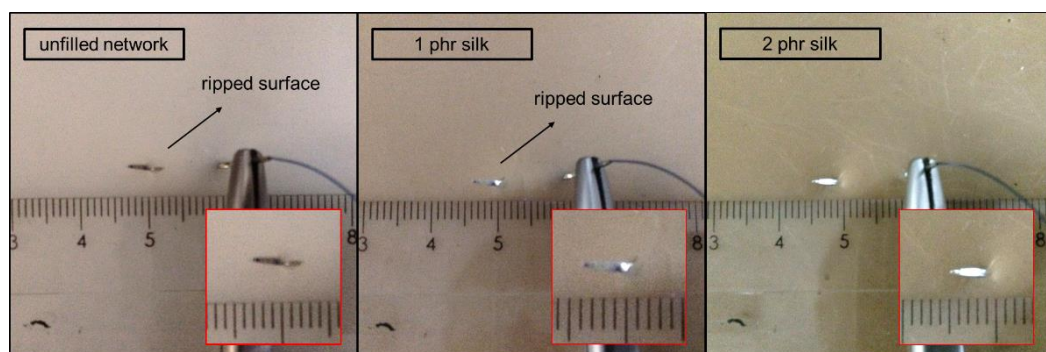


Figure 5.9 Suture equipment evaluation of the unfilled network and filled network of polydimethylsiloxane.

The suturing test evaluates the durability of the suture pad against the suture needle for human skin. From the picture shown in Figure 5.9, the suturing process leaves unfilled polydimethylsiloxane with the ripped surface. The polydimethylsiloxane filled with silk fiber reduces the ripped surface proved that the addition of silk fiber improves the tear resistance of the suture pad against suture equipment. This result suggests that the silk fiber play a role as a barrier reinforcement for the suture needle. The polydimethylsiloxane filled 2 phr of silk fiber shows an absent of ripped surface, which means the composite with 2 phr silk fiber has enough durability as a reinforcement of the composite for suture pad application.



5.3.4 Suture Pad Economical Evaluation

The material cost of a suture pad from silk reinforced polydimethylsiloxane is shown in Table 5.2. This sample dimension of the silk reinforced polydimethylsiloxane suture pad is 10 x 10 x 1 cm.

Table 5.2. The material cost of silk reinforced polydimethylsiloxane suture pad.

Materials	Price/kg (THB)	Materials per sample (g)	Price per sample (THB)
RTV 2-230	350	70	25
Silicone Oil	380	54	21
Silk	1720	0.4	1
Total			47

In comparison, the market price of the commercially available suture pad shown in Table 5.3. The price for commercially available suture pad in the market depends on the size and the quality of the materials.

Table 5.3. The price list of commercially available suture pads

Product name	Dimension (cm)	Price (THB)	References
Brosan	17 x 12	735	amazon.com
Ergode	22 x 16 x 2	398	amazon.com
BornToEdu	16 x 13	459	amazon.com
Skin Suture Pad	18 x 10 x 5	1735	tokopedia.co.id
Skin Model Suture	18 x 11 x 2	1302	tokopedia.co.id



CHAPTER VI

CONCLUSIONS

The polydimethylsiloxane with short silk fiber fabrication is successful. The density measurement confirms well-dispersed fiber reinforcement inside the polydimethylsiloxane network by showing neglectable air voids inside each sample of the silk reinforced polydimethylsiloxane composite. Tensile stress increase by the addition of silk fibers on the polydimethylsiloxane. This result suggests splendid interfacial bonding between silk fiber and polydimethylsiloxane. It proves that the polydimethylsiloxane successfully manages to transfer the load into the silk fibers as well. The decreasing value of elongation at break is due to the substantial differences in flexibility between the silk fiber and polydimethylsiloxane; however, the stiffness of the material increase as the fiber aspect ratio and content increase.



