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STUDY OF TENSILE PROPERTIES, MORPHOLOGY AND CHEMICAL RESISTANCE OF THERMOPLASTIC POLYURETHANE/POLYDIMETHYLSILOXANE BLENDS

Miss Ratirat Sinweeruthai

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By	Miss Ratirat Sinweeruthai
Field of Study	Chemical Engineering
Thesis Advisor	Assistant Professor Siriporn Damrongsakkul, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of Faculty of Engineering
(Professor Somsak Panyakeow, Dr. Eng.)

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....Member
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รติรัตน์ สินวีรุทัย : การศึกษาสมบัติภายใต้แรงดึง โครงสร้างและการทนต่อสารเคมีของพอลิเมอร์ผสมระหว่างเทอร์โมพลาสติกพอลิยูรีเทนกับพอลิไดเมทิลไซโลเซน (STUDY OF TENSILE PROPERTIES, MORPHOLOGY AND CHEMICAL RESISTANCE OF THERMOPLASTIC POLYURETHANE/POLYDIMETHYLSILOXANE BLENDS) อ.ที่ปรึกษา : ผศ.ดร.ศิริพร ดำรงค์ศักดิ์กุล, 157 หน้า, ISBN xxx-xxx-xxx-x

งานวิจัยเรื่องนี้มุ่งเน้นที่จะศึกษาสมบัติภายใต้แรงดึง ลักษณะโครงสร้างและการทนต่อสารเคมีของพอลิเมอร์ผสมของเทอร์โมพลาสติกพอลิยูรีเทน (TPU) กับพอลิไดเมทิลไซโลเซน (PDMS) พอลิเมอร์ผสมที่ปริมาณของพอลิไดเมทิลไซโลเซนต่ำๆ (0-1%) นี้ถูกเตรียมขึ้นโดยวิธีการหลอมละลายในเครื่องอัดรีดแบบสกรูคู่ จากการศึกษาสมบัติภายใต้แรงดึง อาทิ ค่าความแข็งแรงที่จุดแตกหัก ค่าเปอร์เซ็นต์การยืดตัวที่จุดแตกหัก ค่าโมดูลัสของยังและค่าพลังงานในการแตกหัก พบว่าพอลิเมอร์ผสมจะให้ค่าเปอร์เซ็นต์การยืดตัวที่จุดแตกหักเพิ่มขึ้นถึงประมาณ 30% เช่นเดียวกับค่าโมดูลัสของยังที่เพิ่มขึ้นประมาณ 40% ในช่วงค่าความเข้มข้นของพอลิไดเมทิลไซโลเซนที่เหมาะสมประมาณ 0.6%-0.8% ถ้าความเข้มข้นเกินกว่านี้แล้วจะมีผลให้สมบัติดังกล่าวมีค่าลดลง ขณะที่ค่าความแข็งแรงที่จุดแตกหักและค่าพลังงานในการแตกหักมีค่าลดลงประมาณ 20% และ 10% ตามลำดับ โดยผลที่ได้จากการทดสอบสมบัติภายใต้แรงดึงจะสอดคล้องกับลักษณะโครงสร้างบนบริเวณผิวรอยแตกของพอลิเมอร์ผสมที่วิเคราะห์ด้วยกล้องจุลทรรศน์แบบส่องกราด (SEM) ซึ่งพบว่าลักษณะการแตกหักแบบเส้นใยยืดมีปริมาณที่น้อยลงเมื่อปริมาณ PDMS ในพอลิเมอร์ผสมเพิ่มขึ้น ผลจาก SEM ยังพบว่าเฟสของ PDMS มีการกระจายตัวอยู่ในโครงสร้างหลักของ TPU และเมื่อปริมาณของ PDMS ในพอลิเมอร์ผสมเพิ่มขึ้นจะส่งผลให้เฟสของ PDMS ที่กระจายตัวมีขนาดเล็กลง

ในส่วนของการศึกษาผลการทนสารเคมีที่มีต่อสมบัติภายใต้แรงดึงและลักษณะโครงสร้างของพอลิเมอร์ผสมของ TPU กับ PDMS ได้ทำการเลือกสารเคมีที่นำมาใช้ในการทดสอบ 3 ชนิด ได้แก่ น้ำ, กรดซัลฟูริก (3% โดยปริมาตร) และโซเดียมไฮดรอกไซด์ (10% น้ำหนักต่อปริมาตร) พบว่าสารละลายโซเดียมไฮดรอกไซด์มีผลรุนแรงมากที่สุดต่อสมบัติภายใต้แรงดึงและลักษณะโครงสร้างของ TPU และพอลิเมอร์ผสมเมื่อเปรียบเทียบกับผลที่เกิดจากการแช่ในน้ำและสารละลายซัลฟูริก โดยพบว่าค่าความแข็งแรงที่จุดแตกหักและค่าพลังงานในการแตกหักของ TPU บริสุทธิ์หลังจากการแช่ในสารละลายโซเดียมไฮดรอกไซด์มีค่าลดลงประมาณ 42% และ 55% ตามลำดับ โดยผลจากปริมาณ PDMS ในพอลิเมอร์ผสมของการทนด่างต่อสมบัติภายใต้แรงดึงจะมีแนวโน้มไปในทิศทางเดียวกับผลที่ได้จากการทดสอบสมบัติภายใต้แรงดึงก่อนแช่ในสารเคมี กล่าวคือ ปริมาณ PDMS ที่มีผลในการปรับปรุงสมบัติภายใต้แรงดึงของพอลิเมอร์ผสมภายหลังการแช่ด่างให้ดีขึ้นจะมีค่าไม่เกิน 0.8% ผลของสมบัติภายใต้แรงดึงของสารหลังจากแช่ในสารละลายโซเดียมไฮดรอกไซด์สอดคล้องกับผลของน้ำหนักของพอลิเมอร์ผสมที่ลดลงและลักษณะโครงสร้างการแตกหักที่ปรากฏมีเส้นใยยืดที่น้อยมากและจะมีอนุภาคขนาดเล็กหลุดออกมาและติดอยู่บริเวณผิวหน้าของชิ้นงาน โดยปรากฏการณ์นี้คาดว่าเป็นผลมาจากปฏิกิริยาการกัดกร่อนที่เกิดขึ้นระหว่างผิวหน้าของตัวอย่างกับสารละลายโซเดียมไฮดรอกไซด์

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต..
สาขาวิชา วิศวกรรมเคมี ลายมือชื่ออาจารย์ที่ปรึกษา..................................
ปีการศึกษา 2544 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม............................

##4170473921 : MAJOR CHEMICAL ENGINEERING

KEY WORD: POLYMER BLENDS/TPU/PDMS/MORPHOLOGY/CHEMICAL RESISTANCE

RATIRAT SINWEERUTHAI : STUDY OF TENSILE PROPERTIES, MORPHOLOGY AND CHEMICAL RESISTANCE OF THERMOPLASTIC POLYURETHANE/POLYDIMETHYLSILOXANE BLENDS THESIS ADVISOR : ASSISTANT PROFESSOR SIRIPORN DAMRONGSAKKUL, Ph.D. 157 pp. ISBN xxx-xxx-xxx-x.

This work is aimed to study the tensile properties, morphology and chemical resistance of thermoplastic polyurethane (TPU) and polydimethylsiloxane (PDMS) blends. The blends at low content (0%-1.0%) of PDMS were prepared by melt mixing using a twin screw extruder. The properties of the blends including the ultimate tensile strength, the elongation at break, Young's modulus, energy to break and the physical property were studied systematically. The resultant blends show an increase in the elongation at break up to 30% and in Young's modulus up to 40% at the optimum PDMS concentration at around 0.6%-0.8%, beyond which the properties diminish. While the ultimate tensile strength and the energy to break are decreased about 20% and 10%, respectively. The results are in agreement with the morphology of the fractured surface of TPU/PDMS blends observed by Scanning Electron Microscope (SEM) that there are less fibrous characteristics when increasing PDMS content in the blends. The SEM micrographs of the blends show dispersed phase of PDMS in matrix TPU and the domain size of PDMS phase is smaller when increasing PDMS content from 0.2% to 0.8%.

For the study of the effects of chemical resistance to the tensile properties and morphology of TPU/PDMS blends, three types of chemical reagents, i.e. water, sulfuric acid (H_2SO_4, 3% v/v) and sodium hydroxide (NaOH, 10% w/v) are selected. The results on the chemical resistance to tensile properties and morphology of the blends show that NaOH solution has strongest effect to the tensile properties and morphology of virgin TPU and the blends comparing to water and H_2SO_4 solution. It was found that the ultimate tensile strength and the energy to break of virgin TPU after base immersion is strongly decreased by 42% and 55%, respectively. The effect of PDMS contents in the blends on the base resistance to tensile properties is similar to results before immersion, i.e. the effective PDMS contents in the blends that can generally improve tensile properties of the blends after immersion in NaOH does not excess 0.8%. The results are in agreement with the weight loss of TPU/PDMS blends after base immersion and the morphology of the fractured surface of TPU/PDMS blends after base immersion that exhibits very small amount of fibrous characteristic and there are some small particles detached at the surface. This could be the result of an occurrence of a corrosive reaction between the sample surface and NaOH solution.

Department	Chemical Engineering	Student's signature...
Field of study	Chemical Engineering	Advisor's signature...
Academic year	2001	Co-advisor's signature......................................

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Finally, the author wishes to convey her deep appreciation to her family.

CONTENTS

PAGE

CHAPTER

PAGE

PAGE

PAGE

PAGE

LIST OF TABLES

TABLE PAGE

LIST OF TABLES (continuous)

LIST OF TABLES (continuous)

TABLE PAGE

LIST OF FIGURES

FIGURE PAGE

LIST OF FIGURES (continuous)

FIGURE PAGE

LIST OF FIGURES (Continuous)

FIGURE PAGE

LIST OF FIGURES (Continuous)

FIGURE PAGE

LIST OF FIGURES (Continuous)

FIGURE PAGE

CHAPTER I

INTRODUCTION

1.1 Introduction

Polymer blends have emerged as an important group of polymeric materials since the late 1970s and have experienced substantial growth since the 1980s. Interests in polymer blending are reflected in the numbers of patent and research publications by both industry and academia. Blending of polymeric materials has been shown to be an useful and cost effective route, in comparison with the synthesis of new polymers, for enhancing material properties and developing materials with desired performance.

During the past decades, thermoplastic polyurethane (TPU) has received considerable attention from both the scientific and industrial communities. Applications of TPU include automotive exterior body panels, medical implants such as the artificial heart, membranes, ski boot and flexible tubing. TPU features the best physical properties of all elastomer. TPU exhibits high modulus, abrasion resistance, excellent resistance to ageing (ozone), atmospheric factors, typical solvents and oils. Moreover, TPU is capable of bearing greater load than other rubber. But the properties of TPU can be changed by the environment in that a physical or chemical process may occur. There are three environmental effects considered particularly with polyurethane elastomers: the effect of heat, swelling by immersion in certain fluids and hydrolytic resistance. In certain fluids such as alcohols, acids, bases, ketones and ester, polyurethanes tend to have swelling, degradation and reduction in some mechanical properties.

From above mentioned, it is interesting to study the polymer blend of TPU and other polymers. Polydimethysiloxanes (PDMS) was chosen to blend with TPU because

PDMS, frequently referred to by the generic name of silicone, is a polymer with a unique combination of properties resulting from the presence of an inorganic siloxane backbone and organic methyl groups attached to silicon. This chemical configuration produces polymers which have good chemical stability, good oxidative resistance and good chemical stability. Thus, this research is aimed to study the tensile properties and the morphology of TPU/PDMS blends. The effects of chemical reagent on the tensile properties and the morphology of TPU/PDMS blends is investigated.

1.2 Objectives

1.2.1 To develop the polymer blends of thermoplastic polyurethane and polydimethysiloxane by melt mixing method.

1.2.2 To study the tensile properties and morphology of thermoplastic polyurethane and polydimethysiloxane blends.

1.2.3 To study the chemical resistance on the tensile properties and morphology of thermoplastic polyurethane and polydimethysiloxane blends.

1.3 Scope of work

1.3.1 To study melt mixing method of thermoplastic polyurethane and polydimethysiloxane blends.

1.3.2 To find the proper processing conditions of blending in an internal mixer and a twin screw extruder.

1.3.3 To study the following behaviour and properties of the blends of TPU and PDMS:

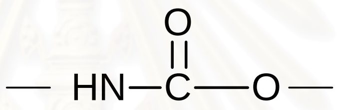
- Thermal properties (by TGA)
- Miscibility (by DSC)
- Tensile properties
- Chemical resistance to tensile properties
- Morphology (by SEM)

CHAPTER II

THEORY

2.1 Polyurethanes

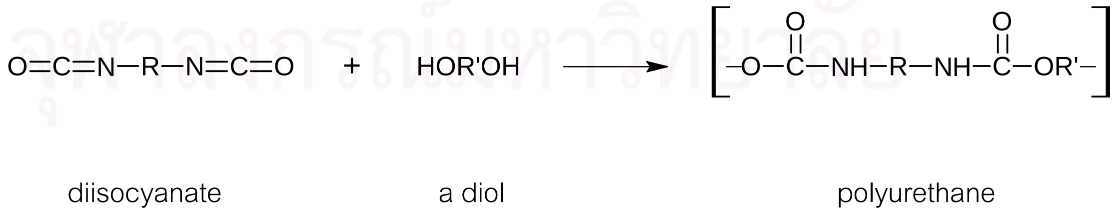
Polyurethanes are defined as polymers which contain urethane groups in the main polymer chain.



$$-HN-\overset{\overset{\displaystyle O}{||}}{C}-O-$$

Figure 2.1 The urethane link. [Hepburn, 1982]

A urethane group, as shown in Figure 2.1, is formed by the chemical reaction between an alcohol and an isocyanate. Polyurethane results from the reaction between alcohols with two or more reactive hydroxy groups per molecule (diols or polyols) and isocyanates that have more than one reactive isocyanate group per molecule. The case of the reaction of a diisocyanate with a diol is presented in the following equation:



$$O{=}C{=}N-R-N{=}C{=}O \quad + \quad HOR'OH \longrightarrow \left[-O-\overset{\overset{\displaystyle O}{||}}{C}-NH-R-NH-\overset{\overset{\displaystyle O}{||}}{C}-OR'-\right]$$

2.1.1 Polyurethane Elastomer

A urethane elastomer can be regarded as a linear block copolymer of the type shown in Figure 2.2. It is consisting of alternating polyurethane and polyol segments. This segmented polymer structure can vary its properties over a very wide range of strength and stiffness by modification of its three basic building blocks: long chain ester or polyether polyol, diisocyanate, and chain extender (glycol, water or diamine). Essentially the hardness range covered is that of soft jelly-like structures to hard rigid plastics. These polymers can be considered in terms of long (1000–2000 nm) flexible segments and much shorter (150 nm) rigid units which are chemically and hydrogen bonded together, the whole undergoing orientation on extension as indicated in Figure 2.3.

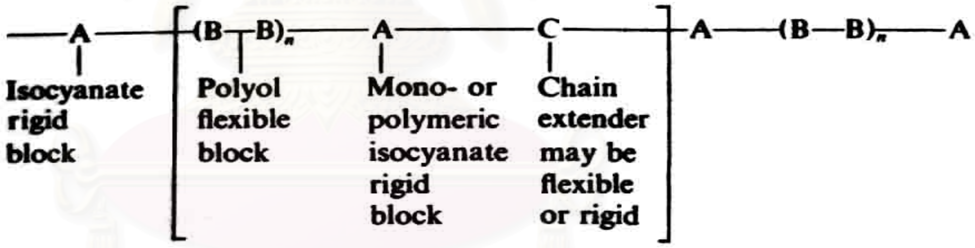


Figure 2.2 The basic unit in a urethane block copolymer. [Hepburn, 1982]

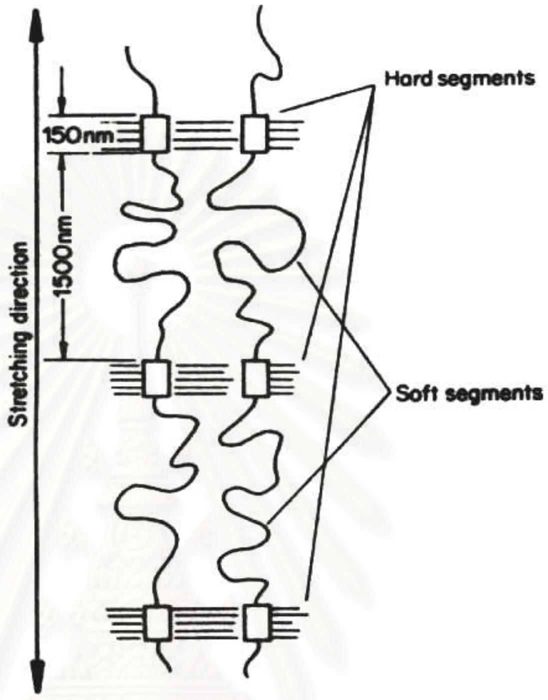


Figure 2.3 Flexible and rigid segments in a polyurethane elastomer. [Hepburn, 1982]

The usual route of chemical formation for all urethane is illustrated in Figure 2.4. It is referred to as the prepolymer method, as the “final” polymer is formed in two separate steps. Initially the diisocyanate and polyol are reacted together to form an intermediate polymer of molecular weight 15000 -20000 which is called a ‘prepolymer’ and is normally a thick viscous liquid or low melting point solid of low or no strength. This prepolymer, sometimes shelf-stabilized by means of 0.01-0.1% of an acid chloride for storage purposes, is then converted into the final high molecular weight polymer by further reaction with a diol or diamine chain extender; this step is usually referred to as the chain extension stage, though sometimes the term crosslinking is used if this better represents the elastomeric character of the final polymer. Alternatively the entire polymer formatiom may be carried out by simultaneously mixing of polyol, diisocyanate and chain extender together, whereupon the reaction is referred to as the 'one shot process' of polyurethane formation as schematically represented in Figure 2.5.

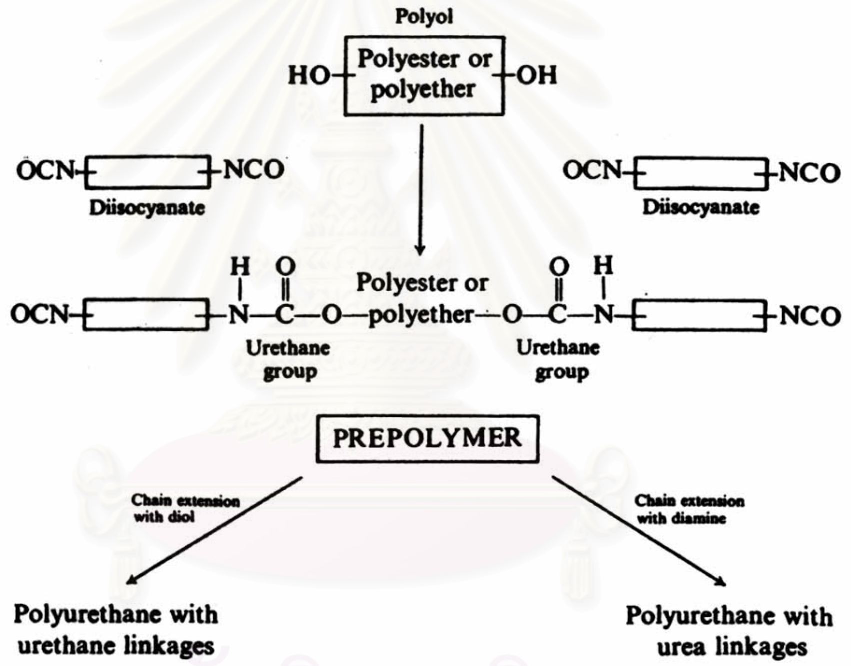
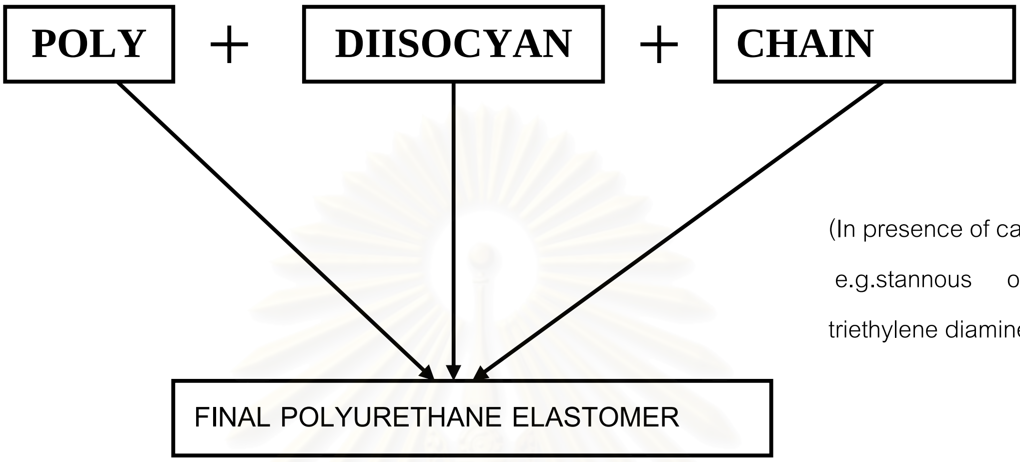


Figure 2.4 Prepolymer route for the formation of the polyurethane elastomer. [Hepburn, 1982]



(In presence of catalysts, e.g.stannous octoate with triethylene diamine)

Figure 2.5 One shot process for polyurethane elastomer preparation. [Hepburn, 1982]

The polyurethane elastomers can be classified in terms of [Wirpsza, 1993]:

I. Macrostructure: Considering the structure, polyurethane elastomers can be divided as interpenetrating polymer network (IPN), etc.

II. Type of group presented: Considering the type of group presented, polyurethane elastomers can be divided as ester, ether, amide, etc.

III. NCO-index value and method of processing: Considering the method of processing, polyurethane elastomers can be subdivided into three main groups as shown in Table 2.1:

2.1.1.1 Cast Elastomers: Polyurethane elastomers are formed by a liquid casting procedure which led to the designation cast elastomers.

2.1.1.2 Millable polyurethane elastomers: They are usually based on low molecular weight polymer about 20,000–30,000. Millable polyurethane elastomers can be crosslinked with the help of TDI dimer, sulphur or peroxide [Wirpsza, 1993].

2.1.1.3 Thermoplastic polyurethane (TPU): TPU are supplied as granules or pellets for processing by thermoplastic processing technique.