Furthermore, the tear resistance test by using suture thread display significant enhancement in durability by the addition of silk fibers. Although, the excessive addition of silk fibers make the composite stiffer and hard to suture. The hardness test confirms that the most suitable suture pad is polydimethylsiloxane reinforced with 2 phr of silk fibers according to its surface texture as well. Finally, the results show that

the short silk fiber reinforced polydimethylsiloxane composite is exceptionally suitable for suture pad application



REFERENCES

- Chaplin, M. (2003, 18 January 2019). Hydrophobic Hydration. Retrieved from http://www1.lsbu.ac.uk/water/hydrophobic_hydration.html
- Cheung, H.-Y., Lau, K.-T., Tao, X.-M., & Hui, D. (2008). A potential material for tissue engineering: Silkworm silk/PLA biocomposite. *Composites Part B: Engineering*, 39(6), 1026-1033. doi:10.1016/j.compositesb.2007.11.009
- Derler, S., Schrade, U., & Gerhardt, L. C. (2007). Tribology of human skin and mechanical skin equivalents in contact with textiles. *Wear*, 263(7-12), 1112-1116. doi:10.1016/j.wear.2006.11.031
- Gasior-Glogowska, M., Komorowska, M., Hanuza, J., Maczka, M., Zajac, A., Ptak, M., . . . Szotek, S. (2013). FT-Raman spectroscopic study of human skin subjected to uniaxial stress. *J Mech Behav Biomed Mater*, 18, 240-252. doi:10.1016/j.jmbbm.2012.11.023
- Kaewprasit, K., Promboon, A., Kanokpanont, S., & Damrongsakkul, S. (2014). Physico-chemical properties and in vitro response of silk fibroin from various domestic races. *J Biomed Mater Res B Appl Biomater*, 102(8), 1639-1647. doi:10.1002/jbm.b.33142
- Kenley. (2018). Kenley Suture Practice Kit - Medical Student Suturing Pad - Pocket Size Surgical Training Kit with 11 Incisions & Wounds – 3 Layers for Fake Skin, Fat & Muscle - Gift for Med School Students. Retrieved from <https://www.amazon.com/Kenley-Suture-Pad-Replicate-Incisions/dp/B0773OFYO1>
- Koh, L.-D., Cheng, Y., Teng, C.-P., Khin, Y.-W., Loh, X.-J., Tee, S.-Y., . . . Han, M.-Y. (2015). Structures, mechanical properties and applications of silk fibroin materials. *Progress in Polymer Science*, 46, 86-110. doi:10.1016/j.progpolymsci.2015.02.001
- Langer, K. (1861). On the anatomy and physiology of the skin. *British Journal of Plastic surgery*(The Imperial Academy of Science, Vienna.).

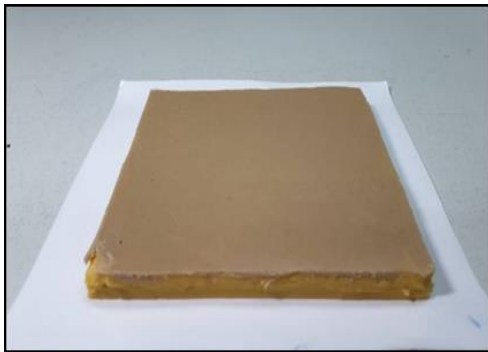
- Lassila, L., Keulemans, F., Sailyoja, E., Vallittu, P. K., & Garoushi, S. (2018). Mechanical properties and fracture behavior of flowable fiber reinforced composite restorations. *Dent Mater*, *34*(4), 598-606. doi:10.1016/j.dental.2018.01.002
- Liu, G. R. (1998). A step-by-step method of rule-of-mixture of fiber and particle reinforced composite material.
- Marks, J. G., & Miller, J. J. (2017). *Lookingbill and Marks' Principles of Dermatology E-Book*: Elsevier Health Sciences.
- Matrix, M. Skin structure. Retrieved from <https://marinematrix.com/skin-and-nutrition/>
- Mendoza-Acevedo, S., Villa-Vargas, L. A., Mendoza-León, H. F., Alemán-Arce, M., & Munguía-Cervantes, J. E. J. S. y. v. (2017). Improved method to reduce interfacial defects in bonding polydimethylsiloxane layers of microfluidic devices for lab-on-chip applications. *30*(2), 25-29.
- Mi, H.-Y., Jing, X., Huang, H.-X., & Turng, L.-S. (2018). Novel polydimethylsiloxane (PDMS) composites reinforced with three-dimensional continuous silica fibers. *Materials Letters*, *210*, 173-176. doi:10.1016/j.matlet.2017.09.018
- Ni Annaidh, A., Bruyere, K., Destrade, M., Gilchrist, M. D., & Ottenio, M. (2012). Characterization of the anisotropic mechanical properties of excised human skin. *J Mech Behav Biomed Mater*, *5*(1), 139-148. doi:10.1016/j.jmbbm.2011.08.016
- Ottenio, M., Tran, D., Ni Annaidh, A., Gilchrist, M. D., & Bruyere, K. (2015). Strain rate and anisotropy effects on the tensile failure characteristics of human skin. *J Mech Behav Biomed Mater*, *41*, 241-250. doi:10.1016/j.jmbbm.2014.10.006
- Prakash, S., Loganathan, D., Babu, K. S., Babu, G. D., Khrisan, V. G., & Gopi, G. (2016). Mechanical Behaviour of Silk Fabric Reinforced Eco-Friendly Polymer Matrix Composite. *Int. J. Chem. Sci.*
- R. C. M. P. Aquino, S. N. M. (2003). Evaluation of the critical fiber length of piassava (*Attalea funifera*). *Journal of Material Science & Engineering*.
- Rusa, C. C., Bridges, C., Ha, S.-W., & Tonelli, A. E. (2005). Conformational Changes Induced in Bombyx mori Silk Fibroin by Cyclodextrin Inclusion Complexation. *Fiber and Polymer Science Program, North Carolina State University, Raleigh, NC 27695-8301, United States; William G. Enloe High School, Raleigh, NC, United States.* doi:10.1021/ma050340a