Table 2.1 Review of preparation and processing of various polyurethane elastomers.[Wirpsza, 1993]

Preparation technique	Prepolymer		One - shot	
Components	Oligomerol + diisocyanate		Oligomerol + diisocyanate(s) + extender + catalyst	
Intermediate	NCO - terminated (stable) prepolymer			
Additional treatment	Degassing under vacuum, for 30 min at 80-100 °C			
Additional component	Extender (Glycol or liquid diamine) + catalyst			
Additional treatment	Degassing (2 – 5 min)		Degassing	
Processed material	Liquid PUR (unstable)		Polyurethane elastomer (stable)	
Process technique	Mould casting	RIM	Milled	Thermoplastic
Addition treatment	Post – curing (e.g. annealing)	Post – curing (e.g. annealing)	Processing techniques typical of rubber (press forming, extrusion vulcanization)	Processing techniques typical of thermoplasts (injection moulding, extrusion, calendering)
Type of PU elastomer	Cast	Cast, injection moulded	Milled	Thermoplastic, elastoplast

2.1.2 Thermoplastic polyurethane

Thermoplastic polyurethane elastomers (elastoplastics) are at the same time thermoplastic and highly elastic rubber. They consist of essentially linear primary polymer chains. The structure of these primary chains comprises a preponderance of relatively long flexible chain segments which have been joined end-to-end by rigid segments through covalent chemical bonds. The flexible segments are diisocyanate coupled, low melting polyester or polyether chains. The rigid segments include single diurethane bridges resulting when a diisocyanate molecule couples two polyester or polyether molecules, but more particularly they are longer, high melting urethane chain segments formed by reaction of diisocyanate with the small glycol chain extender component.

2.1.2.1 Classification of Thermoplastic polyurethane

TPU may be broadly divided into two groups [Wirpsza, 1993].

2.1.2.1.1 Linear, non-crosslinked thermoplastic polyurethane elastomers

They are similar to cast polyurethane elastomers, but with a higher permanent set, obtained at isocyanate group index (NCO-index) =1.0. The properties depend largely on the molar ratio of extender to oligomerol (Table 2.2).

2.1.2.1.2 Crosslinkable thermoplastic polyurethane elastomers

They are obtained with a slight excess of isocyanate groups (NCO-index = 1.04 - 1.12) and crosslinked by allophanate or biuret links. Above 90 °C - 120°C the crosslinks reversibly rupture to yield a linear polymer which, upon formation and cooling, recrosslinks as the result of the reaction of free isocyanate group with the urethane and urea group. Thermoplastic polyurethane must be given along heated post cure to activate these few and dormant residual NCO groups, i.e. a typical cure would be 10 hr at 110°C in a hot air oven.

Table 2.2 Effect of extender on poly(butylene adipate) (RMM 1000) and MDI (NCO-index=1.0) based thermoplastic linear polyurethane. [Wirpsza, 1993]

Property	Extender					
	Ethylene glycol			1,4 - Butanediol		
	Mole ratio of extender to oligoesterol					
	0.3	1	2	0.3	1	2
Hardness/IRHD	65	73	90	72	87	95
Tensile strength/MPa	41	48	40	33	55	45
Elongation at break /%	700	560	350	800	570	480
300% modulus/MPa	3	6	23	3	9	25
Permanent/%	60	10	30	80	47	70

2.1.2.2 Properties and Applications

Thermoplastic polyurethane products are the first synthetic materials with rubber elasticity that could be processed by thermoplastic method. They have the typically high quality properties, i.e., the tensile strength reaches 60 MPa, and the elongation at break up to 600-900%. They have excellent tear, abrasion, impact, and wear resistance. Additionally, thermoplastic polyurethanes are resistant to ultraviolet light, outdoor weather exposure, hydrocarbon, and aromatic oils. However, TPU are changed by the effect of heat that temperatures above ambient, there is a temporary reduction of properties due to a weakening of the physical bonds within the polymer and immersion in certain fluids. The effect of organic materials on thermoplastic polyurethane is dependent on the chemical group presented in these materials, i.e. alcohols, acids, ketones and ester tend to cause swelling and degradation at high temperatures.

The applications of thermoplastic polyurethane are both numerous and varied. Most depend on the excellent toughness and wear resistance with broad temperature range for use. The applications of TPU include automotive part, shoes, wheels, industrial wheels, medical implants, and flexible tubing.

2.2 Polysiloxane

Polysiloxanes, frequently referred to by the generic name silicones, are unique among inorganic and semi-inorganic polymer. Since they combine the inorganic silicon atom with the organic carbon atom. Like carbon, silicon has a great ability to combine with other elements. But unlike carbon, it is incapable of forming double bonds to create long silicone-to-silicon polymer skeletal structure. Silicone are used in a variety of commercial applications including: tubing, prosthetic devices, gaskets, wire insulation, construction sealants, adhesives, fire stops, greases, heat transfer fluids, surfactants, antifoams, release agents, lubricants, anticracking agents, diffusion pump fluids, etc. Many of these products are based on polydimethylsiloxane (PDMS).

2.2.1 Silicone Forms

The principal industrial silicone polymers can be classified as fluids, resins, and elastomers, as presented in Figure 2.6 [Frye, 1994].

2.2.1.1 Silicone fluids are linear chains of polydimethysiloxane whose molecular weights determine their viscosity. They are known for their high temperature stability, high compressibility, relatively constant viscosity over temperature, and general inertness. They are used in vinyl polishes and high-temperature greases as heat-transfer fluids, and in plastic molding as release agents.

2.2.1.2 Silicone resins are highly branched polymers that cure to solids. They are resemble glass but are somewhat softer and usually soluble in solvent until cured. The degree of hardness when cured depends on the extent of crosslinking. Silicone resins are used as high temperature paint additives, electrical molding compounds, masonry water repellants, abrasion-resistant coatings for plastic, etc.

2.2.1.3 Silicone Elastomers are prepared from linear silicone oil or gums and reinforced with a filler and then vulcanized. Silicone elastomers are manufactured in several forms: heat-cured rubber, liquid injection molding elastomers, etc.

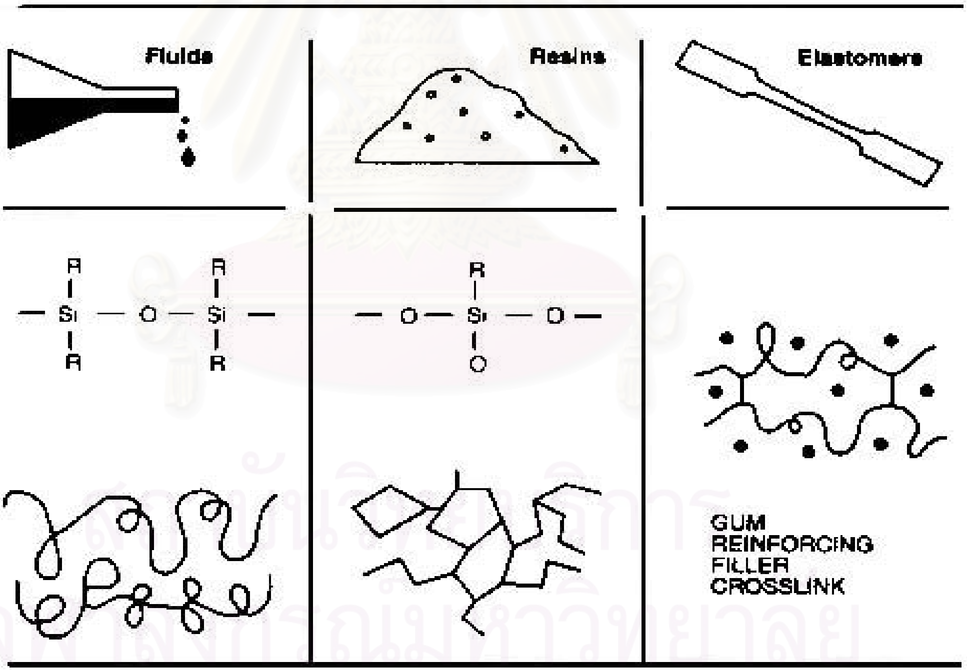


Figure 2.6. Silicone forms: Fluids, resins, elastomers. [Frye, 1994]

2.2.2 Polydimethylsiloxane

Polydimethysiloxanes (PDMS) are polymers with a unique combination of properties resulting from the presence of an inorganic siloxane backbone and organic methyl groups attached to silicone. The chemical configuration (as shown in Figure 2.7) gives polymers which have low glass transition temperature (-124^{o}C), low melting temperature (-40^{o}C) so that PDMS is fluid over a wide range of temperature. PDMS has good thermal stability, good oxidative resistance and good chemical stability. Several structures features make the siloxane backbone one of the most flexible in all of polymer science. The reasons for this extraordinary flexibility can be seen from Figure 2.7. Frist, because of the nature of the bonding, the Si-O skeletal bond has a length (1.64Å) which is significantly larger than that (1.53Å) of the C-C bond found in most organic polymers. As a result, steric interferences or intramolecular congestion are diminished. Also, the oxygen skeletal atoms are as small as an atom can be and still have the divalency needed to continue a chain structure. Finally the Si-O-Si bond angle of around 143^{O} is much more open than the usual tetrahedral bonding (∼110^{O}), and torsional rotations can occur without incurring a serious energy penalty. These structural features have the effects on increasing the dynamic flexibility of the chain. They also increase its equilibrium flexibility, which is the ability of a chain to take on a compact shape when in the form of a random coil.

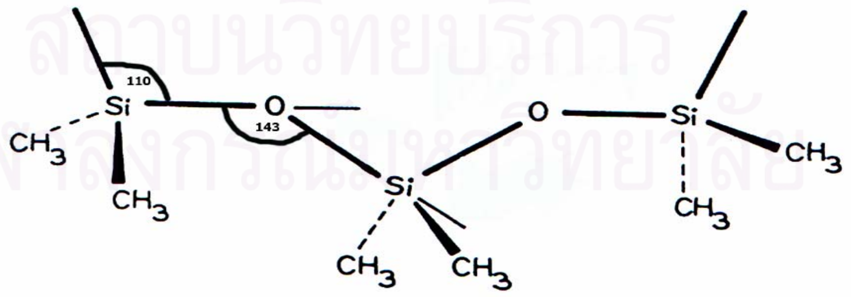


Figure 2.7 Sketch of the PDMS chain, showing some structure information relevant to its high flexibility. [Mark *et al*, 1992]

2.3 Polymer blends

Polymer blend is a mixture of at least two polymers or copolymers. The main purpose of blending polymer is to develop a new polymeric material which has specific properties different from those of the pure polymers at a lower cost instead of synthesizing a new polymer that requires more money, time and efforts.

2.3.1 The preparation of the blends

Preparation of polymer blends can be accomplished by several methods [Walsh, 1985].

2.3.1.1 Melt Mixing

Melt Mixing can be performed by mixing the mixture in the melt state. Mixing in the melt state is the method for the preparation of polymer blends in a large scale. The advantage of this method is being free from foreign components, i.e. solvents.

The disadvantage of melt mixing is that both components must be in the melt state, which means that the temperature may be high enough to cause degradation. Mixing equipment for melt invariably involves metal surfaces which move in opposition; for this reason, bearings and seals are always required. Another disadvantage of melt mixing is the cost of the equipment. Also even laboratory-size mixing equipment, it generally works well only with a large amount of material, i.e. 50 grams or more. If mixing quantities of less than 1 gram is required, melt mixing is hardly feasible.

For laboratory-scale mixing, a number of devices are available, for example, electrically heated two-roll mill, brabender mixer, extruder, and rotational rheometer.

2.3.1.2 Casting From Common Solvents

This method is done by dissolving the polymer components in a suitable solvent and then removing the solvent from the mixture.

Casting of the blends from a common solvent is the simplest mixing method available and is widely practiced in a laboratory scale. Very small quantity of experimental polymers can be handled easily. The resulting product, a film, is immediately useful for thermal analysis, dynamic mechanical analysis, etc. If pure solvents and clean glassware are used, contamination can be precluded. In most cases, temperatures never exceed ambient, so degradation is not a problem.

The most severe problem with casting is the influence of the solvent and the casting history on the resulting product. In spite of the fact that most of the solvent can be removed from a cast film, the nature of the film depends strongly on the solvent and the conditions used during casting. To avoid concentration and temperature gradients during the removal of solvent, casting is best done in thin films and with slow solvent removal.

There are a number of methods for casting thin films from polymer solutions. One easy method is to spread the solution over a glass plate by rolling a rod wound with wire. Most researchers simply cast dilute solutions into flat dishes. If films at very uniform thickness are needed, the solution can be cast onto mercury substrate. Covering the cast solution with an inverted dish slows the evaporation of the solvent and promotes uniform films.

2.3.1.3 Freeze Drying

In the freeze drying process a solution of the two polymers is quenched down to a very low temperature and the solvent is frozen. Solvent is then cleanly removed by sublimation from the frozen material. Dilute solutions must be used and the solution volume must be kept low for good heat transfer. The freeze drying process involves the following three stages:

- Frozen solution by low temperature cooling.
- Dried by direct sublimation of the frozen solvent
- Stored in the dry state under controlled conditions.

An advantage of this method is that a resulting blend will be independent of the solvent. Freeze drying seems to work best with solvents having high symmetry, i.e. benzene, dioxane, naphthalene, etc. This is also the limitation of this method. Such the powder form of the blend after solvent removal is usually not very useful and further shaping must be performed. While not complex, freeze drying requires a good vacuum system for low-boiling solvents.

2.3.1.4 Emulsions

The handling polymers as emulsions have many advantages as same as the used of solution casting. Films can be casted; mixing requires no expensive equipment; high temperature is not needed.

Emusions of polymers are not always available or easy to make. While emulsion polymerization is highly advanced, it is not applicable to all monomers.

2.3.1.5 Mixing via Reaction

Co-crosslinking and interpenetrating polymer networks (IPN) formation are specialty methods for forming blends. The idea of these methods is to force a degree of miscibility by reactions between the polymers.

2.3.2 Miscibility Characteristics of the blends

Mixing is the process that makes blends by putting several components together so that the blends become homogeneous or heterogeneous with small domain sizes. Blends can be classified into three categories as belows:

2.3.2.1 Miscibility

Miscibility is the state of a single phase where the level of molecular mixing is adequate to yield expected macroscopic properties of single phase material.

2.3.2.2 Partial miscibility

Partial miscibility exhibits at least two miscibility phases where each phase may comprise a high concentration of one component with a smaller dissolved portion of the other.

2.3.2.3 Immiscibility

Immiscibility is a state of two phases in which each phase comprises individual component and exhibits both macroscopic and/or microscopic properties of that component.

Miscibility characteristic mainly depends on several parameters such as composition, methods of mixing, temperature, pressure and volume of mixing.

2.3.3 The Phase Diagram of Polymer Blends

For general usage, if the phase separation curves are available, the working conditions and the processing parameters of the blend can be properly determined. The phase separation curve can be obtained from the diagram called “Phase Diagram” which usually is a plot of temperature versus composition of the blend. Pressure and other process parameters also have some effects on phase separation, but these parameters hardly change in normal ambient conditions. In real polymer blend systems, many types of phase diagrams can be found as shown in Figure 2.8 [Kroschwitz, 1990]. The shade area in Figure 2.8 represents phase separation while the unshaded area represents homogeneous region.

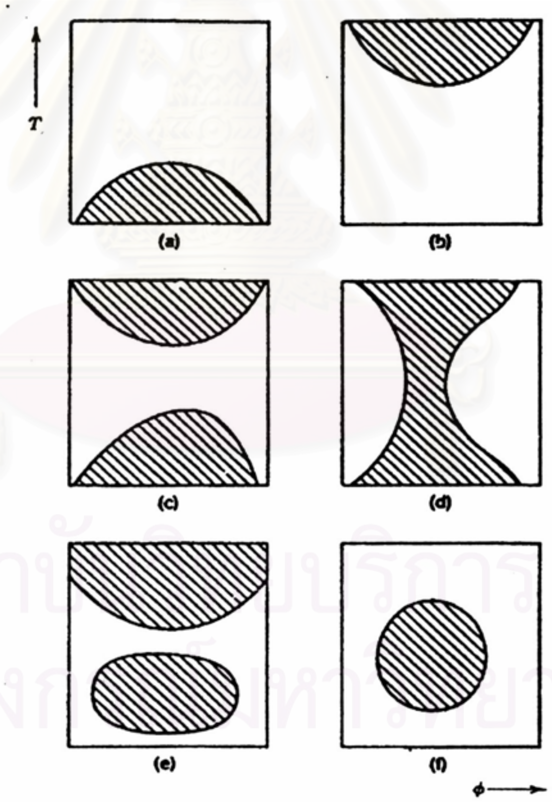


Figure 2.8 Schematic representation of six possible phase equilibria diagrams for binary mixtures in which the shaded areas represent phase separation. [Kroschwitz, 1990]

Figure 2.8(a) represents a system in which there is an upper critical solution temperature (UCST) behavior of typical polymer blends in which an initially homogeneous mixture undergoes phase separation upon lowering of temperature (increasing temperature increase miscibility).

When the blend goes from one phase to two phases as the temperature is raised, this behavior is called the lower critical solution temperature (LCST) behavior (Figure 2.8(b)). This is basically opposite from UCST behavior.

Figure 2.8(c) illustrates the combination of both upper and lower critical solution phase boundaries, that is most commonly found in nonpolar polymer solutions

Figure 2.8(d) shows the convergence of upper and lower critical boundaries for an immiscible system to form an hourglass-shaped phase boundary. This type of phase diagram is the common phase diagram for the commercial polymer alloys.

Figure 2.8(e) illustrates the existence of upper, lower, and quasilower critical phase boundaries. This type of phase diagram can be observed in polar polymer solutions.

Figure 2.8(f) shows the immiscibility loop with upper and lower critical phase boundaries inverted.

2.3.4 Determination of Miscibility

To determine the miscibility of polymer blends, the variety of experimental techniques are used. Some techniques, such as calorimetric, dilatometric, dynamic mechanical, dielectric, are based on the determination of the number and the location of the glass transition temperatures (T_g). Other techniques are based on scattering or microscopy technologies. Melting point (T_m) depression is another method used to determine the miscibility. Each technique has its own advantages, resolutions, cost, difficulties, assumptions and availabilities. Figure 2.9 presented a summary of different techniques used for the assessment of miscibility of polymer blends [Gedde, 1995]. It also suggested the suitability of each technique in relation to the domain size of the blend.

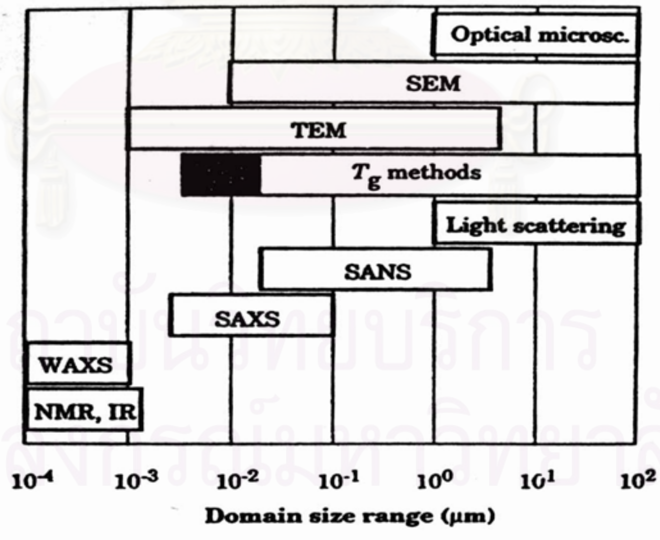


Figure 2.9 Size range cover by different experimental techniques for the assessment of miscibility. [Gedde, 1995]

2.3.4.1 Glass transition determination

There are many methods by which T_g of polymer may be determined. Examples are differential thermal analysis (DTA), thermal optical analysis (TOA), differential scanning calorimetry (DSC), dynamic mechanical measurement, dielectric measurement, and dilatometry. Some of the most widely used methods of T_g measurement in polymer blends are described belows [Walsh, 1985].

2.3.4.1.1 Differential Scanning Calorimetry (DSC)

The T_g is usually determined by a differential scanning calorimetry (DSC). DSC is the technique that monitors enthalpy changes (heat flow into or out) of a material (sample and reference) as a function of temperature or time. The sample and the reference are heated or cooled at a constant rate. The resulting temperature difference signal can then be recorded versus time or sample temperature [Fava, 1980]. An inflection in the plot is observed at the T_g because an increase in the specific heat of the polymer is accompanied by the increased molecular motion. This technique has the advantage of small sample requirements (typically 5-20 mg), rapid measurement blend and high sensitivity.

2.3.4.1.2 Dynamic Mechanical Measurement

Dynamic mechanical measurements have been widely used in the study of polymer miscibility. With this technique, a dynamic modulus can be measured as a function of temperature over a range of frequencies. From traditional torsion pendulum measurements, the dynamic shear loss modulus (G”) and the dynamic shear storage modulus (G’) may be obtained as a function of temperature at a nominal frequency in the vicinity of 1 Hz. The torsion pendulum consists of an internal source (disk or rod) connected to a polymer specimen which is firmly fixed at the other end. The inertial source is angularly displaced and released, allowed the specimen to vibrate freely. The resultant damped sinusodial wave is then determined using a suitable recording device [Olabisi, 1979].

The T_g of the blends is defined as the temperature corresponding to the maximum in G" or $\tan\delta$ ($\tan\delta$ = G"/G') at the main relaxation, which marks the onset of main chain segmental mobility corresponding to the glass transition.

This technique has more stringent sample requirements than calorimetry, that only films or fibers made from the blends can be studied. However, it is sometimes preferred because of a widely held belief that it is more sensitive than calorimetry.

2.3.4.1.3 Dielectric Relaxation

The electrical properties of polymers are analogous to mechanical properties in that the dielectric constant, ε', is similar to compliance, the dielectric loss factor, ε'', is similar to mechanical loss, and the dielectric strength is analogous to tensile strength. The dielectric loss factor and the dissipation factor, $\tan\delta$ ($\varepsilon'/\varepsilon''$), are of primary interest as they are commonly used to ascertain polymeric transition such as the glass transition. The ε', ε'' can be measured by placing the sample between parallel plate capacitors and alternating the electric field [Sperling, 1992]. The experimental advantage of obtaining transition data from electrical measurements over dynamic mechanical testing is in the ease of changing frequency.

The major disadvantage is the difficulty in determining the transitions of nonpolar polymers. Generally, nonpolar polymers will require slight modification, such as oxidation, to provide sufficient polarity to resolve adequately secondary loss transition as well as glass transition in blends [Olabisi, 1979].

2.3.4.1.4 Dilatometry

The earliest used method of determining T_g in polymers, dilatometry, has been infrequently employed in blend studies because of the greater speed and versatility of modern thermal analysis instrumentation.

A dilatometer consists of a glass bulb with an attached small capillary. The dilatometer is then placed in a temperature bath, and the temperature changed at a uniform rate so that a plot of volume as a function of temperature is obtained. An inflection point indicates the position of the glass transition [Eisenberg, 1993]. In contrast to DSC, dilatometry requires larger samples and more time and care in sample preparation and measurement.