- Sang-Ryeoul Ryu, D.-J. L. (2001). Effects of fiber aspect ratio, fiber content, and bonding agent on tensile and tear properties of short-fiber reinforced rubber. *KSME International Journal*.
- Silva, V. P., Goncalves, M. C., & Yoshida, I. V. P. (2006). Biogenic silica short fibers as alternative reinforcing fillers of silicone rubbers. *Journal of Applied Polymer Science*, 101(1), 290-299. doi:10.1002/app.23324
- Silver, F. H. (2001). Viscoelastic properties of human skin and processed dermis.
- Soo Kim, E. (2011). Effect of incorporation of carbon fiber and silicon carbide powder into silicone rubber on the ablation and mechanical properties of the silicone rubber-based ablation material. *Journal of Applied Polymer Science*, 120(2), 831-838. doi:10.1002/app.33139
- Valentini, L., Bittolo Bon, S., Mussolin, L., & Pugno, N. M. (2018). Silkworm silk fibers vs PEEK reinforced rubber luminescent strain gauge and stretchable composites. *Composites Science and Technology*, 156, 254-261. doi:10.1016/j.compscitech.2017.12.031
- Vogel, H. (1987). Age dependence of mechanical and biochemical properties of human skin. I: Stress-strain experiments, skin thickness and biochemical analysis. 3(1), 67-91.
- Wu, W., & Wang, J. (2018). Effect of KH550 on the Preparation and Compatibility of Carbon Fibers Reinforced Silicone Rubber Composites. *Silicon*, 10(5), 1903-1910. doi:10.1007/s12633-017-9700-4
- Wu, W., & Zuo, H. (2018). Silicone Rubber Composites Modified by Chopped Basalt Fibers Treated with Coupling Agent. *Silicon*, 10(6), 2555-2559. doi:10.1007/s12633-018-9790-7
- Yue, Y., Zhang, H., Zhang, Z., & Chen, Y. (2013). Tensile properties of fumed silica filled polydimethylsiloxane networks. *Composites Part A: Applied Science and Manufacturing*, 54, 20-27. doi:10.1016/j.compositesa.2013.06.016
- Zahid, M., Heredia-Guerrero, J. A., Athanassiou, A., & Bayer, I. S. (2017). Robust water repellent treatment for woven cotton fabrics with eco-friendly polymers. *Chemical Engineering Journal*, 319, 321-332. doi:10.1016/j.cej.2017.03.006