2.3.4.2 Scattering

A quick but not totally reliable method to determine that a polymer blend forms a single phase or multiphase is by its transparency [Olabisi, 1979]. Discontinuous domains in the polymer blends are often large enough to refract light, forming a translucent or an opaque blend when two transparent polymers are mixed. In a miscible one-phase blend of two amorphous polymers (transparent polymer), no domains are presented to refract light and, hence, the blend may be transparent. By the scattering method, one may reach erroneous conclusions if :

1. The refractive indexes of polymer A and polymer B are similar.
2. The domains are smaller than that of the wavelength of light, the light is not scattered, and a two phase blend can be transparent.
3. Either component of an initially transparent miscible blend later crystallizes, the blend may become opaque.

To improve this technique, the uses of an x-ray and a neutron scattering instead of light scattering provide much insight into the blend morphology as the very small domains can be accessed. Furthermore, small-angle neutron scattering has emerged as a powerful tool for investigating many aspects of polymer blends [Olabisi, 1979].

2.3.4.3 Microscopy

Microscopy is the name given to a group of experimental methods which permit magnification of morphological structures to make details visible [Gedde, 1995]. Microscopy provides detailed information about miscibility and phase morphology, i.e. the actual geometry of the phases. The microscopic methods can be divided into three categories as follows:

2.3.4.3.1 Optical Microscopy

The optical microscope is obtained by two lens systems, referred to as the objective and the eyepiece. The objective generates a magnified real image of the specimen. The real image is further magnified by the eyepiece and a magnified real image is formed at the retina of the eye [Gedde, 1995]. Optical microscopy resolves structures down to about 1 μm. The sample may need staining prior to examination. In other cases, where the refractive index mismatch is sufficiently large, direct examination can be made in the microscope using phase-contrast as interference-contrast optical microscopy.

2.3.4.3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) uses the technique of a focus electron beam to scan the sample surface. Maximum resolution is obtained with a high accelerating voltage, small probe size and high beam current. These conditions may result in beam damage to sensitive specimen. The depth of focus decreases with increasing magnification and is about 1 μm at 10,000× magnification. Magnifications up to about 100,000× are possible. In addition to having a higher resolution than optical microscopy, SEM has a much large depth of field. Samples are thinly coated with a metal to provide a conductive layer [Woodward, 1995].

2.3.4.3.3 Transmission Electron Microscopy (TEM)

The transmission electron microscope (TEM) is built according to the same principle as the optical microscope, with a condenser len, an objective len and projector len (the analogue of the eyepiece). A magnified image is obtained on a fluorescent screen or on a hairpin tungsten filament or a lanthanum boride (LaB_6) filament heated with a low-voltage source. The potential of the filament is highly negative and the electrons are accelerated towards an anode held at a small position potential [Gedde,1995].

Transmission electron microscope involves complex and tedious preparation of the samples necessary to reveal the microphase. But the resolution of TEM is superior to optical microscopy and SEM.

2.4 Processing Technique

2.4.1 High Intensity Internal Batch Mixer

One of the earliest and most common high intensity internal batch mixers, still widely used in the plastics and rubber industries, is the Banbury mixer.

The Banbury mixer (Figure 2.10) consists of a mixing chamber shaped like a figure eight with a spiral lobed rotor in each chamber. The shape of the rotor is such that it induces axial mixing along the rotor toward the center. The mixture is fed to the mixing chamber through a vertical chute in with an air or hydraulic driven ram is located. The lower face of the ram is part of the mixing chamber. The homogenized mixture is discharged through a slide or "door-door" at the bottom. There is a small clearance between the rotors, which usually operate at different speeds, and between the rotors and the chamber wall. In these clearances dispersive mixing takes place. The shape of the rotors and the motion of the ram during operation ensure that all fluid particles undergo high intensive shearing flow in the gaps. Both rotors and chamber walls are temperature controlled.

The physical properties of the mixture can be changed during the mixing process and intensive mixing is often used to improve certain properties.

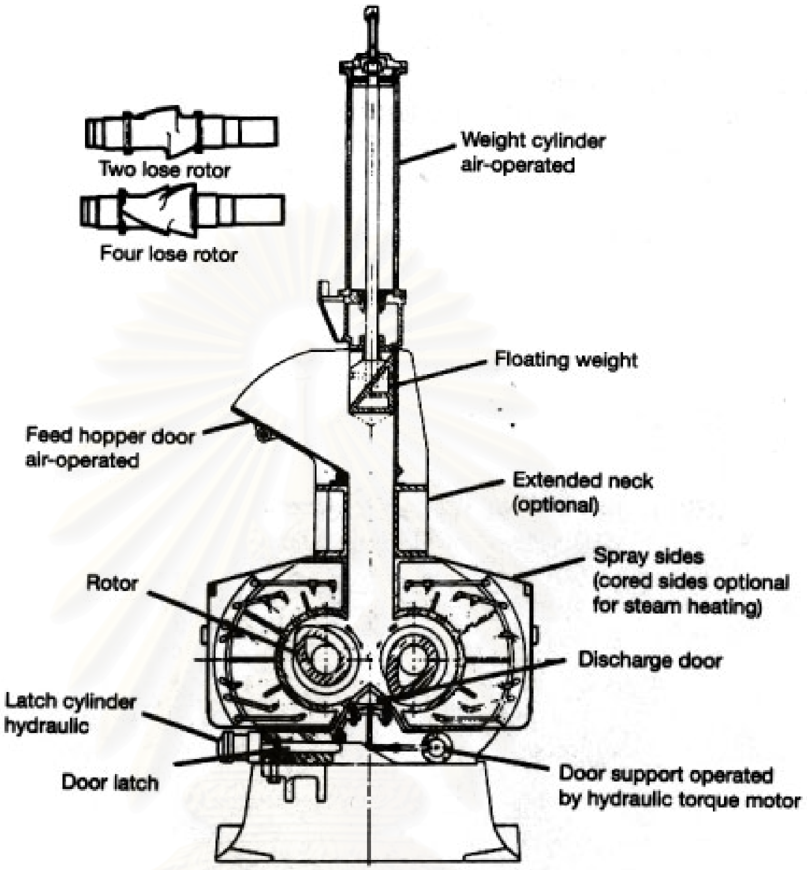


Figure 2.10 Cross-section of a Banbury mixer. The inset shoes two of several common types of rotors that operate in pairs to intensively mix rubber and thermoplastics. [Belofsky, 1995]

2.4.2 Twin Screw Extruder

Polymer Blending can be performed through melt mixing by other processing techniques such as single screw extruder, twin screw extruder, internal mixer, two roll mill, etc. One of the important considerations for the use of a twin screw extruder is that the mixing mechanism ensures that all of the materials have the same shear history. In addition, the shear produced by the conveying action is much less than that for a single screw machine and furthermore, it is controllable. Usually the amount of shear imparted by the pumping screws is less than that desired, the independent control of the shear and the conveying effects are the major reasons that these machines are used extensively to extrude heat-sensitive and shear-sensitive polymer such as rigid PVC.

Twin screw extruders are utilized in certain operations because they offer specific advantages. These include:

- Increased output at low screw speed,
- Improved pumping control over wide range of operating conditions,
- Decreased viscous dissipation and internal heat generation,
- Ability to handle materials that are difficult to feed such as powder,
- Lower power requirements,
- A completely versatile processing technique,
- A continuously operating process,
- Low cost of operation and easier quality control,
- Greater product uniformity,
- Low contact time in the extruder.

Twin screw extruders are often used to achieve improved dispersing and mixing, as in the compounding of additives. However, the twin screw extruder has disadvantages of processing less flexibility in switching to a new mixture, and the machine is expensive.

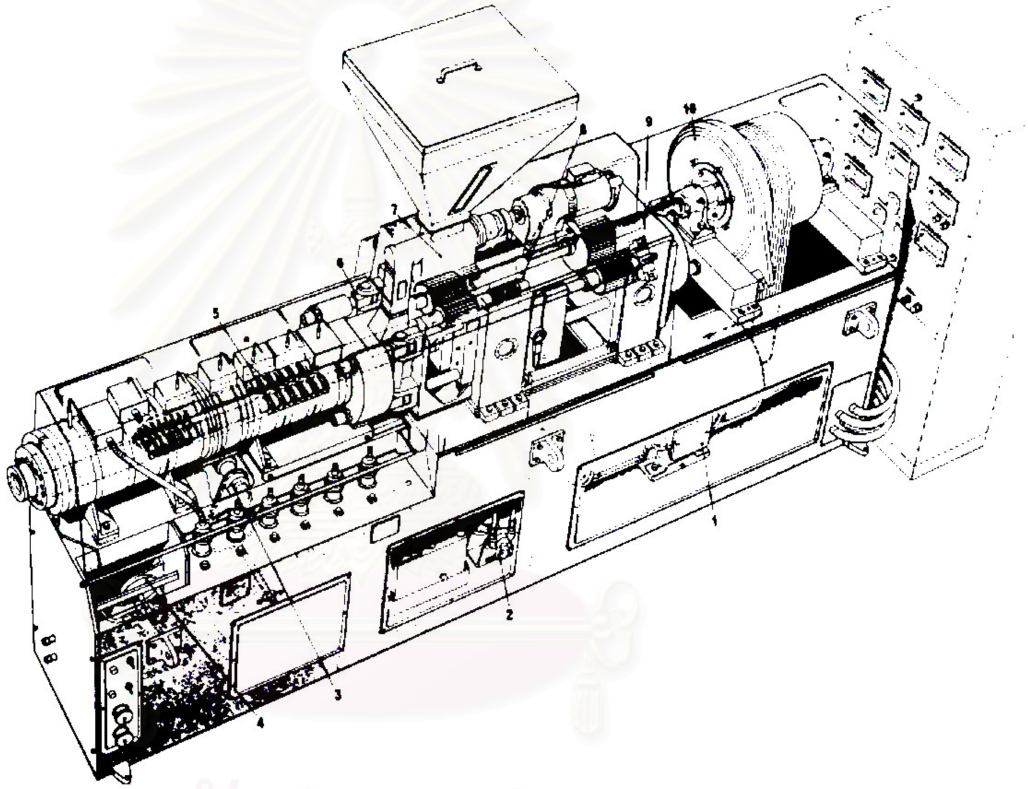


Figure 2.11 ZSK corotating intermeshing twin screw extruder with corresponding barrel elements [Tadmor,1979]

Twin screw extruders are frequently used when processing needs exceed the capabilities of single screw extruders. The twin screw mechanisms can be co-rotating or counter-rotating, intermeshing or non-intermeshing. Co-rotating, intermeshing extruders are the most widely used for commercial processing as shown in Figure 2.11. Next in significance are counter-rotating, intermeshing; and counter-rotating, non-intermeshing machines. Twin screw extruders can be classified into intermeshing or non-intermeshing and co-rotating or counter-rotating, as summarized in Figure 2.12.

2.4.2.1 Co-rotating, intermeshing extruders

The extruders have the roots and flanks of one screw continuously wiped by the crest of the adjacent screw. The polymer follows a figure-eight path as it moves along the screw, with polymer surfaces being constantly renewed. Residence time (heat and shear history) is short and well-defined for each particle, facilitating good process control.

2.4.2.2 Counter-rotating, intermeshing extruders

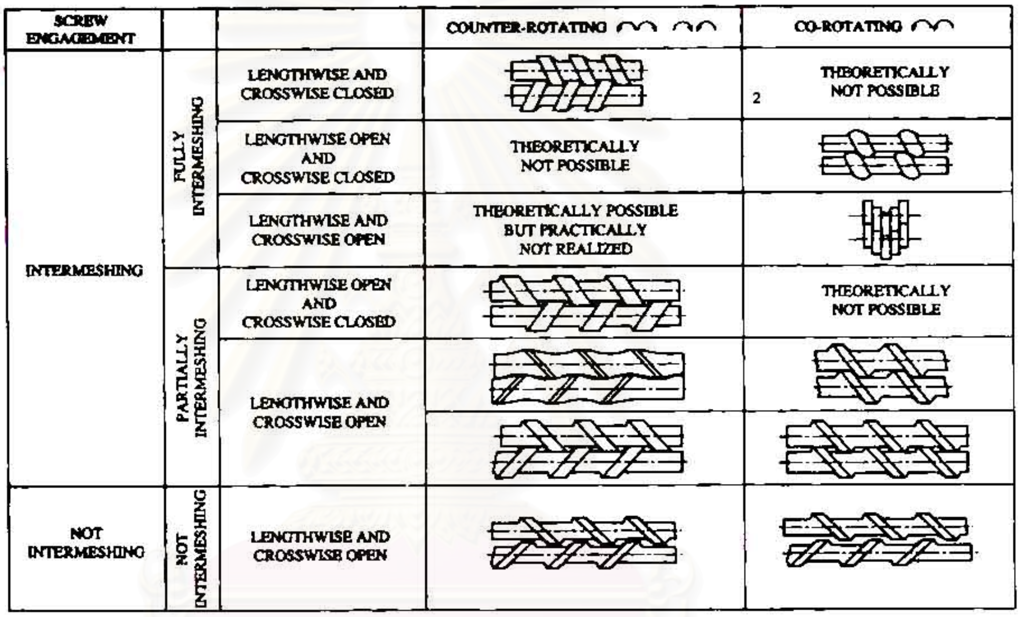
Typically, the counter-rotating is outward at the top and inward at the bottom. The material essentially moves as a unit volume in a closed chamber. Material in the wedge area undergoes a motion similar to that involve in calendering.

2.4.2.3 Counter-rotating, non-intermeshing extruders

The continuous mixer uses a rotor design that combines the transport effects of the screw with the dispersive mixing capability of a winged rotor, similar in design to a Banbury (batch) mixer. This simple design controls shear rate by motor speed and variable pressure discharge valve.

2.4.2.4 Counter-rotating, tangential extruders

The extruder essentially operates as two single screw extruder side by side. The screw pitch of both screws is opposed so that the drag flow from the two screws pumps the polymer in the same direction.



SCREW ENGAGEMENT			COUNTER-ROTATING	CO-ROTATING
INTERMESHING	FULLY INTERMESHING	LENGTHWISE AND CROSSWISE CLOSED		2 THEORETICALLY NOT POSSIBLE
		LENGTHWISE OPEN AND CROSSWISE CLOSED	THEORETICALLY NOT POSSIBLE	
		LENGTHWISE AND CROSSWISE OPEN	THEORETICALLY POSSIBLE BUT PRACTICALLY NOT REALIZED	
	PARTIALLY INTERMESHING	LENGTHWISE OPEN AND CROSSWISE CLOSED		THEORETICALLY NOT POSSIBLE
		LENGTHWISE AND CROSSWISE OPEN		
NOT INTERMESHING	NOT INTERMESHING	LENGTHWISE AND CROSSWISE OPEN		

Figure 2.12 Comparison of commercial twin screw extruder arrangements.
[Griskey, 1995]

2.4.3 Compression Molding

Compression molding is used principally for thermosetting plastics, and much less commonly for thermoplastics. The process of compression molding may be simply described in Figure 2.13. Compression molding consists of forcing a certain amount of polymer into the desired shape of the mold cavity, not by injecting it into a closed molding, but by closing one half of the mold on the other. The mold is heated, and an appropriate amount of molding material is loaded into the lower half of the mold. The two parts of the mold are brought together under pressure. The pressure and temperature can be varied considerably depending upon the thermal and rheological properties of the polymers. In practice, the polymer is often preheated to reduce the temperature different from the mold and to assist easy flow in the mold. In addition, a slight excess of material is usually placed in the mold to insure its being completely filled. The compound, softened by heat, is thereby welded into a continuous mass having the shape of the cavity. The mass then must be hardened, so that it can be removed with out distortion when the mold is opened. The advantages of compression molding over other processing techniques are:

- Polymers flow over shorter distances thus reducing frozen-in stresses.
- Polymer are not forced through small gates, which can lead to reduction in mechanical properties.
- Mold maintenance cost is low.
- Tooling costs are inexpensive because of the simplicity.
- Material is not wasted because of the absence of sprues and runners.

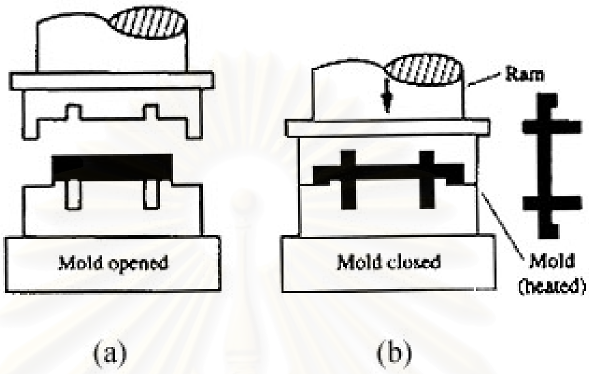


Figure 2.13 Schematic of compression molding (a) Open, preform in place; (b) closed. [Griskey, 1995]

2.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is generally used for determining the melting temperature, glass transition temperature, degree of crystallinity, and heat of fusion of polymers. This test measures the thermal energy absorbed (endothermic) or given off (exothermic) by the sample. The sample and the reference are placed in thin metal (aluminum) pans, with the thermocouple sensor below the pans. DSC measurements can be made in two ways: by measuring the electrical energy provided from heaters below the pans necessary to maintain the two pans at the same temperature or by measuring the heat flow as a function of sample temperature. Either type of DSC is performed at a constant heating rate under a nitrogen atmosphere.

Although DSC is used routinely in polymer characterization studies, the analyst needs to be aware of variable factor that can distort the results. It is well known that the first heating curve is significantly influenced by the thermal history of the sample that the polymer is subjected to during processing. Therefore, the second heating scan must be performed to introduce constant thermal history to the samples.

2.6 Thermogravimetric Analysis (TGA)

Thermogravimetry is one of the thermal analysis methods which examines the mass change of a sample as a function of temperature in the scanning mode or as a function of time in the isothermal mode. To perform the test, a small amount of sample with exact weights is hung from a balance and heated in the small furnace on the TGA unit according to a predetermined temperature program. As all materials ultimately decompose on heating, and the decomposition temperature is a characteristic property of each material, TGA is an excellent technique for the characterization and quality control of materials. TGA can be used to follow the reactions at which sample weight is changed including desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition.

The advantages of TGA can be summarized as follows:

- The sample can be studied over a wide temperature range using various temperature programmes;
- Almost any physical form of sample can be accommodated using a variety of sample vessels;
- A small amount of sample (0.1 μg – 10 mg) is required;
- The atmosphere in the vicinity of the sample can be standardized
- The time required to complete an experiment ranges from several minutes to several hours.

However, the disadvantage of TGA is that it cannot be used to study melting temperature, glass transition temperature or crystallization since TGA examines the mass change of the sample as a function of temperature in the scanning mode or as a function of time in the isothermal mode while some phenomena of the sample, such as melting , glass transition and crystallization, occurs without any mass changes. TGA curves are normally plotted with the mass change expressed as a percentage on the vertical axis and temperature or time on the horizontal axis.

2.7 Scanning Electron Microscopy (SEM)

Scanning electron microscopy first became widely available in the late 1960s. They are quite sophisticated instruments but are relatively easy to operate and the information they provide comes in the form of magnified images and is normally easy to interpret. SEM uses the technique of a focus electron beam to scan the sample surface [Woodward,1995]. The electron beam is controlled by lenses consisting of magnetic fields. Rotational symmetric electromagnets focus the electron beam in the same way as convex lens do in optical microscopes [Gedde, 1995]. The polymer specimen to be examined by SEM was first coated with a thin layer of gold to provide a conductive layer. SEM provides more detailed information on the morphology; domain down to a size of 10 nm can be resolved. SEM is becoming the most popular method of observation of polymer blends. The great advantages of this technique are: rapidity, great depth of focus, relatively simple image interpretation, and easy of sample preparation. But there are limitations which are caused by specimen charging that occurs in the SEM when the subject is non conductive, and by structural damage caused by the high energy electron beam when it impinges on the specimen.

2.8 Tensile Properties

The most important mechanical property of a plastic is its tensile stress-strain curve (Figure 2.14). This curve is obtained by "stretching" material in a testing machine and measuring its extension and the load required to reach this extension. The force and the extension of samples can be converted to stress and strain by calculations using the original dimensions and the increase in length. Figure 2.14 shows a general stress-strain curve for a plastic such as polyethylene demonstrating various elements of tensile behavior. Initially the modulus is high, until a point is reached where the plastic “yields” or deforms. Prior to the yield point, the elongation is reversible. At the yield point, enough stress has been applied to cause the molecules to untangle and flow over one another, and further elongation is irreversible. Eventually the sample breaks.

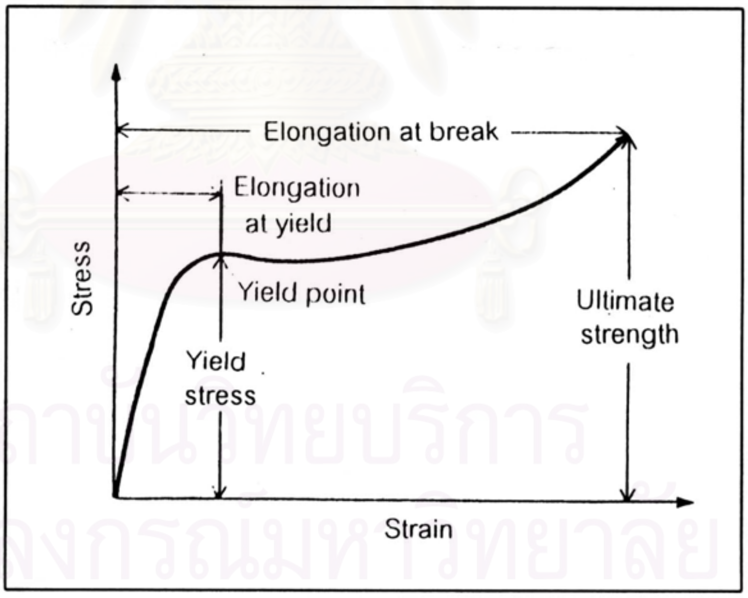


Figure 2.14 General tensile stress-strain curve for a typical thermoplastic. [Haung, 1988]

2.8.1 Stress

Stress is the force applied to produce deformation in a unit area of a test specimen. The standard unit of measure in Pascal or pound per square inch.

2.8.2 Strain

Strain is the ratio of elongation or deformation to the gauge length of the test specimen, that is the change in length per unit of original length. It is expressed as a dimensionless number.

2.8.3 Tensile Strength

Maximum tensile stress sustained by the test specimen during a tensile test. Ultimate tensile strength is stress at which the specimen breaks or fractures. It shall be calculated by dividing the maximum load by the original minimum cross-section area of the specimen. The result shall be expressed in force per unit area, usually megapascals.

2.8.4 Elongation

The increase in the length of a test specimen that is expressed as a percentage of the initial gauge length is called the percentage of elongation.

2.8.5 Ultimate Elongation

Ultimate elongation or percent elongation at break is the strain at which the material breaks. It shall be calculated by dividing the extension at the moment of rupture of the specimen by the initial gage length of the specimen and multiplying 100.

2.8.6 Modulus of elasticity or Young's Modulus

Modulus of elasticity or young’s modulus is the linear slope of the stress-strain curve. Normally at low extension or low strain, the stress-strain relationship of plastics shows linear behavior known as linear viscoelasticity. However, plastics generally show nonlinear behavior of the stress-strain relationship. Therefore, modulus values for plastic are determined at very low extension which the stress-strain curve is often reasonably straight line. All elastic modulus values shall be computed using the average initial cross-sectional area of the test specimens in the calculations. The result shall be expressed in pascal. The modulus of elasticity is applied to describe the stiffness or rigidity of plastic.

2.8.7 Yield point

The yield point is the first point on the stress-strain curves at which an increase in strain occurs without an increase in stress. After the yield point the specimen exhibits non-recoverable behavior. Thus, this point would normally represent the limit of elasticity. The stress at the yield point is specified as the tensile strength at yield or yield stress. Tensile strength at yield is an often-quoted property, especially if it has a higher value than the ultimate tensile strength at break.

2.8.7 Area under the stress-strain curve

The area under the stress-strain curve from the origin to the breaking point is proportional to the energy required to break the plastic and is sometimes referred to as the toughness of the plastic. .

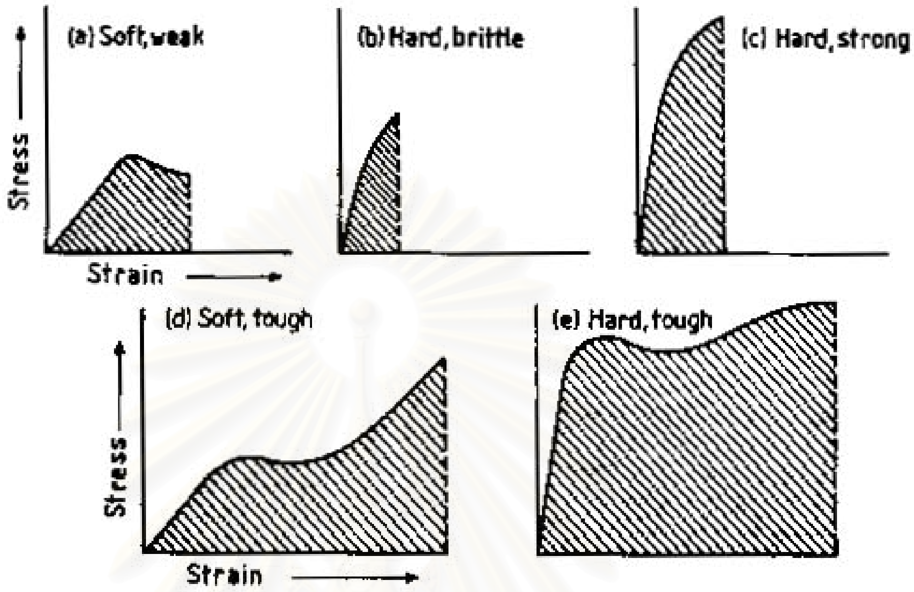


Figure 2.15 Stress-strain behavior of various types of plastics. [Brown, 1981]

Carswell and Nason have described five forms of material behavior which can be expressed by the stress- strain diagrams (Figure 2.15) [Roger, 1981]. In Figure 2.15, a soft and weak material is characterized by low modulus, low yield strength and moderate elongation at break (a). A hard and brittle material such as general purpose phenolic is characterized by high modulus and low elongation (b). A hard and strong material such as polyacetal has high modulus, high yield stress, usually high ultimate strength, and low elongation (c). A soft and tough material such as polyethylene shows, low yield stress, but very high elongation at break (d). A hard and tough material such as polycarbonate is characterized by high modulus, high yield stress, high elongation at break and high ultimate strength (e).

CHAPTER III

LITERATURE REVIEWS

Literature on the blends of TPU and PDMS

Hill, D.J.T., *et al*. (1996) have clearly shown that significant improvements in the performance of thermoplastic polyurethane (TPU) can be achieved through the blending of standard, commercially available polyurethane and commercial siloxane fluid (Polydimethysiloxane, PDMS). TPU are based on poly(tetramethylene oxide) (PTMO) soft segments, 4,4'-diphenylmethane diisocyanate (MDI) hard segments and 1,4-butanediol chain extended. PDMS with a molecular weight of 134 kg/mol is a fluid with a viscosity of 10^5 centistoke. A brabender twin screw extruder was used to melt blend the PDMS with the TPU at maximised shear. Temperatures in the four zones of the extruder were in the range 160°C – 220°C, and the extruder was run at 30 rpm. The resultant polyurethanes show improvements in wear resistant of up to 25% (c.f. virgin polyurethane) for an optimal PDMS concentration of 1.5-2.0%, beyond which the properties diminish rapidly. The mechanical properties of the blend have been even more significantly enhanced, by up to 40% for tensile strength and 50% for elongation at break.

Bremner, T., *et al*. (1997) have studied a packing model in system of TPU/PDMS blends from the resultant mechanical and wear properties of Hill, D.J.T., *et al*. (1996). Their research found the changes in the mechanical and wear properties are not due to surface modification alone, but are largely due to modification of the bulk by PDMS. A model is presented that accounts for the observed for relationships between the physical properties and the PDMS concentration in the blends. It was proposed that the addition of PDMS facilitates an improved packing efficiency in the polyurethane soft domain, leading to improved material performance. Beyond an optimum PDMS concentration of 1.5-2.0%, phase separation of PDMS becomes significant, plasticization sets in, and mechanical properties then begin to diminish rapidly.

Literature on the blends of TPU and other polymers

Santos, R. de J., *et al*. (1993) have found that the mechanical properties of polymer blends are dependent not only on the chemical nature but also on the morphology of polymer blends which can be determined by electron microscopy techniques. They have presented an optimization of the etching technique as an aid in the investigation of phase structures of blends composed of thermoplastic polyurethane elastomer (TPU) and Acrylonitrile–butadiene–styrene (ABS resin) by Scanning electron microscopy (SEM). Polymer blends were prepared on a two-roll mill at 80^{o}C and 15 rpm, for 30 min. Each mixture was etched by using Methyl Ethyl Ketone (MEK) at room temperature for periods of 2, 3 and 4 hr. The results were observed by SEM before and after the treatment with MEK. In TPU/ABS blends, the domains of the ABS dispersed phase at the fractured surface are not visible by the SEM technique unless etched samples have been used. Etching by MEK of the fractured surface of TPU/ABS blends for 3 hr has revealed the dispersed phase morphology. The average size of ABS domains was found to be proportional to the ABS content in the blends.

Yue, M.Z. and Chian, K.S. (1996) have studied the mechanical properties and morphology of thermoplastic polyurethane elastomer (TPU) with poly(vinylidene fluoride) (PVDF) blends. Polymer blends were prepared in an internal mixer at 170^{o}C. The results were incompatible at all compositions. The blends showed layered-type structures, due to their immiscibility, which resulted in the low mechanical properties in the blends. PVDF disrupted the intermolecular chain interactions in TPU resulting in lowering of the mechanical properties in the blends. Result showed that the 50:50 blend has lowest mechanical strength. At high levels of PVDF (>50%), the mechanical strength increased proportionally to PVDF. It was also found that both breaking strain and the energy at break of these blends decreased with increasing PVDF content.

Zerjal, B., *et al*. (1996) have studied the miscibility in thermoplastic polyurethane elastomer (TPU) with poly(styrene–co–acrylonitrile)(SAN) blends by differential scanning calorimetry (DSC) and dielectric spectroscopy. Blends were prepared by melt mixing in a Brabender kneading chamber (rotation speed 50 rpm) at 468 K for 10 min. From DSC measurements it could be concluded that values of the glass transition temperature (T_g) of TPU in TPU/SAN blends increases linearly with increasing weight fraction of SAN to the composition 50/50, while value of T_g of SAN in the blends decreases with increasing weight fraction of TPU.

Ahn, T.O., *et al*. (1997) have studied the influence of interchange reactions on the miscibility of thermoplastic polyesterurethanes and polycarbonate (PC) binary blend. The miscibility of TPU and PC blends was observed by differential scanning calorimetry (DSC). A series of TPU with various hard segment contents was prepared using 4,4'-diphenylmethane diisocyanate and 1,4-butanediol, (poly (MDI-BD)), as the hard segment and poly(ethylene adipate)diol or poly(butylene adipate)diol, whose number – average molecular weight is 2000, as the soft segment. The blend of TPU and PC were obtained by casting the pyridine solution (2-5w/v%) of the polymers. The miscibility between PC and poly (MDI-BD) or TPU containing a polyester soft segment was enhanced by interchange reactions at high temperature.

Potschke, P., *et al*. (1997) have studied the influence of the component viscosities on the blend morphology and mechanical properties of thermoplastic polyurethanes and polyolefines blends. Blends were produced by melt mixing using a twin screw extruder. The screw speed was 150 rpm, the output was 10 kg/h, melt temperature was 230°C and residence time was about 50 s. In the blend system thermoplastic polyurethanes and polyolefines interactions between the blend components cannot be detected by DSC, DMA, selective extraction and SEM. The tensile strength shows a U-shaped curve with a minimum between 40 and 60 wt % of polyolefin. At similar viscosity ratios (η_d / η_m), blends with polyether based TPU (TPU-eth) have a finer morphology than blends with polyester based TPU (TPU-est). Blends with TPU-eth show a lower decrease in tensile strength with blend composition than blends with TPU-est.

Xie, J., *et al*. (1997) have studied the morphology of binary and ternary blends composed of poly(styrene-co-acrylonitrile) (SAN), thermoplastic polyurethane (TPU) and poly(ethylene-co-vinyl acetate) (EVA). The morphology of polymer blends was characterized by scanning electron microscopy (SEM). Chloroform or hot acetone, hexane/toluene (2/1 v/v) and NaOH/CH_3OH (1 wt%) were found to be selective etching agents for SAN, EVA and TPU, respectively. With either TPU or SAN as the minor component, the resulting blends always show uniform morphology with fine dispersion of the minor component, while blends of SAN and EVA show rough phase structure with poor phase adhesion. These results are in accordance with the difference in the mechanical properties of SAN/TPU and SAN/EVA. In addition, for SAN/TPU/EVA blends, if TPU is only a minor component, it is preferentially located at the interphase, playing the role of a compatibilizer. As the amount of TPU increases, the compatibility is gradually improved.

Ha, C.S., *et al*. (1998) have studies the fracture toughness and properties of plasticized PVC and thermoplastic polyurethane (TPU) blends. Two kinds of TPU are based on polyether but different hardness, as TPU70 (shore A hardness 70) and TPU90 (shore A hardness 90). PVC/TPU blends at various weight ratio at 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, and 0/100 were prepared by melt blending in a laboratory-made bench kneader under experimental conditions of 60 rpm, 170^{o}C for 8 min. The physical properties such as thermal stability, tensile properties, abrasion resistance, and flame retardance of plasticized PVC except hardness were greatly enhanced by adding TPU. Additionally, the morphological studies by SEM showed clearly the dimple rupture topology of the PVC/TPU70 blends, while the PVC/TPU90 blends did not.

Kim, Y., *et al*. (1998) have studied the dynamic mechanical properties and morphology on the compatibility of plasticized PVC and thermoplastioc polyurethane (TPU) blends. Two kinds of TPU are based on polyether but different hardness, as TPU70 (shore A hardness 70) and TPU90 (shore A hardness 90). Their work was found that TPU with a lower hardness is more compatible with plasticized PVC than with a higher hardness in the composition range at 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, and 0/100 of plasticized PVC and TPU blends.

Jaisankar, S.N. and Radhakrishnan. G., (2000) have studied the compatibility effect of SMA (styrene maleic anhydried) on the morphology and mechanical properties of thermoplastic polyurethane (TPU) and poly(styrene-c-acrylonitrile)(SAN) blends. It was investigated using Fourier transform infrared spectra (FT-IR), Differential scanning calorimetry (DSC) and Scanning electron microscopy (SEM). The blends were prepared by melt mixing in a two-roll mill at 220^{o}C - 235^{o}C at milling time 10-12 min. The resultant TPU/SAN blends of composition 70/30 and 50/50 show better mechanical properties than other blend ratios. Addition of SMA (5 wt%) improved the miscibility as evidenced by uniform phase from the SEM micrographs. Also TPU/SAN/SMA 70/30/5 showed better compatibility than other blend ratios.

Literature on the blends of PU and other polymers

Samios, C.K., *et al*. (2000) have studied the compatibllization of polyurethane (PU) with poly(ethylene terephthalate) (PET). PU are based on polyester with soft segments consisting of poly(butylene adipate), and hard segments fromed by the addition of 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol. The resultant PU/PET blends show good mechanical properties that indicate good blend compatibility. SEM micrographs of specimens fractured at ambient temperature (between the T_g of the components) was found that at high PET contents, features of glassy fracture with shear bands predominate while at higher PU contents it is a fibrous texture. Morphology examination revealed good dispersed and strong interface adhesion.

Archondouli, P.S., and Kalfoglou, N.K., (2001) have studied the compatibllization and properties of poly(ethylene terephthalate) (PBT) and polyurethane (PU) blends. TPU are based on polyester soft segments, and 4,4'-diphenylmethane diisocyanate (MDI) with 1,4-butanediol hard segments. The morphology examination revealed good component dispersion and strong interface adhesion. Thermal property and Dynamic mechanical properties (DMA) indicated partial component mixing and mechanical compatibility typical of polymeric alloy.

Literature on the structure of segmented polyurethane

Li, Y., *et al*. (1992) have studied the effects of temperature and annealing of segmented polyurethane. The multiphase structure and related relaxations of a segmented polyurethane were characterized by using a combination of differential scanning calorimetry (DSC) and synchrotron small-angle X-ray scattering (SAXS). The results showed a soft segment glass transition temperature (T_g) which is significantly higher than the T_g (-84°C) of the pure soft segment, suggesting an incomplete phase-separation behavior for the soft segment. Synchrotron SAXS was also used to study the postannealing effects on the segmented polyurethane with a well-defined thermal history. The structural changes were irreversible upon annealing. Thermal postannealing did not have a significant effect on the multiphase structure once the structure development has reached equilibrium and interaction among the hard segments has reached a certain degree of strength. However, postannealing could promote perfection inside the hard segment domain or further phase separation of some hard segments inside the soft segment matrix. The structures from the samples which have not reached equilibrium or have very weak interaction among the hard segments could be changed dramatically by postannealing. The only way to change the existing structure entirely is to melt the sample. The mobility of the hard segment, the viscosity of the system, and the interaction between the hard segments are three key factors which control the structure in segmented polyurethanes.

Pompe, G., *et al*. (1998) have studied the influence of processing condition on the multiphase structure of segmented polyurethane. The resulting phase morphology of thermoplastic polyurethane elastomer is not only influenced by the chemical structure, but also by the processing condition. The polymorphism of hard segment (HS) crystallites of commercial polyurethane was investigated in dependence on the melting processing conditions using wide–angle x-ray scattering (WAXS) and differential scanning calorimetry (DSC). The thermoplastic polyurethane is used linear block copolymer based on polyethylene adipatediol, 1,4-butanediol (BD) and 4,4'-diphenylmethanediisocyanate (MDI), with hard segment content of about 60 wt% and a shore D hardness of 60. The TPU was extruded by use of a co-rotating, intermeshing twin screw extruder. The screw speed was 150 rpm, the output 10 kg/hr. The maximum melt temperature was 240 ^{o}C, the residence time was about 50 s. In the TPU studied in this paper two different morphologies of the MDI/BD-based hard segment crystallites were visible. The content of the different crystallite types strongly depends on the maximum processing temperature. The assignment of the two different crystallite types to the different melting regions is possible by comparing the differential scanning calorimetry (DSC) melting behavior with the wide angle X-ray scattering (WAXS). Analysis of results permits the assignment of HS crystallites of so-called ' type II ' with high WAXS intensity to those melting above 220 ^{0}C. Additionally, the tensile strength was correlated to the phase morphology.

CHAPTER IV

EXPERIMENT

4.1 Materials

4.1.1 Thermoplastic polyurethane (TPU)

Thermoplastic polyurethane (TPU) used in this study is S385A series with the trade name of Skythane, obtained from SK Chemicals Co, Ltd. The TPU has average molecular weight about 250,000 measured in the condition of polystyrene standard in dimethylformamide (DMF). The specific gravity of TPU is 1.21. S385A is the polyester-based thermoplastic polyurethane of which the hard segment is 4,4'-diphenylmethane diisocyanate (MDI) extended with 1,4-butanediol (BO). The chemical structure of the hard segment of TPU is shown in Figure 4.1. The soft segment is polyester polyol and 1,4-butanediol.

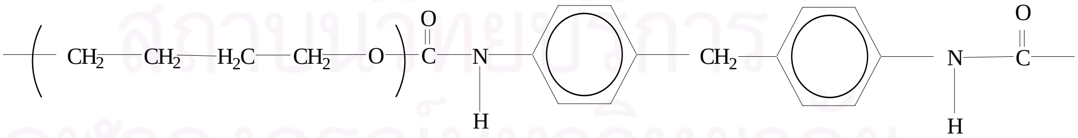


Figure 4.1. Chemical structure of hard segment of thermoplastic polyurethane

4.1.2 Polydimethylsiloxane (PDMS)

Polydimethylsiloxane (PDMS) used in this study was obtained from Dow Corning Co, Ltd. PDMS appears in a form of transparent fluid with a viscosity of 60,000 centistoke. The specific gravity of PDMS is 0.977. The chemical structure of polydimethylsiloxane is shown in Figure 4.2.

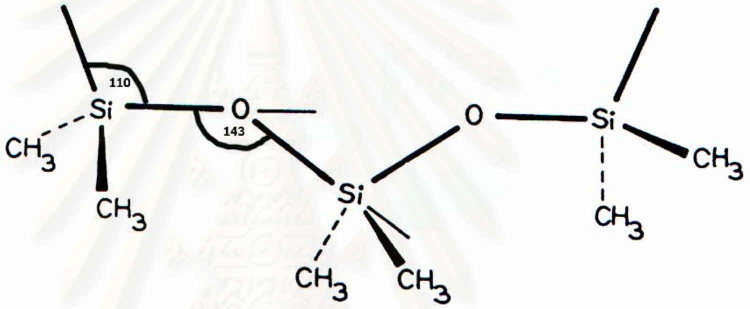


Figure 4.2 Chemical structure of polydimethylsiloxane [Hepburn, 1982].

4.2 Sample Preparation

Experimental procedures of TPU/PDMS blends are summarised according to Figure 4.3.

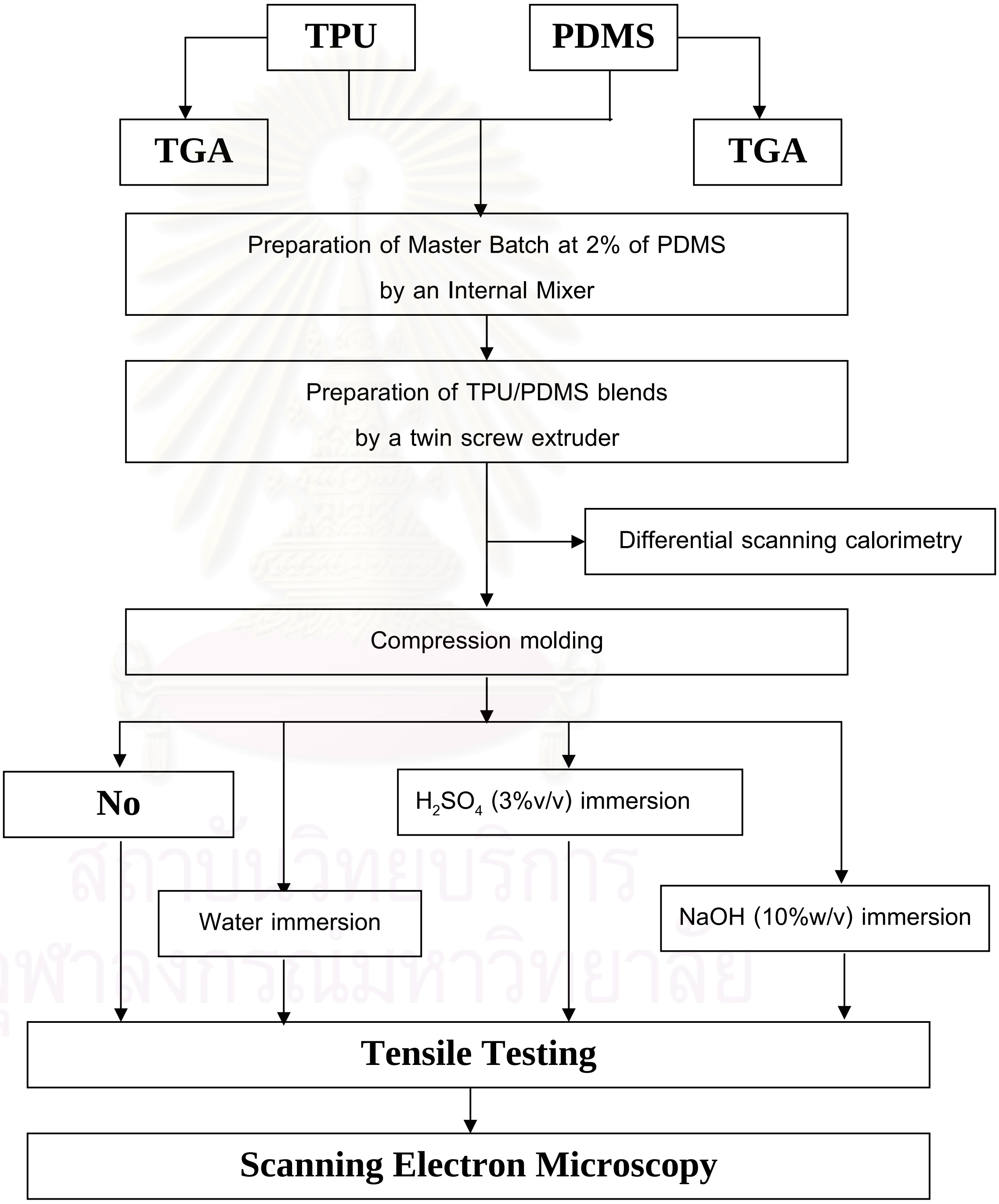


Figure 4.3. The schematic diagram of experimental work.

4.2.1 Master Batch

Master batch of TPU/PDMS blends at 2% by weight of PDMS was prepared using the internal mixer of Haake “Rheomix3000p“ fitted with roller rotors (at National Metal and Materials Technology Center, MTEC). The internal mixer used in this experiment is shown in Figure 4.4. TPU and PDMS were melt-blended in the internal mixer at 190°C for 10 min with the rotor speed of 30 rpm. After that the master batch of TPU/PDMS blends was compressed and cut into pieces.