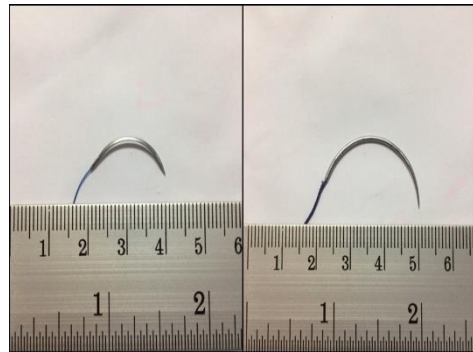
- Zhang, Z., Tingaut, P., Rentsch, D., Zimmermann, T., & Sebe, G. (2015). Controlled Silylation of Nanofibrillated Cellulose in Water: Reinforcement of a Model Polydimethylsiloxane Network. *ChemSusChem*, 8(16), 2681-2690. doi:10.1002/cssc.201500525
- Ziraki, S., Zebarjad, S. M., & Hadianfard, M. J. (2016). A study on the tensile properties of silicone rubber/polypropylene fibers/silica hybrid nanocomposites. *J Mech Behav Biomed Mater*, 57, 289-296. doi:10.1016/j.jmbbm.2016.01.019



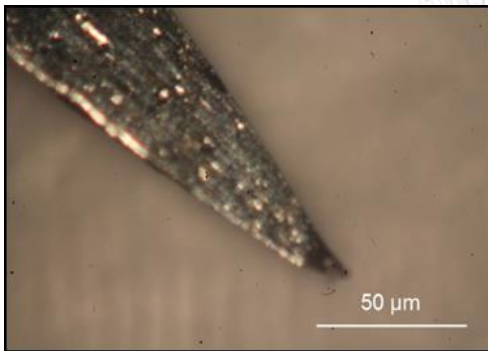
APPENDIX



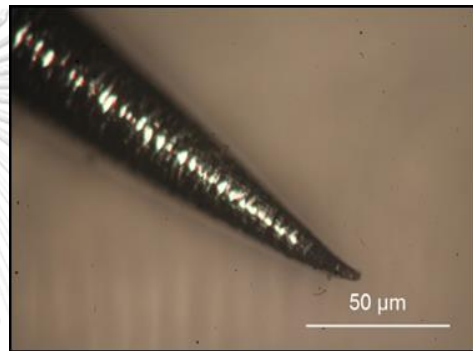
Silk-PDMS suture pad



Suture needles



Sharp edge suture needle



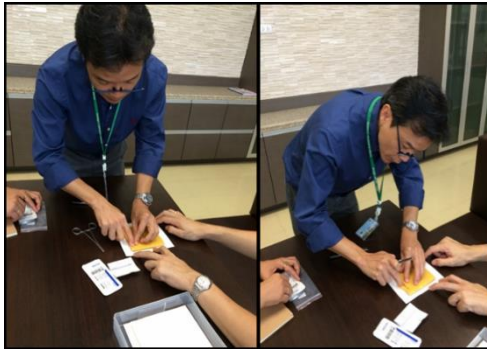
Cone shape suture needle



Suture pad evaluation by Assoc. Prof. Dr Tipaporn Wonghongkul at Faculty of Nursing Chiang Mai University



Suture pad evaluation by Assoc. Prof. Dr Tipaporn Wonghongkul at Faculty of Nursing Chiang Mai University



Suture pad evaluation by Assoc. Prof. Dr. Ruangsak Lertkhajonsuk of Obstetric and Gyneaecology King Chulalongkorn Memorial Hospital



Suture pad evaluation by Assoc. Prof. Dr. Ruangsak Lertkhajonsuk of Obstetric and Gyneaecology King Chulalongkorn Memorial Hospital



VITA

NAME	Radhitya Banuaji Prastowo
DATE OF BIRTH	09 September 1994
PLACE OF BIRTH	Semarang
INSTITUTIONS ATTENDED	Chulalongkorn University
HOME ADDRESS	Jln. Pujowiyoto RT02/RW06, Purbalingga, Jawa Tengah, Indonesia.
AWARD RECEIVED	Awardee ASEAN Scholarship Chulalongkorn University