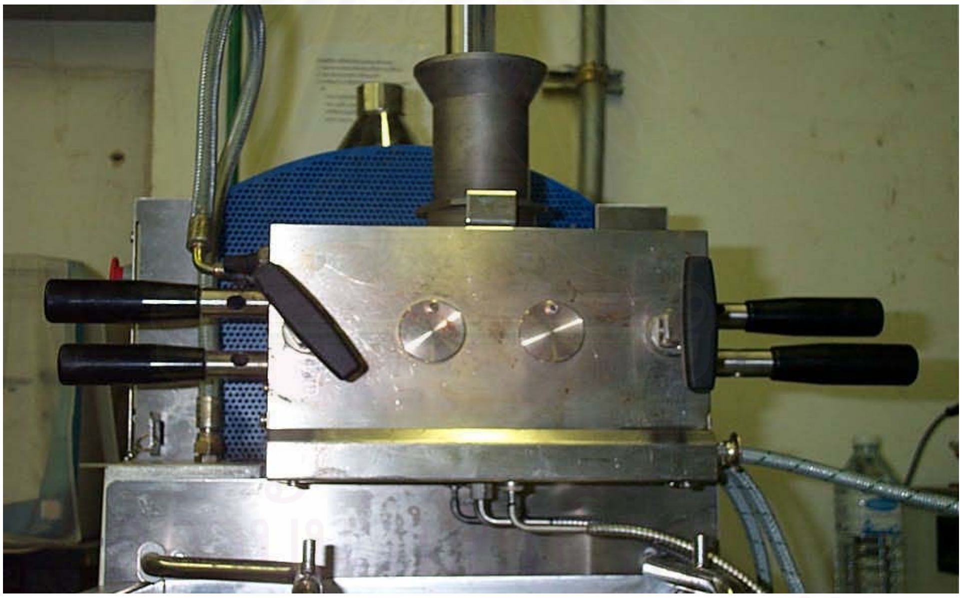


Figure 4.4. Photographic illustration of the internal mixer "Rheomix3000p".

4.2.1 Final blends of TPU/PDMS

The TPU/PDMS blends at various PDMS contents were prepared using the counter-rotating twin screw extruder of Haake (at Energy Management Technology Division, The School of Energy and Materials, King's Mongkut University of Technology). The master batch at 2% PDMS was used to blend with the virgin TPU to obtain the blends with the final PDMS concentration of 0.2%-1% in 0.2% increments. The temperature in the four zones of the extruder was operated in the range of 170°C-180°C and the extruder was run at 30 rpm. The temperature profiles of the counter-rotating twin screw extruder during the processing are shown in Figure 4.5. The extruded blends were cooled down in water and they were finally cut into pellet form. The virgin TPU sample was also treated in the same preparation procedure in order to use as the reference sample.

By blending master batch with virgin TPU in the twin screw extruder, the maximum concentration of PDMS in the TPU/PDMS blend is at 1% of PDMS since the excess amount of PDMS more than 1% resulted in the unmelt TPU pellet from the die of the extruder.

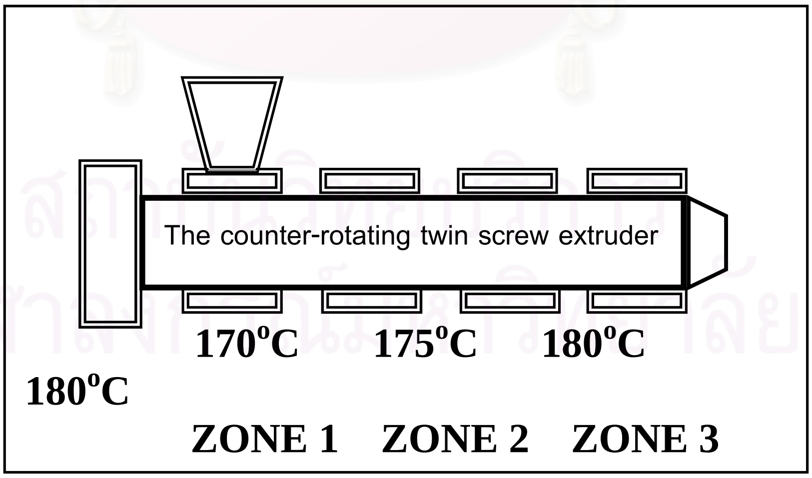


Figure 4.5 The temperature profiles of the counter-rotating twin screw extruder.

4.2.2 Compression Molding

Before compression, virgin and blended TPU were dried in an oven at 60°C for 2 hr. All extruded samples were prepared using compression molding on "Scientific" (at National Metal and Materials Technology Center, MTEC). The samples were compression molded at 200°C for 25 min, compressed at the pressure 100 kg/cm^3 for 2 min, and then cooled down in water at 25°C for 3 min. The size of the mold is 20 cm in width, 25 cm in length, and 1mm in depth. Finally, compressed sheet was cut into a standard size for tensile testing. Figure 4.6 shows photographic of cutter for tensile testing (at Rubber Research Institute).

Figure 4.6 Photographic illustration of cutter for Tensile Testing.

4.3 Measurement

4.3.1 The Measurement of Thermogravimetric analysis (TGA)

TGA was used to investigate the thermal stability of TPU and PDMS. TGA determination was performed by Shimadzu in TGA-50 model (at Petrochemical Engineering Laboratory, Department of Chemical Engineering, Chulalongkorn University) with a heating rate of 10°C/min and the temperature range from room temperature to 800°C. A sample weighed about 15 mg was used for TGA measurement. Results of decomposition temperatures are determined from the onset temperature. Thermograms are shown in the forms of thermogravimetry (TG) curve comparing to derivative thermogravimetry (DTG) curve.

4.3.2 The Measurement of Differential Scanning Calorimetry (DSC)

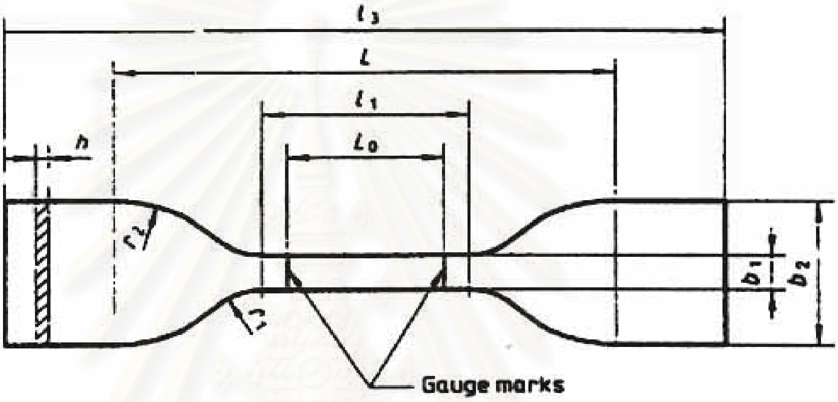
Differential scanning calorimetry (DSC) was used to investigate thermal transition of TPU, PDMS and 1% of TPU/PDMS blends. A differential scanning calorimetry study was performed by PERKIN-ELMER DSC7 (at the Department of Science, Mahidol University) with a heating rate of 10°C/min and a cooling rate of -10°C/min covered the temperature range from -150°C to 250°C. A sample weighed about 10 mg was used for each measurement. The second heating cycle was used to evaluate the glass transition temperature of the samples. Results of glass transition temperatures are determined from the mid point temperature.

4.3.3 Tensile Measurement

Tensile properties were measured using "Lloyd instrument model LR 5K" (at Rubber Research Institute) as shown in Figure 4.7. The test conditions follow ISO 527-1 of the British Standards Institution (BSI). For tensile testing, dumbbell shaped samples (type II) were used with the dimensions shown in Figure 4.8.

Figure 4.7. Photographic illustration of tensile testing in Lloyd model LR 5K.

The determination of tensile properties was performed at the constant crosshead speed of 500 mm/min with a 500 N load cell. The results from the tests include ultimate tensile strength, elongation at break, Young's modulus and energy to break. Reported data are the average value of 5 measurements. Raw measured data are provided in Appendix.



Dimensions	Type II, mm
b_1 - Width of parallel-sided portion	6
b_2 - Width at ends	25
h - Thickness	1 or under
L_0 - Gage length	25
L_1 - Length of narrow parallel-sided portion	33
L_2 - Initial distance between grips	80
L_3 - Overall length	115 or more
r_1 - Small radius	14
r_2 - Large radius	25

Figure 4.8 Dimension of tensile test specimen followed ISO 527-1 of BSI.

4.3.4 Resistance to Chemical Reagents

Chemical resistance of all samples was tested following ASTM D543-95. Chemical reagents used in this study were distilled water, Sulfuric acid (H_2SO_4, 3% v/v), Sulfuric acid (H_2SO_4, 30% v/v), and Sodium hydroxide (NaOH, 10% w/v). In the experiment, virgin TPU and blended TPU were immersed in chosen chemical reagents at 25 ^{o}C for 168 hr, after that, the virgin TPU and blended TPU were dried and taken for tensile testing as described in section 4.3.3.

4.3.5 Scanning Electron Microscopy (SEM)

Scanning Electron microscopy (SEM) was used to study the morphology of virgin TPU and blended TPU. SEM was carried out with a JEOL JSM-6400 (at Scientific and Technological Research Equipment Center, Chulalongkorn University). In scanning electron microscope, a fine beam of electron was first scanned across the surface of an opaque specimen. Once such an electron beam touches the surface, a difference of electron density in the specimen results a variety of scattering electron and photon emission. Those electrons are detected, modified and used to modulate the brightness of the second beam scanned synchronously in cathode ray tube (CRT). Before the analysis, the samples were coated with a thin film of gold to produce secondary electrons and to prevent charging.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Thermal Properties and Miscibility of TPU/PDMS blends

5.1.1 Thermalgravimetric analysis (TGA)

Thermalgravimetric analysis (TGA) is generally used to determine thermal decomposition temperature of polymers that is useful to characterize the thermal stability of material under a variety of conditions. The thermograms of thermoplastic polyurethane (TPU) and polydimethylsiloxane (PDMS) are shown in Figure 5.1 and 5.2, respectively. The TG curve of TPU indicates three ranges of decomposition temperature, determined from the onset points of a mass change as follows:

- First decomposition temperature at 290 °C,
- Second decomposition temperature at 390 °C and
- Final decomposition temperature at 460 °C.

Normally polyurethane decomposition is initiated in the hard segments (urethane group). The decomposition temperature of the urethane bond is in the range of 150°C to 250°C, depending on the polyurethane structure, i.e. the polyester polyurethanes based on MDI and butanediol start to decompose at about 300°C [Wirpsza, 1993]. The second stage of decomposition refers to the flexible segments and urethane groups linked to an aliphatic group. In the third stage, ester groups in the flexible segments undergo decomposition. The highest decomposition temperature of a polyesterurethane based on MDI and polyesterdiol is reported at 400°C [Wirpsza, 1993].

The TG curve of PDMS, in Figure 5.2, shows the onset of decomposition temperature at 340°C. Comparing to the TG curve of TPU, the maximum temperature that can be used to melt mixing of TPU and PDMS should not exceed 290°C which is the initial temperature of TPU decomposition.

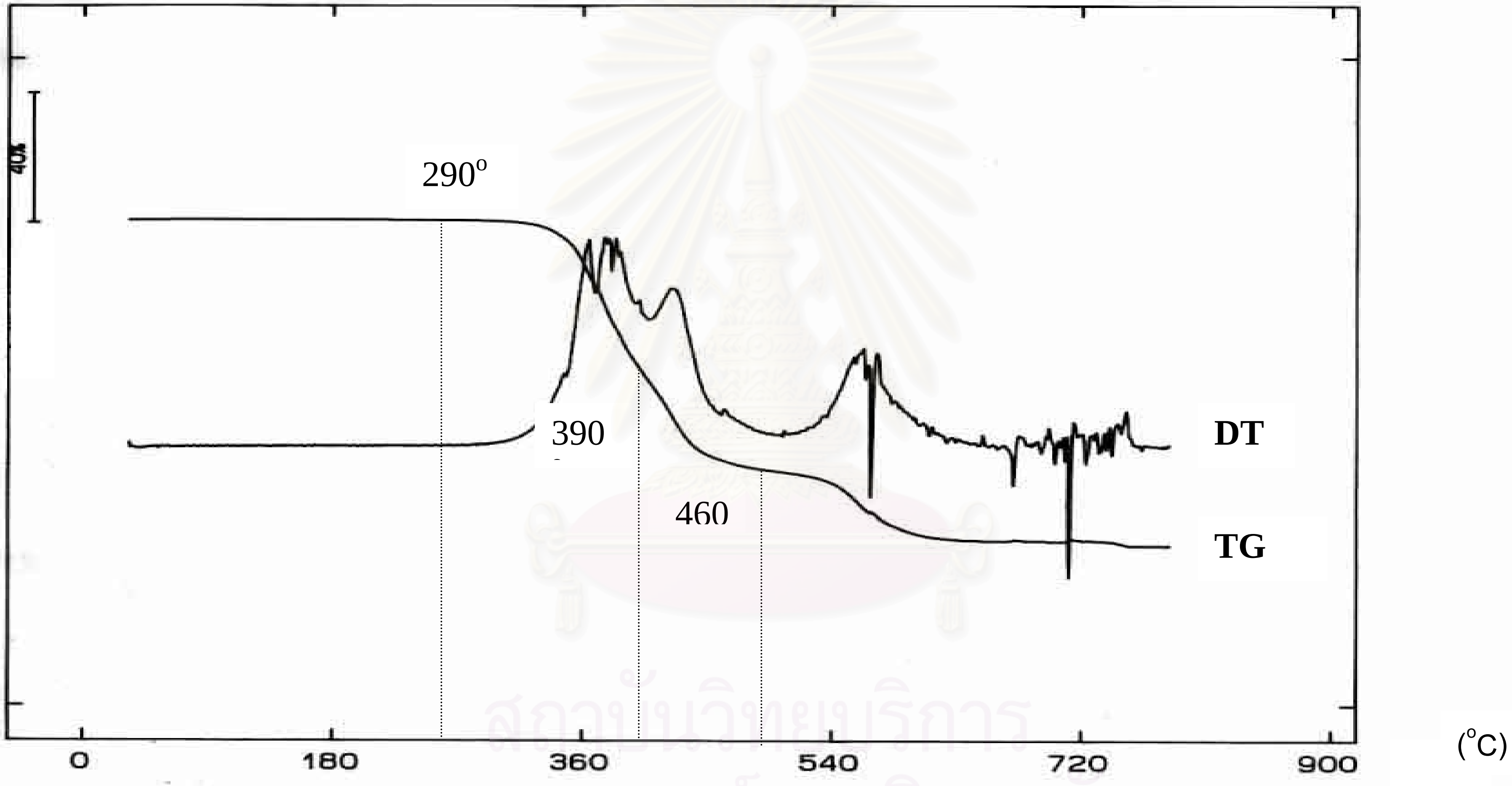


Figure 5.1 TG curve and the corresponding DTG curve of thermoplastic polyurethane.

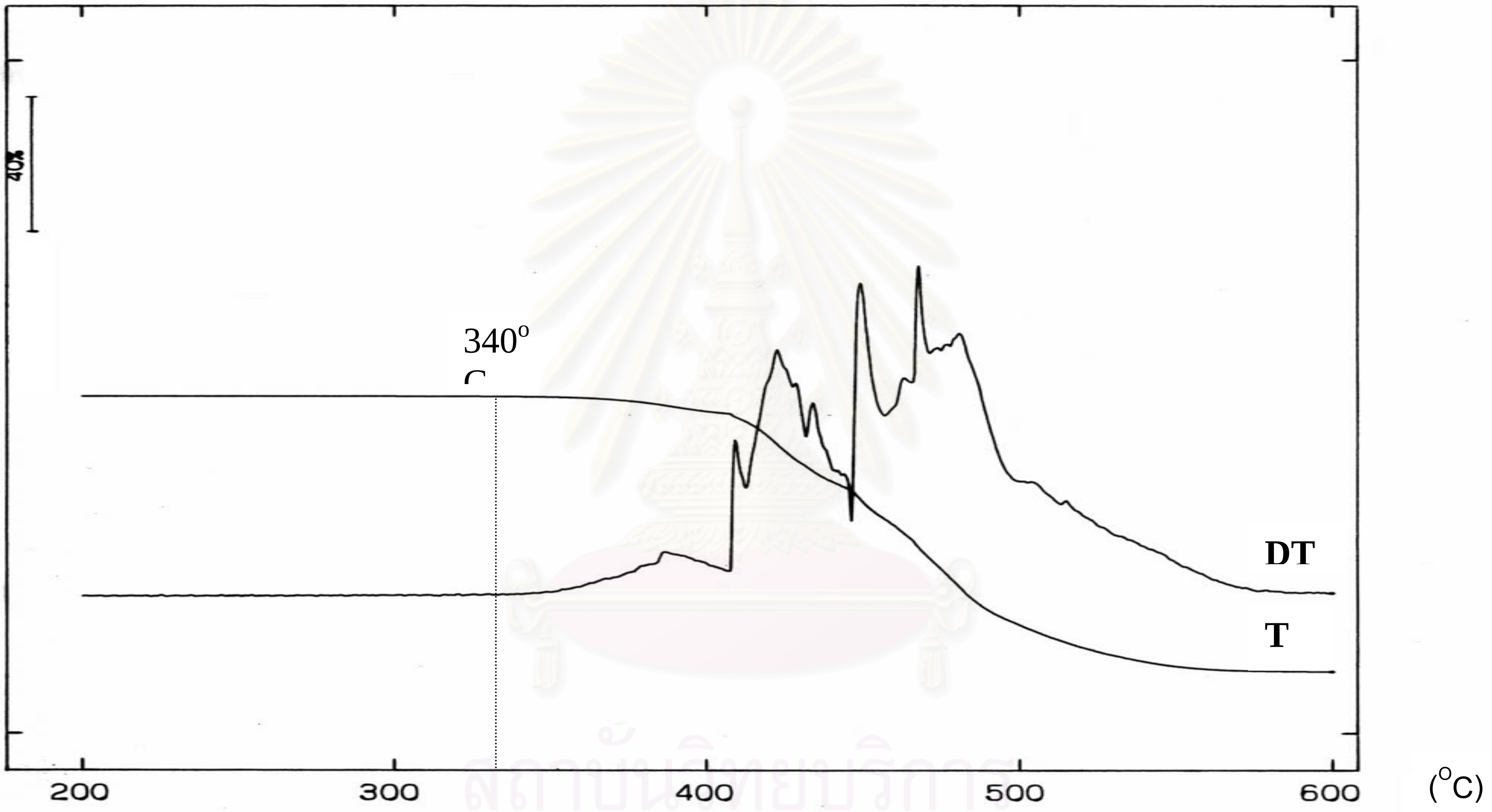


Figure 5.2 TG curve and the corresponding DTG curve of Polydimethylsiloxane

5.1.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was used to study the miscibility of thermoplastic polyurethane and polydimethylsiloxane blends in addition to determine glass transition temperature (T_g) of TPU and PDMS. DSC thermograms of TPU and PDMS from the second heating cycle are shown in Figure 5.3 and Figure 5.4, respectively. The glass transition temperatures of TPU and PDMS are -23.4°C and -126.6°C, respectively.

It is noted from Figure 5.4 that there is an exothermic peak at -87°C and a double endothermic peak at -39°C. The exothermic peak corresponds to the crystallization of PDMS while the endothermic peak normally represents the melting temperature. However, in this case, the exhibition of the double endothermic melting peak may occur from differences in crystallite size distribution, melting-recrystallization of the original crystallites and their subsequent melting or different crystalline forms of the polymer [Stephen, 1993].

The miscibility of polymer blends can be estimated by shifts of the glass transition temperature of the blend from those of the pure components. DSC thermograms of TPU/PDMS blends at 1% of PDMS is shown in figure 5.5. The glass transition temperature of the blend is determined at -24.1°C which is very closed to that of the virgin TPU. This is because TPU is the major component in the blend (99%). On the other hand, PDMS composition in the blend is very low so that the glass transition of PDMS rich phase in the blend can not be detected by DSC technique. It is therefore impossible to determine the miscibility of TPU/PDMS blends using DSC.

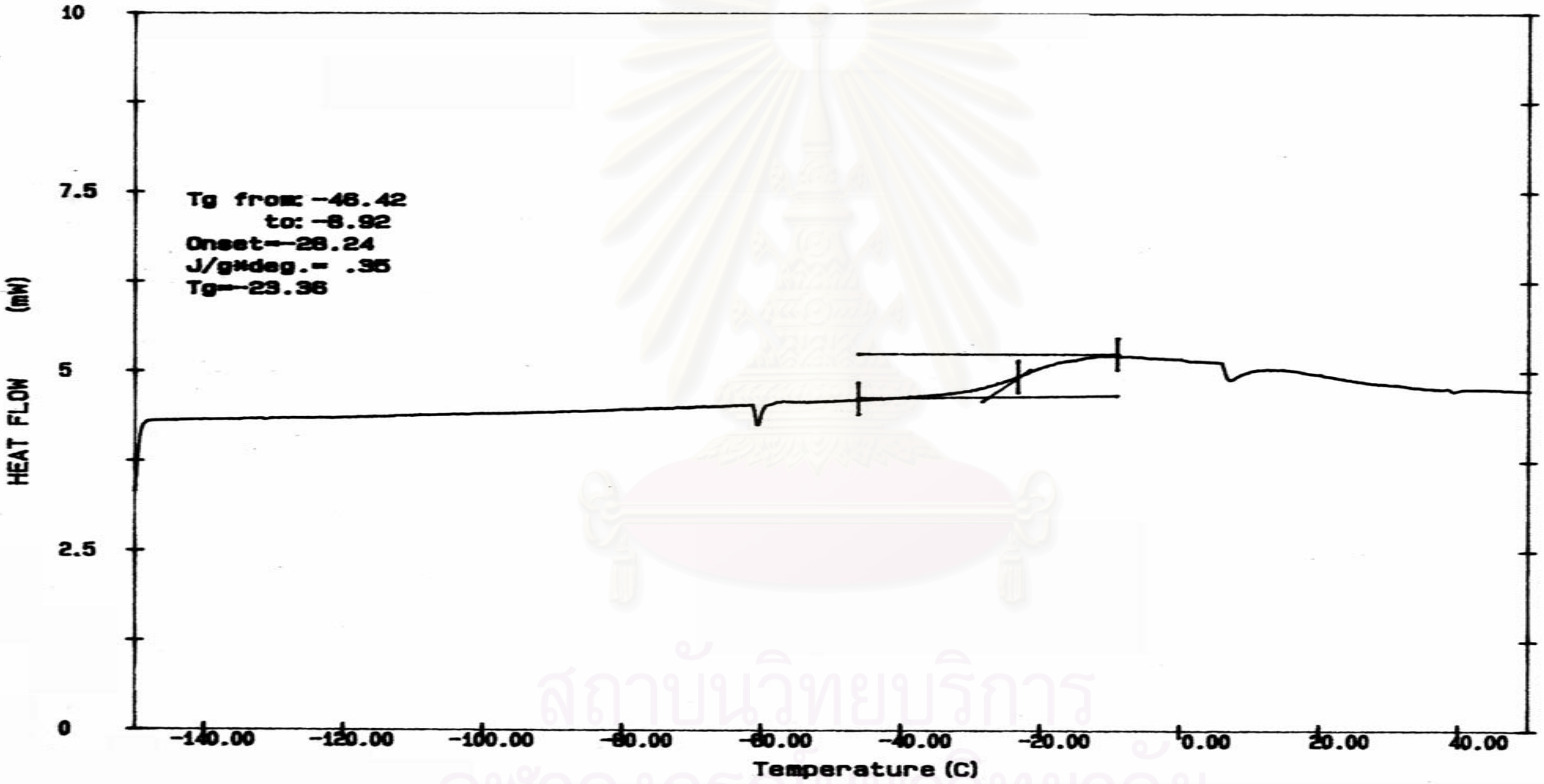


Figure 5.3. DSC themogram of thermoplastic polyurethane.

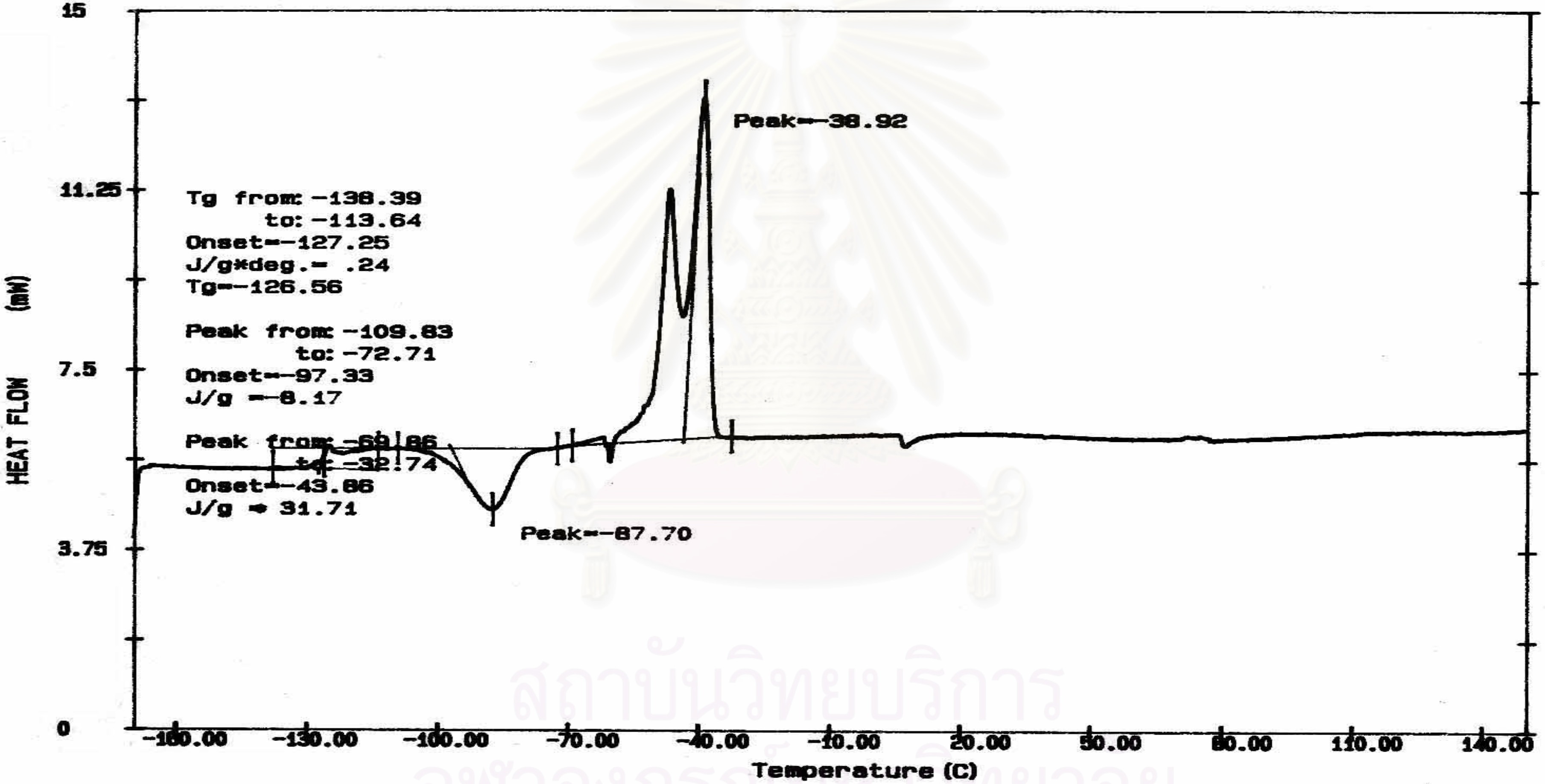


Figure 5.4. DSC themogram of polydimethylsiloxane.

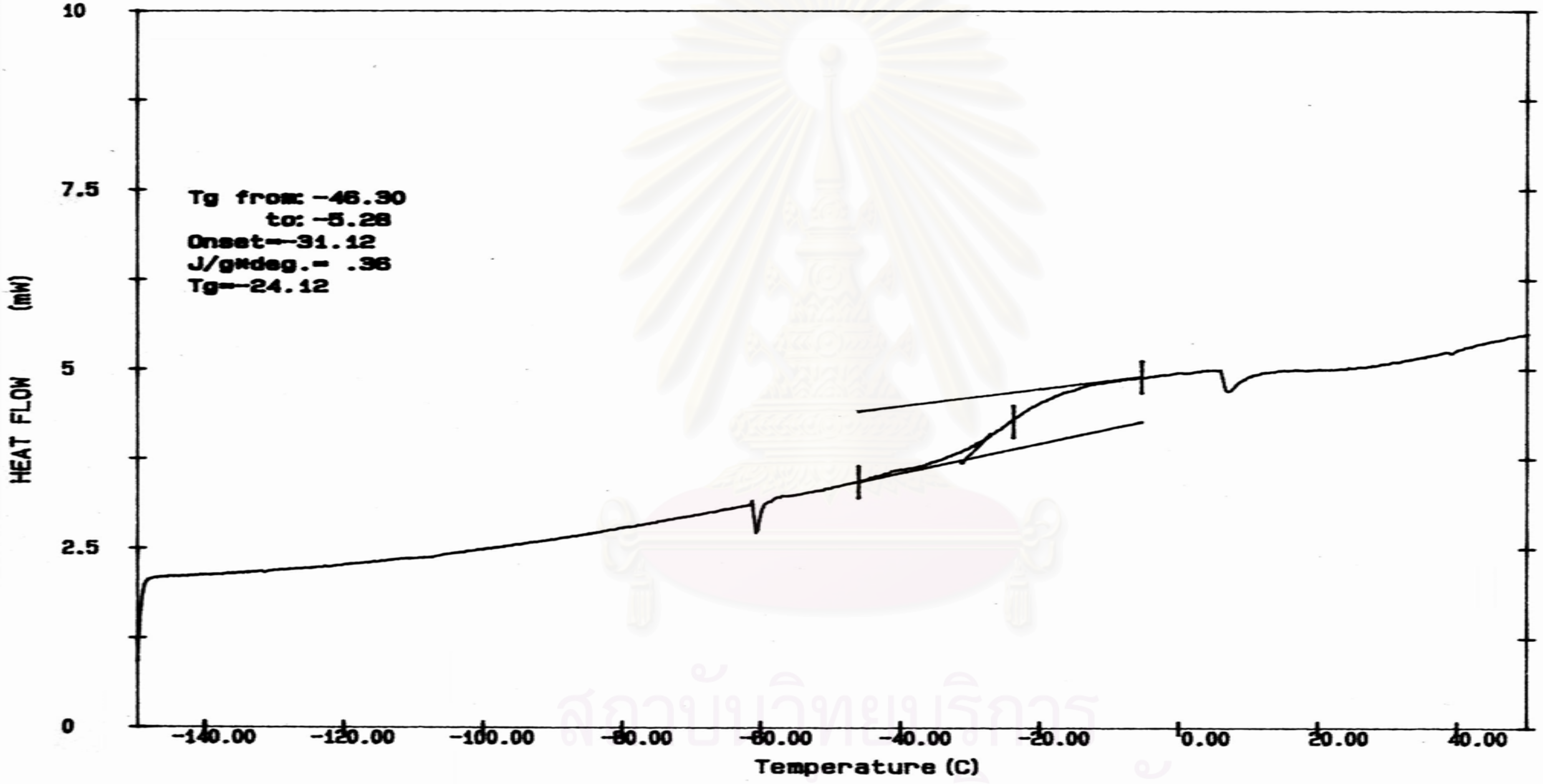


Figure 5.5. DSC themogram of TPU/PDMS blends at 1% of PDMS.

5.2. Physical Appearance of TPU/PDMS blends

5.2.1 TPU/PDMS blends

The color of virgin TPU is transparent and the surface of virgin TPU is smooth with high elasticity. While blending TPU with PDMS, the color of blended TPU becomes cloudy and it gets more cloudy when the amount of PDMS in the blends is increased. Surface appearance of blended TPU is still smooth with high elasticity.

5.2.2 TPU/PDMS blends after immersion in water

Weight change of sample after immersion in chemical reagents is shown in Table 5.1. The weight of all samples after immersion in water, comparing to those before water immersion, tends to slightly increase about 0.3%-0.6%. The surface appearance of samples at all compositions after immersion in water was the same as the samples before immersion but the color of virgin TPU and blended TPU after immersion in water is pale yellow. While the color of samples before immersion is transparent for virgin TPU and cloudy for blended TPU. This may imply that water immersion has no significant effect on the color and appearance of virgin TPU and blended TPU.

Table 5.1 Comparison of weight changes of virgin TPU and blends TPU after immersion in chemical reagents.

% PDMS	% weight change			
	Water	H_2SO_4 (3%)	NaOH (10%)	H_2SO_4 (30%)
0	+0.3	+0.3	-15.5	-1.2
0.2	+0.4	+0.3	-9.5	-1.3
0.4	+0.4	+0.4	-13.9	-0.4
0.6	+0.4	+0.3	-13	-0.9
0.8	+0.6	+0.5	-14.3	-0.8
1.0	+0.3	+0.4	-13	-0.9

Notes : + means increasing weight compared to that before immersion
- means decreasing weight compared to that before immersion

5.2.3. TPU/PDMS blends after immersion in H_2SO_4 (3% v/v) and H_2SO_4 (30% v/v)

In Table 5.1, the weight of all samples after immersion in H_2SO_4 (3%), comparing to those before immersion is the same as that found in the case of after water immersion. The surface appearance of samples at all compositions after immersion in H_2SO_4 (3%) was the same as the samples before immersion but the color of virgin TPU and blended TPU after immersion in H_2SO_4 (3%) is darker yellow than those after water immersion. This may imply that immersion in H_2SO_4 (3%) has no significant effect on the physical appearance of virgin TPU and blended TPU.

In our experiment, the strong acid at higher concentration (H_2SO_4 (30%)) was also used in the test of chemical resistance of virgin TPU and blended TPU. The weight of samples at all compositions after immersion in H_2SO_4 (30%), comparing to those before immersion is decreased by about 1%. Cracking appears on the surface of all samples after immersion in H_2SO_4 (30%), especially on virgin TPU. Color of virgin TPU after strong acid immersion (30%) is darkish yellow and transparent while blended TPU after strong acid immersion (30%) is darkish yellow and cloudy. This implies that immersion in H_2SO_4 at high concentration (30%) has more effect to the color and physical appearance of virgin TPU and blended TPU. In addition, adding PDMS in the virgin TPU can help reducing the crack occurred on the samples after immersion in H_2SO_4 (30%).

5.2.4 TPU/PDMS blends after immersion in NaOH (10% w/v)

In Table 5.1, the weight of samples at all compositions after immersion in NaOH is remarkably decreased about 10-15% comparing to those before immersion. The weight of virgin TPU is most decreased by 15.5% while blended TPU are decreased about 9%-14%. Decreasing weight of virgin TPU and blended TPU after immersion in NaOH may occur from corrosion of NaOH on the surface of samples. Also the surface appearance of samples after immersion in NaOH is rough, similar to network and there are some powders appeared on the surface of all samples. Additionally, the color of NaOH solution after immersion is different from the solution of NaOH before immersion, i.e. solution of NaOH after immersion has some powders suspended while NaOH solution before immersion is similarly transparent to water. The color of samples at all compositions after immersion in NaOH is yellowish and cloudy. This indicates that base immersion has a strong effect on the color and physical appearance of virgin TPU and blended TPU. The addition of PDMS in the TPU blends can reduce the corrosion effect on the physical appearance.

5.3 Tensile Properties

5.3.1 TPU/PDMS blends

The relationship between PDMS content and the tensile properties of the blend of TPU and PDMS is shown in Table 5.2.

Table 5.2 Tensile properties of the blends of TPU and PDMS.

%PDMS	Ultimate tensile Strength (MPa)	% Elongation at break (%)	Young's Modulus(MPa)	Energy to break (N-mm)
0	62.9	485.7	3.4	5798
0.2	50.9	568.9	3.2	5842
0.4	55.7	609.2	4.1	5756
0.6	57.3	622.3	4.7	5141
0.8	51.3	635.4	4.1	5167
1	61.0	581.2	4.2	5126

Ultimate tensile strength of pure and blended TPU at various PDMS contents is shown in Figure 5.6. It can be seen that the value of ultimate tensile strength is decreased when TPU is blended with PDMS at all PDMS contents except at 1% of PDMS. The ultimate tensile strength of the blends with PDMS content at 0.2%, 0.4%, 0.6%, and 0.8% is lower than that of virgin TPU about 19%, 11%, 9%, and 19%, respectively. On the other words, PDMS content at 0.2% has an effect on decreasing the ultimate tensile strength of the virgin TPU but higher PDMS content (from 0.2% to 0.8%) tends to have no more effect on the ultimate tensile strength of the blends, comparing to the TPU blend with 0.2% of PDMS. At PDMS content of 1%, the ultimate tensile strength of blended TPU is rather closed to that of virgin TPU.

Percentage of elongation at break of virgin TPU and blended TPU at various PDMS contents is shown in Figure 5.7. It is noticed that the elongation at break of blended TPU with 0.2% of PDMS is improved from that of pure TPU by 17%. Increasing PDMS content from 0.2% to 0.8% tends to gradually increase the elongation at break, up to about 30% higher than the virgin TPU when 0.8% of PDMS is added. From our results, at PDMS content of 1%, the trend of elongation at break of the blends is similar to that found in the ultimate tensile strength but in an opposite direction, i.e. the value of the elongation at break of the blend with 1% of PDMS is decreased from that of 0.8% of PDMS and seems to be closed to that of virgin TPU.

The Young's modulus of TPU/PDMS blends at various compositions is shown in Figure 5.8. The results on Young's modulus of blended TPU are increased when increasing PDMS content up to 0.6%. Young's modulus of blends with various PDMS contents is higher than virgin TPU about 20% to 40%.

Energy to break of virgin TPU and blended TPU at various PDMS contents is shown in Figure 5.9. It can be seen that energy to break of blended TPU at 0.2% and 0.4% of PDMS are similar to that of virgin TPU. Increasing PDMS content from 0.6% to 1.0% tends to decrease the energy to break. In addition, the stress-strain curve of virgin TPU and blended TPU at various PDMS contents, shown in Figure 5.10, illustrates that virgin TPU and all blended TPU exhibit soft and tough characteristics. Adding PDMS from 0.2% to 0.6% increases the toughness of the samples but further increasing PDMS content seems to has an effect on the opposite direction, i.e. the toughness of the blends is decreased closing to the virgin TPU.

The results on tensile test can be concluded that the ultimate tensile strength of the blended TPU is decreased with increasing PDMS in the range of 0.2% to 0.8% while the elongation at break of blended TPU is gradually increased with increasing PDMS content at the same range. Exception occurs at blended TPU with 1% of PDMS. The ultimate tensile strength is turned to increase closing back to that of virgin TPU while the elongation at break is turned to decrease closing to that of virgin TPU too. Young's modulus of the blended TPU is also increased with increasing PDMS content up to about 0.6% of PDMS while it is turned to decrease at PDMS content higher than 0.6%. Energy to break of virgin TPU and blended TPU with 0.2% to 0.4% of PDMS is consistent but those with 0.6% to 1.0% of PDMS tend to decrease. This could imply that there is an optimum PDMS contents at around 0.6% to 0.8% that has an effect on the tensile properties of TPU/PDMS blends. Higher PDMS content tends to reduce the effect on the tensile properties.

Our study can be compared to the work of Hill, *et al* (1996), who have studied the development of wear-resistant thermoplastic polyurethanes by blending with PDMS. They found that the resultant blended polyurethanes showed improvement in ultimate tensile strength up to 10% to 40%, elongation up to 20% to 50% and Young's modulus up to 10% from virgin TPU when blended with 1.5% to 2.0% of PDMS. This concentration showed optimum properties and the properties diminish rapidly at PDMS concentration above the optimal level since phase separation of PDMS became significant. Their system and results are summarised and compared to our work in Table 5.3. Difference on the result of the ultimate tensile strength is marked while the results on elongation at break and Young's modulus are in agreement. Optimum PDMS concentration in the blend of their work was noted at 1.5%-2% of PDMS that is higher than our optimum PDMS concentration. The differences could be caused from discrepancy in the structure and the characteristics of polymer components and also the mixing method of the blends.

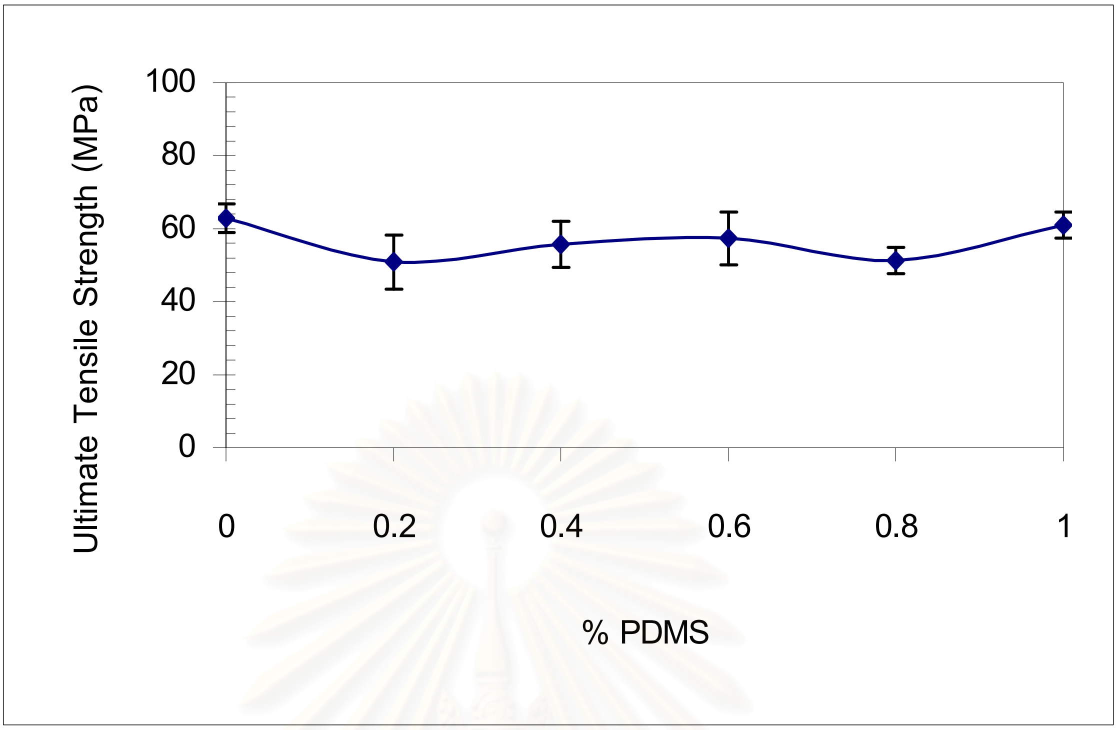


Figure 5.6 Ultimate tensile strength of virgin TPU and blended TPU at various PDMS contents.

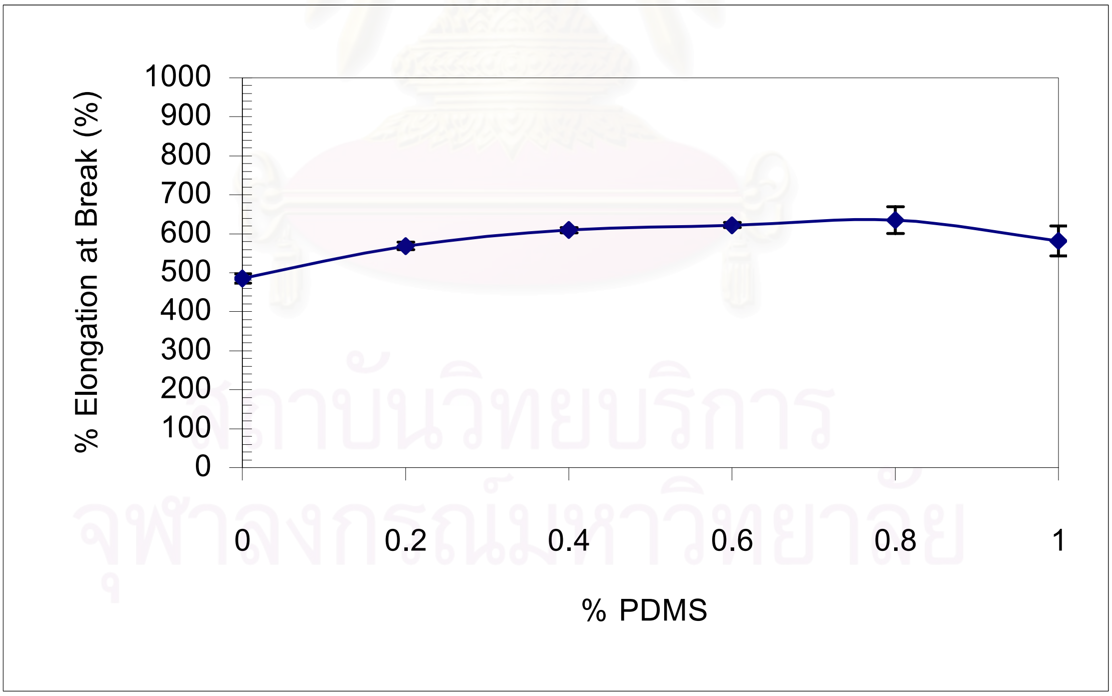


Figure 5.7 The Elongation at break of virgin TPU and blended TPU at various PDMS contents.

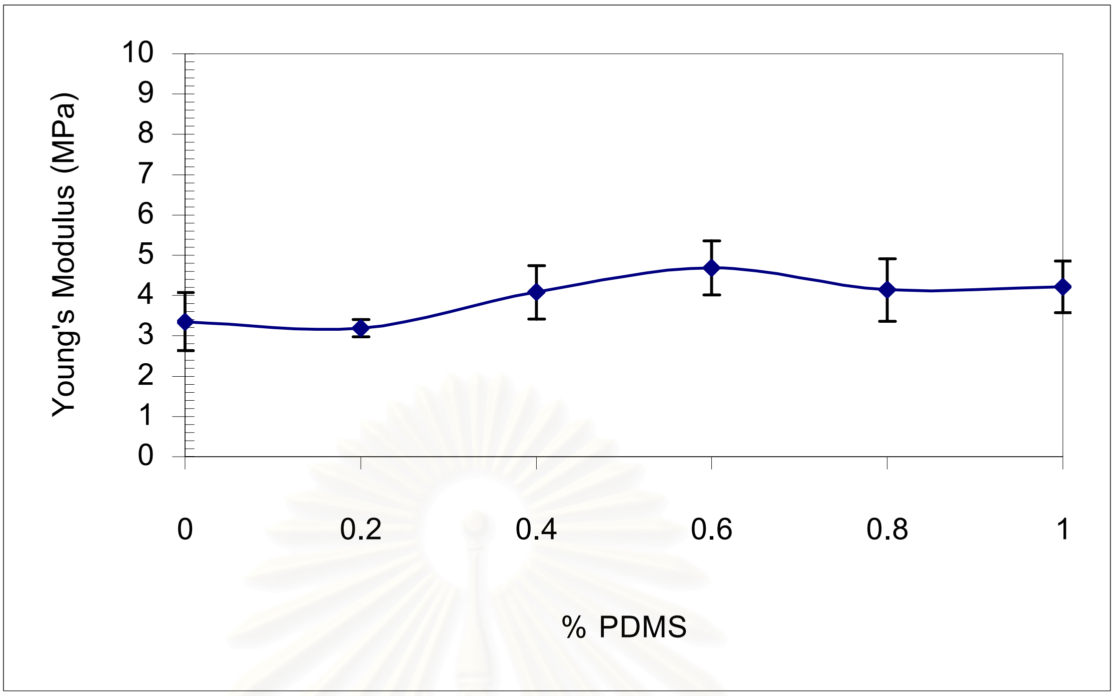


Figure 5.8 Young's modulus of virgin TPU and blended TPU at various PDMS contents.

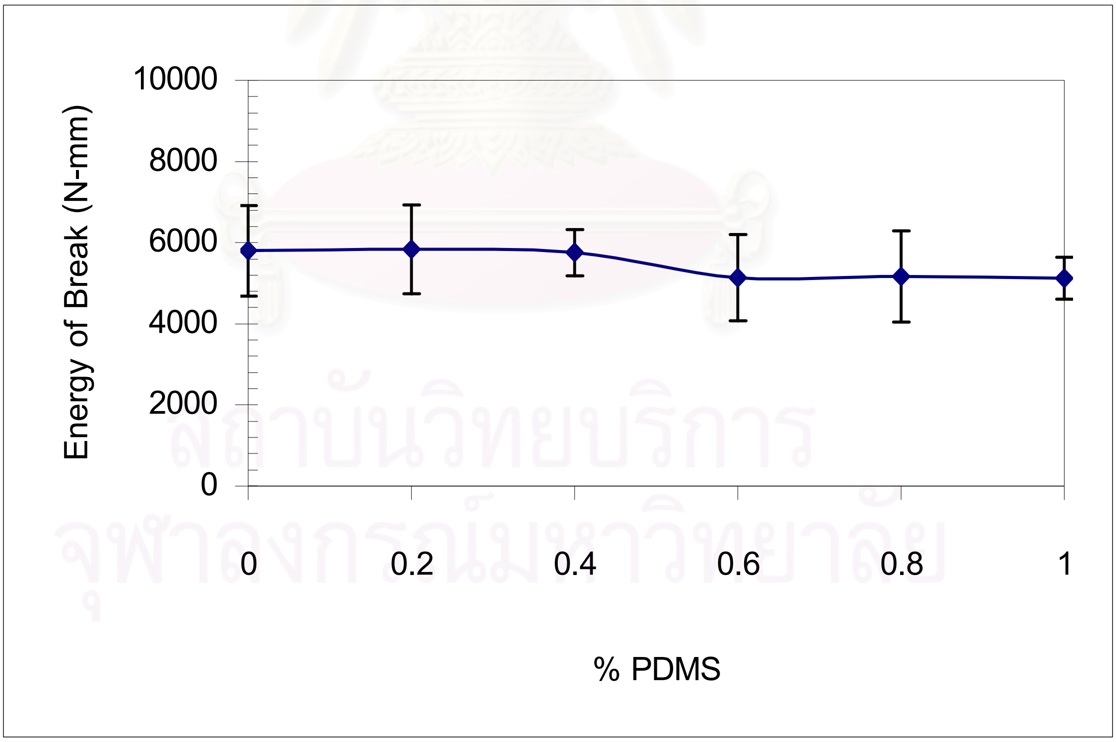


Figure 5.9 Energy to break of virgin TPU and blended TPU at various PDMS contents.

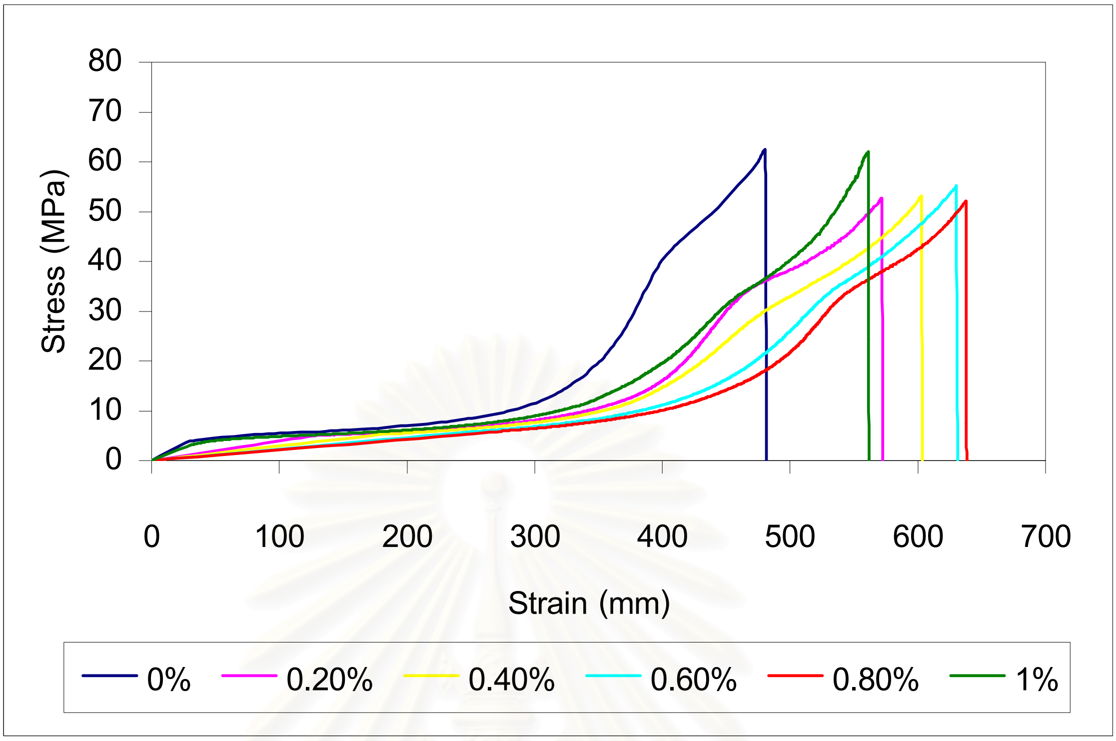


Figure 5.10 Stress-strain curves of virgin TPU comparing to blended TPU at various PDMS contents.

Table 5.3 Comparison of this work with the work of Hill, D. J. T., *et al.* (1996)

	Hill, D. J. T., *et al.* (1996)	This work
Materials		
TPU		
Soft segment	PTMO	Polyol , MDI
Hard segment	MDI, 1,4 – butanediol	1,4 – butanediol, MDI
Molecular weight		250,000 kg/mol
PDMS		
Viscosity (η)	10^5 centistoke	$6*10^4$ centistoke
Molecular weight	134 kg/mol	
Method of Mixing	Twin screw extruder	Internal mixer
	Temperature 160 – 220°C	Temperature 190°C
	Speed 30 rpm	Resident time 10 min
		Speed 30 rpm
		Twin screw extruder
		Temperature 170 – 180°C
		Speed 30 rpm
PDMS concentration	0% - 4% by weight (0.5% increments)	0% - 1% by weight (0.2% increments)
Results		
Ultimate tensile strength	Up 10% - 40% (at 1.5% - 2% PDMS)	Down 10% - 20% (at 0.2% - 0.8% PDMS)
Elongation at break	Up 20% - 50% (at 1.5% - 2% PDMS)	Up 30% (at 0.2% - 0.8% PDMS)
Young's modulus	Up 10% (at 1.5% - 2% PDMS)	Up 20% - 40% (at 0.4% - 0.6% PDMS)
Energy to break		Down 10% (at 0.6% - 1% PDMS)

5.3.2 TPU/PDMS blends after immersion in water

The results on the ultimate tensile strength, elongation at break, Young's Modulus and energy to break of blended TPU at various PDMS contents after water immersion are shown in Table 5.4, 5.5, 5.6, and 5.7, respectively, comparing to the results before water immersion.

Table 5.4 Comparison of ultimate tensile strength of TPU/PDMS blends before and after water immersion.

% PDMS	Ultimate tensile strength (MPa)	
	Before water immersion	After water immersion
0	62.9	56.3
0.2	50.9	60.2
0.4	55.7	59.4
0.6	57.3	55.7
0.8	51.3	62.4
1.0	61.0	54.4

Comparison of the ultimate tensile strength of virgin TPU and blended TPU before and after immersion in water is shown in Figure 5.11. The trend of the ultimate tensile strength of virgin TPU and blended TPU after immersion in water, comparing to those before water immersion, is not significantly obvious. The value of the ultimate tensile strength within the range of error bar of each sample after water immersion is more or less similar to those before water immersion. This indicates that water immersion has no effects on the ultimate tensile strength of the virgin TPU and blended TPU.

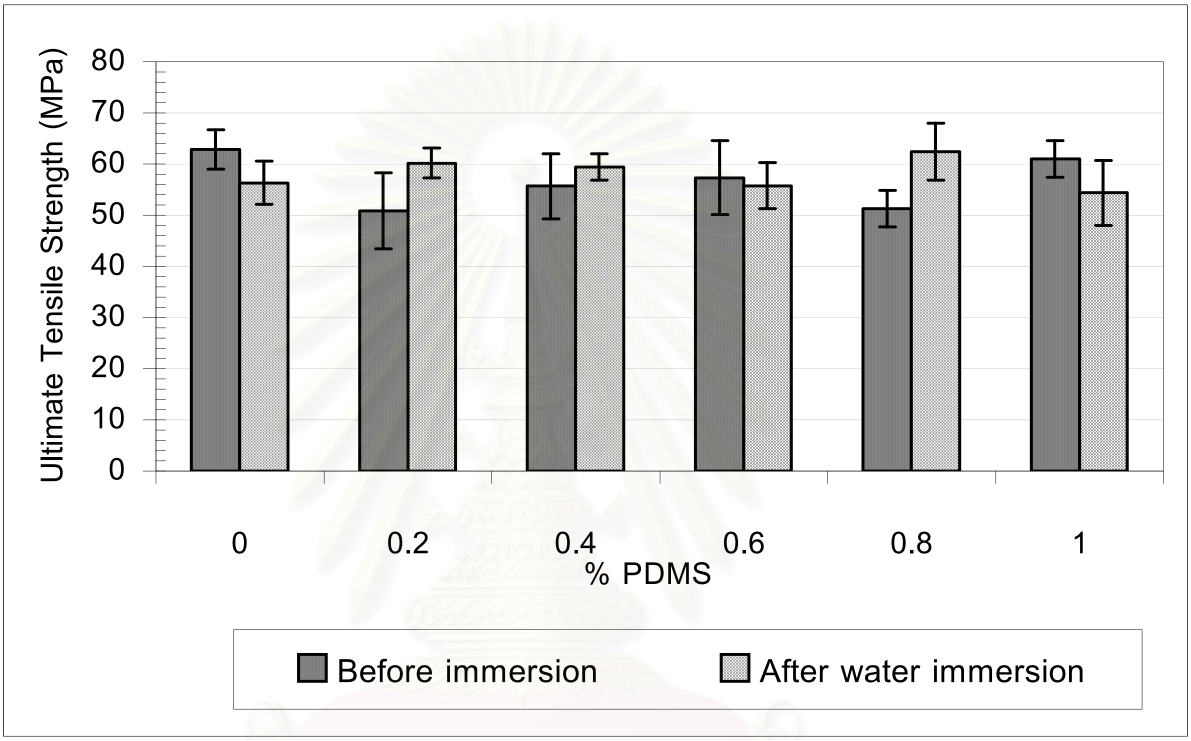


Figure 5.11 Comparison on the ultimate tensile strength of virgin TPU and blended TPU at various PDMS contents before and after water immersion.

The elongation at break of virgin TPU and blended TPU at various PDMS contents before and after water immersion is shown in Table 5.5.

Table 5.5 Comparison of elongation at break of TPU/PDMS blends before and after water immersion.

% PDMS	% Elongation at break	
	Before water immersion	After water immersion
0	485.7	476.3
0.2	568.9	490.3
0.4	609.2	505.4
0.6	622.3	510.8
0.8	635.4	480.4
1.0	581.2	514.0

Comparison of the elongation at break of virgin TPU and blended TPU at various compositions of PDMS before and after water immersion is shown in Figure 5.12. After water immersion, elongation at break of all blended TPU is consistent with that of virgin TPU. The elongation at break of virgin TPU after water immersion is similar to that of virgin TPU before water immersion while these of all blended TPU after water immersion are decreased when they are compared with those before water immersion. The result of virgin TPU indicates that water does not influence on the elongation of virgin TPU but it has an influence on the elongation property of blended TPU by lowering the elongation at break of each blend before immersion.

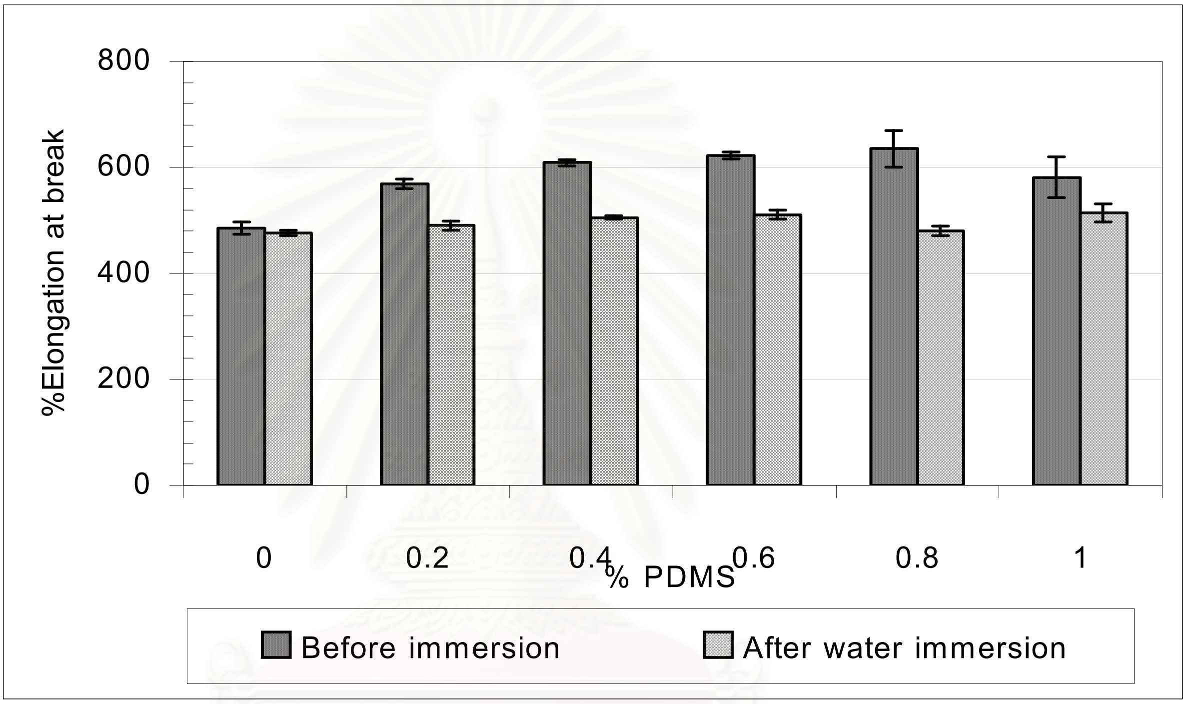


Figure 5.12 Comparison on %elongation at break of virgin TPU and blended TPU at various PDMS contents before and after water immersion.

The results on Young’s modulus of virgin TPU and blended TPU at various compositions of PDMS after water immersion are shown in Table 5.6 and Figure 5.13, comparing to the results before water immersion.

Table 5.6 Comparison of Young’s modulus of TPU/PDMS blends before and after water Immersion.

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% PDMS	Young’s modulus (MPa)	
	Before water immersion	After water immersion
0	3.4	3.3
0.2	3.2	3.2
0.4	4.1	4.1
0.6	4.7	4.1
0.8	4.1	4.3
1.0	4.2	3.6

The trend of the Young’s modulus of virgin TPU and blended TPU after water immersion, comparing to those before water immersion, is not significantly obvious. The value of the Young’s modulus within the range of error bar of each sample after water immersion is more or less similar to those before water immersion. This could imply that water immersion has no effect on the Young’s modulus.

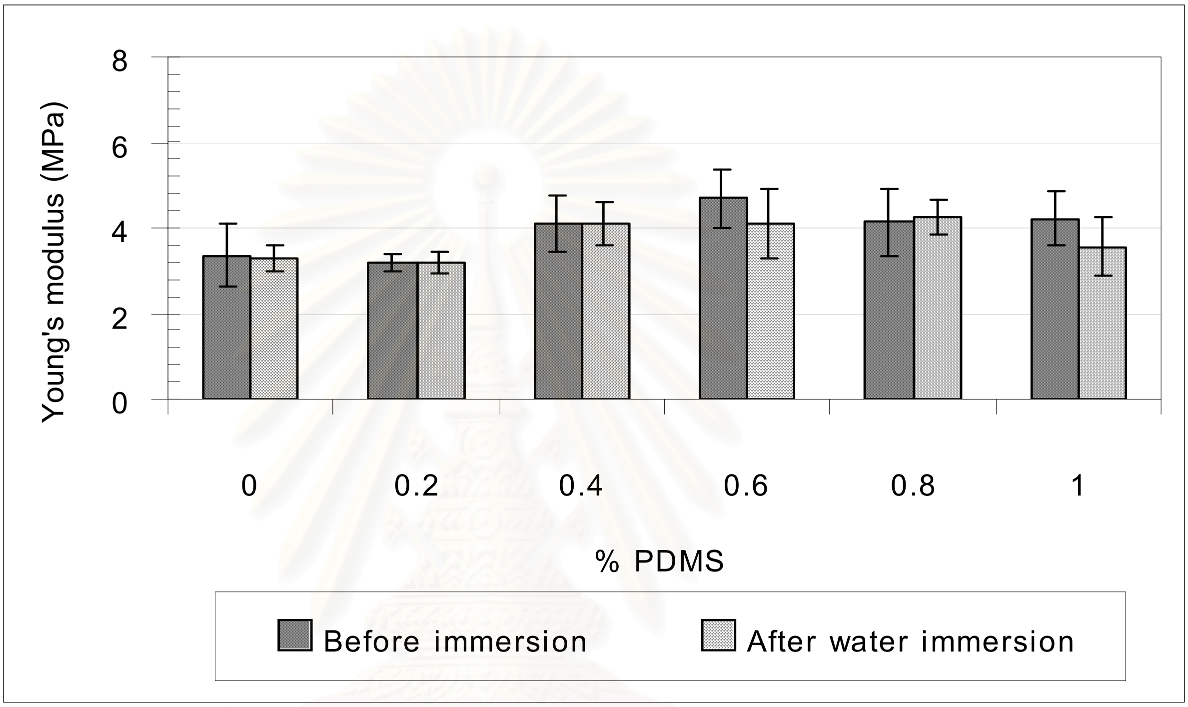


Figure 5.13 Comparison on Young's modulus of virgin TPU and blended TPU at various PDMS contents before and after water immersion.

Energy to break of virgin TPU and blended TPU at various PDMS content before and after water immersion are shown in Table 5.7.

Table 5.7 Comparison of energy to break of TPU/PDMS blends before and after water immersion

% PDMS	Energy to break (N-mm)	
	Before water immersion	After water immersion
0	5798	6059
0.2	5842	6720
0.4	5756	5317
0.6	5141	5522
0.8	5167	5191
1.0	5126	5692

The stress-strain curves of virgin TPU and blended TPU at 0.8% of PDMS before and after water immersion are shown in Figure 5.14. It can be seen the trend of energy to break of virgin TPU and blended TPU after water immersion seems to be slightly more than those before water immersion. This could imply that water immersion has a very slight effect on the energy to break of all samples.

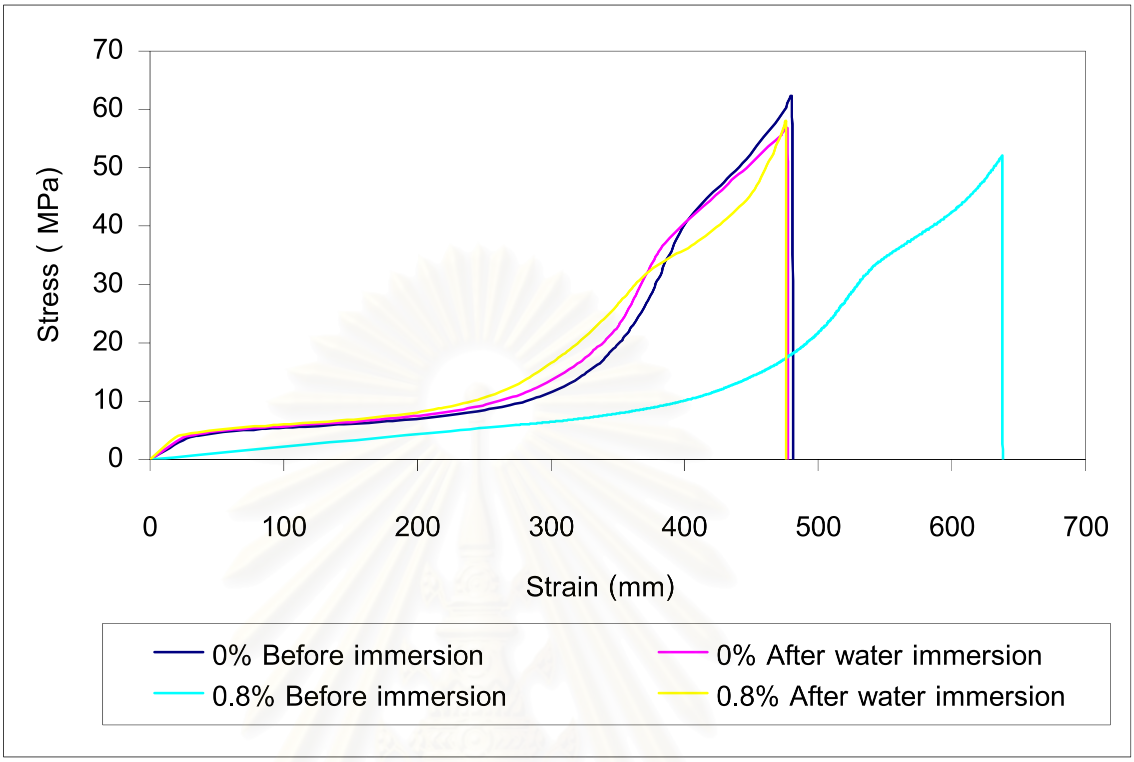


Figure 5.14 Stress-strain curves of virgin TPU and blended TPU at 0.8% of PDMS before and after water immersion.

5.3.3 TPU/PDMS blends after immersion in H_2SO_4 (3% v/v)

The results on the ultimate tensile strength, the elongation at break, Young's Modulus and energy to break of blended TPU at various PDMS contents after acid immersion (3% H_2SO_4) are shown in Table 5.8, 5.9, 5.10, and 5.11, respectively, comparing to the results before acid immersion.

Table 5.8 Ultimate tensile strength of TPU/PDMS blends before and after immersion in H_2SO_4.

%PDMS	Ultimate tensile strength (MPa)	
	Before immersion	After immersion in H_2SO_4
0	62.9	58
0.2	50.9	56.4
0.4	55.7	60.2
0.6	57.3	61.3
0.8	51.3	60.7
1.0	61	60.5

Comparison of the ultimate tensile strength of virgin TPU and blended TPU before and after immersion in acid is shown in Figure 5.15. It can be seen that after acid immersion the value of the ultimate tensile strength within the range of error bar of blended TPU at all PDMS contents is more and less similar to that of virgin TPU. After acid immersion, the PDMS content tends to have no effect on the ultimate tensile strength comparing to that of the virgin TPU.

Comparing the ultimate tensile strength after acid immersion to those before acid immersion, the ultimate tensile strength of virgin TPU after acid immersion seems to be slightly lower than that before acid immersion. This is as generally known that the acid resistance of TPU is not good. For all blended TPU except at 1% of PDMS, the ultimate tensile strength after acid immersion tends to be higher that those before acid immersion. This could imply that PDMS content in blended TPU can improve the ultimate tensile strength after acid immersion comparing to that before acid immersion.

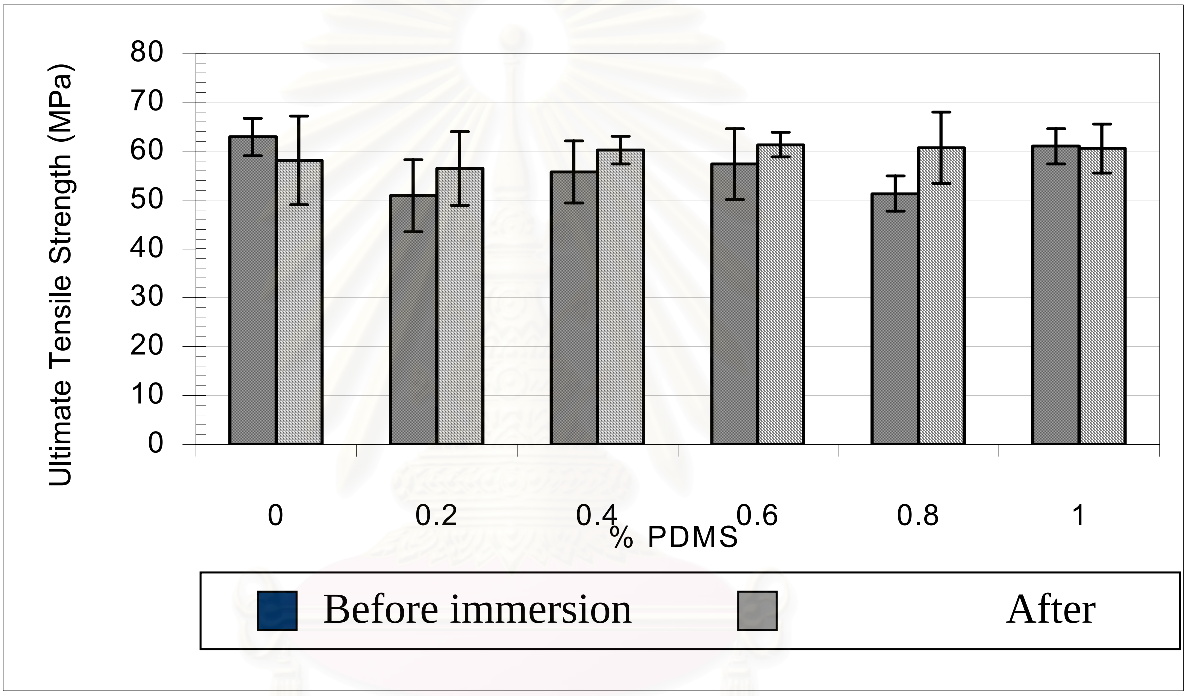


Figure 5.15 Comparison on the ultimate tensile strength of virgin TPU and blended TPU at various PDMS contents before and after immersion in H_2SO_4.

The results of %elongation at break of virgin TPU and blended TPU at various contents of PDMS after immersion in H_2SO_4 are shown in Table 5.9 and Figure 5.16, comparing to the results before immersion in H_2SO_4.

Table 5.9 Elongation of TPU/PDMS blends before and after immersion in H_2SO_4 .

%PDMS	% Elongation at break	
	Before immersion	After immersion in H_2SO_4
0	485.7	541.2
0.2	568.9	541.3
0.4	609.2	571.8
0.6	622.3	562
0.8	635.4	514.6
1.0	581.2	530

After acid immersion, elongation at break of all blended TPU is consistent with that of virgin TPU. This could imply that after acid immersion PDMS content tends to have no effect on the elongation at break comparing to that of the virgin TPU.

Comparing the elongation at break after acid immersion to those before acid immersion, the elongation at break of virgin TPU after acid immersion is higher than that of virgin TPU before acid immersion while these of blended TPU after acid immersion are decreased from those of blended TPU before acid immersion. The results indicate that PDMS contents in blended TPU have no effects on improving the elongation at break after acid immersion comparing to that before acid immersion.

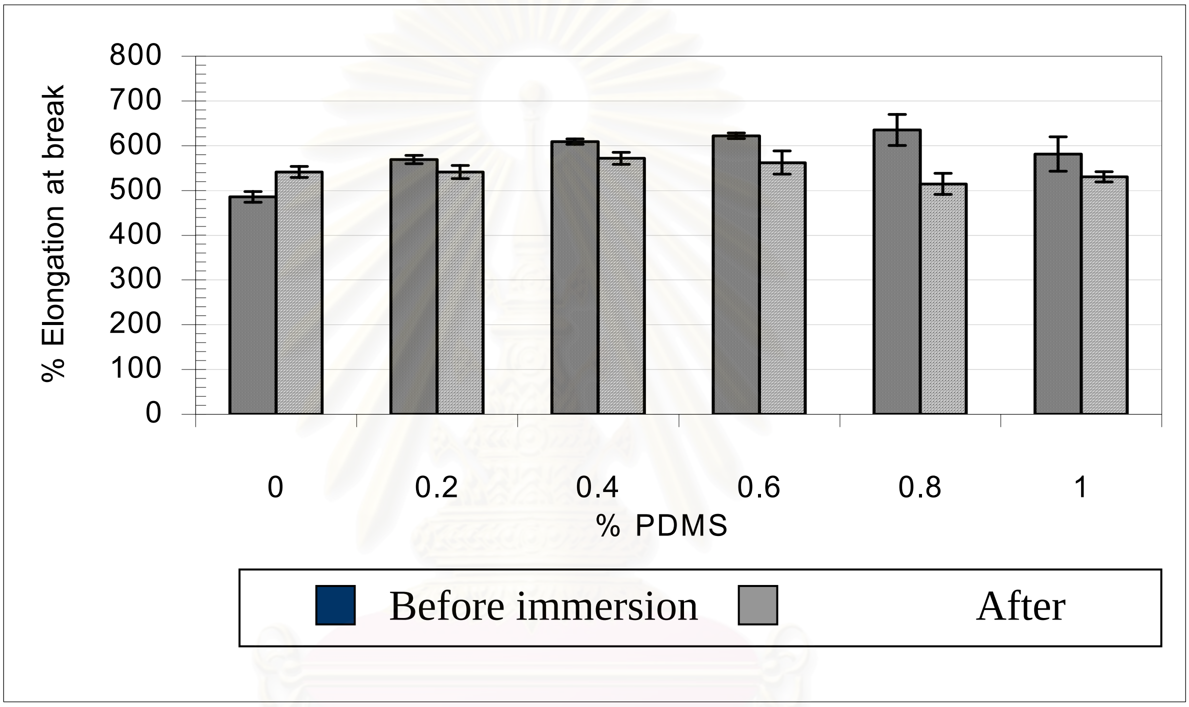


Figure 5.16 Comparison on %elongation at break of virgin TPU and blended TPU at various PDMS contents before and after immersion in H_2SO_4.

The results on Young's modulus of virgin TPU and blended TPU at various contents of PDMS after immersion in H_2SO_4 are shown in Table 5.10 and Figure 5.17, comparing to the results before immersion in H_2SO_4.

Table 5.10 Young's modulus of TPU/PDMS blends before and after immersion in H_2SO_4.

%PDMS	Young's modulus (MPa)	
	Before immersion	After immersion in H_2SO_4
0	3.4	3.2
0.2	3.2	3.5
0.4	4.1	2.9
0.6	4.7	3.1
0.8	4.1	3.7
1.0	4.2	3.7

It can be seen that after acid immersion the values of Young's modulus of all blended TPU do not much differ from that of virgin TPU. Comparing the Young's modulus of virgin TPU and blended TPU after acid immersion to those before acid immersion, it is noticed that, for virgin TPU and blended TPU with 0.2% of PDMS, the Young's modulus is rather consistent. However for blended TPU with 0.4%, 0.6%, 0.8%, and 1% of PDMS, the Young's modulus after acid immersion is lower than before acid immersion by about 29%, 34%, 10%, and 11%, respectively. This could imply that PDMS contents have an effect on lowering the Young's modulus after acid immersion of some TPU blends comparing to that before acid immersion.

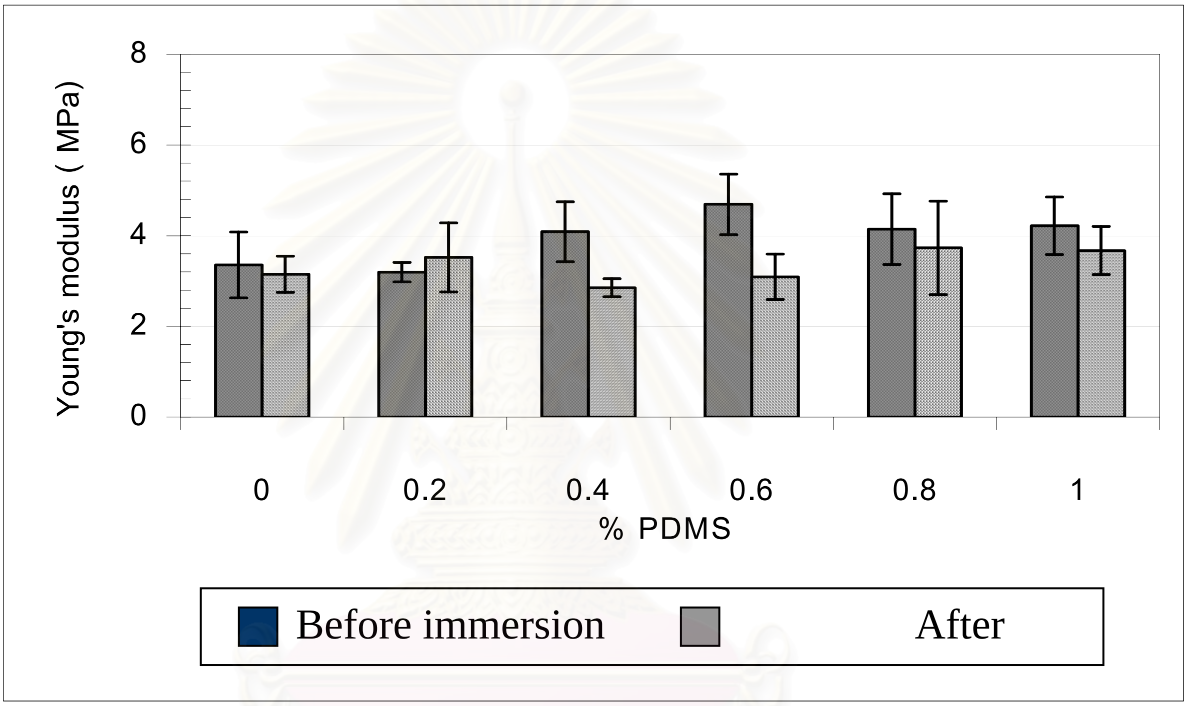


Figure 5.17 Comparison on Young’s modulus of virgin TPU and blended TPU at various PDMS contents before and after immersion in H_2SO_4.

The results on the energy to break of virgin and blended TPU at various contents of PDMS after immersion in H_2SO_4 are shown in Table 5.11 comparing to the results before immersion in H_2SO_4.

Table 5.11. Energy to break of TPU/PDMS blends before and after immersion in H_2SO_4.

%PDMS	Energy to break (N-mm)	
	Before immersion	After immersion in H_2SO_4
0	5798	6307
0.2	5842	5570
0.4	5756	7730
0.6	5141	6944
0.8	5167	6083
1.0	5126	6120

The stress-strain curves of virgin TPU and blended TPU with 0.8% of PDMS before and after acid immersion are shown in Figure 5.18. Comparing the energy to break after acid immersion to those before acid immersion, the energy to break of virgin TPU and most blended TPU after acid immersion is higher than those before acid immersion. This implies that PDMS contents in blended TPU can improve the energy to break or toughness after acid immersion comparing to that before acid immersion.

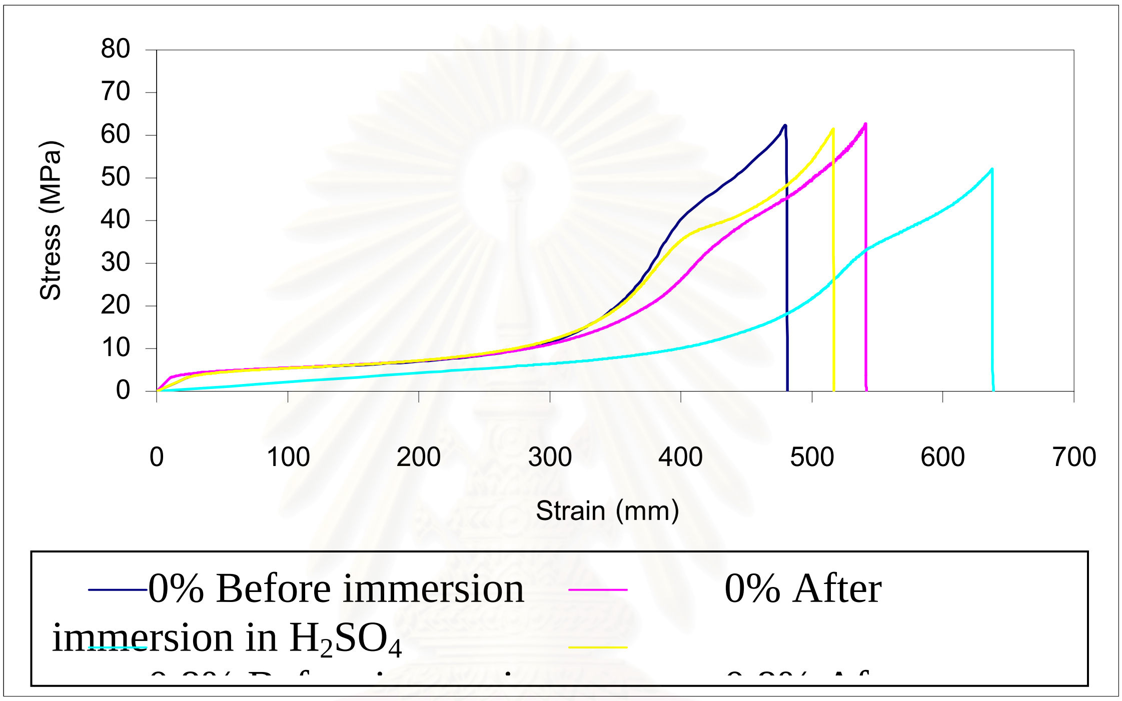


Figure 5.18 Stress-strain curves of virgin TPU and blended TPU at 0.8% of PDMS before and after immersion in H_2SO_4.

5.3.4 TPU/PDMS blends after immersion in NaOH (10% w/v)

The results on the ultimate tensile strength, the elongation at break, Young's Modulus and energy to break of blended TPU at various PDMS contents after base immersion are shown in Table 5.12, 5.13, 5.14, and 5.15, respectively, comparing to the results before base immersion.

Table 5.12. Ultimate tensile strength of TPU/PDMS blends before and after immersion in NaOH.

%PDMS	Ultimate tensile strength (MPa)	
	Before immersion	After immersion in NaOH
0	62.9	36.8
0.2	50.9	43.6
0.4	55.7	41.9
0.6	57.3	42.8
0.8	51.3	38.5
1.0	61.0	31.7

Comparison of the ultimate tensile strength of virgin TPU and blended TPU before and after immersion in base is shown in Figure 5.19. It can be seen that the values of the ultimate tensile strength of TPU after base immersion are increased when TPU is blended with PDMS at all PDMS contents except at 1.0% of PDMS. After base immersion the ultimate tensile strength of the blends with PDMS content at 0.2%, 0.4%, 0.6%, and 0.8% is higher than that of virgin TPU about 19%, 14%, 16%, and 5%, respectively. On the other words, PDMS content at 0.2% has an effect on increasing the ultimate tensile strength of the virgin TPU after base immersion but higher PDMS content (from 0.2% to 0.8%) tends to have no more effect on the ultimate tensile strength of the blends, comparing to the TPU blend with 0.2% of PDMS. This is similar to the effects of PDMS contents on the ultimate tensile strength of blended TPU before immersion discussed in section 5.3.1.

The ultimate tensile strength of virgin TPU and blended TPU after base immersion, comparing to those before base immersion, is remarkably different. The value of the ultimate tensile strength of virgin TPU after base immersion is lower than that before base immersion about 42%. This is the poor chemical resistance of virgin TPU. For blended TPU, the ultimate tensile strength of blended TPU with PDMS (0.2%-1%) are lower than those before base immersion about 14% - 48%. It can be concluded that NaOH immersion has a strong effect on decreasing the ultimate tensile strength of the virgin TPU and blended TPU with PDMS.

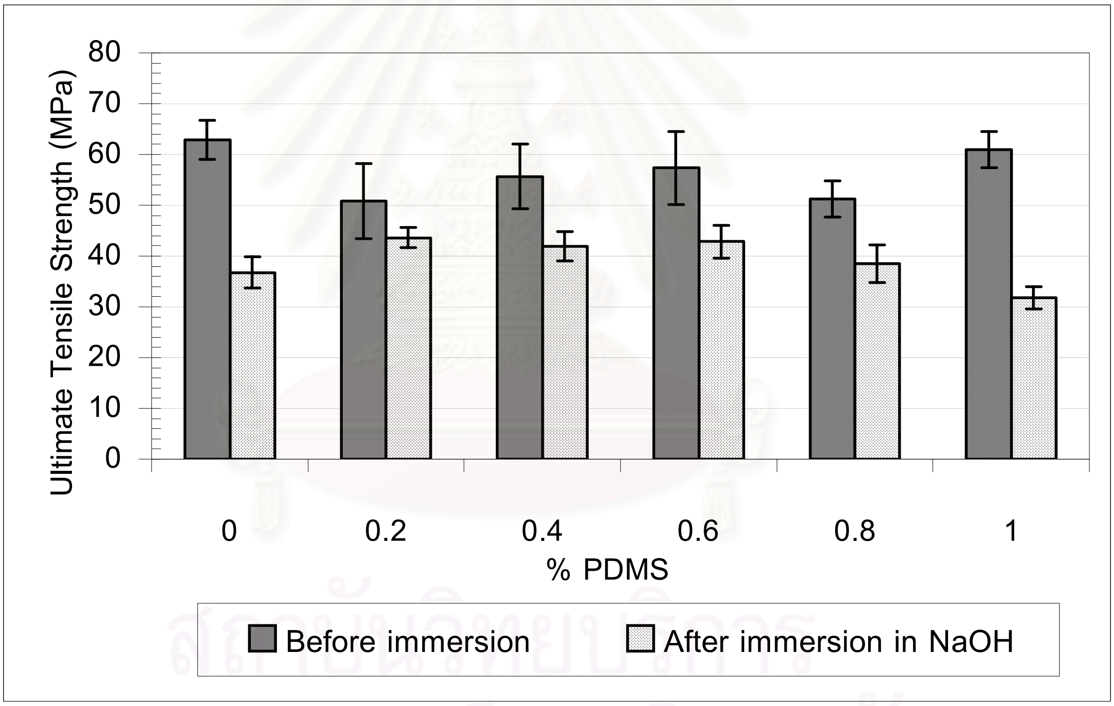


Figure 5.19 Comparison on the ultimate tensile strength of virgin TPU and blended TPU at various PDMS contents before and after immersion in NaOH.

The results of elongation at break of virgin TPU and blended TPU at various PDMS contents after base immersion are shown in Table 5.13 and Figure 5.20, comparing to results before base immersion.

Table 5.13 Elongation at break of TPU/PDMS blends before and after immersion in NaOH.

%PDMS	% Elongation at break	
	Before immersion	After immersion in NaOH
0	485.7	487.0
0.2	568.9	496.9
0.4	609.2	472
0.6	622.3	482.6
0.8	635.4	458.8
1.0	581.2	462.7

After base immersion, elongation at break of all blended TPU is consistent with that of virgin TPU. This could imply that PDMS content tends to have no effect on the elongation at break after base immersion.

The elongation at break of virgin TPU after base immersion is similar to that of virgin TPU before base immersion while those of all blended TPU after base immersion are decreased from those of blended TPU before base immersion about 15% to 40%. The results indicate that base immersion does not influence the elongation of virgin TPU but it has an influence on the elongation property of blended TPU by lowering the elongation at break of each blend before base immersion.

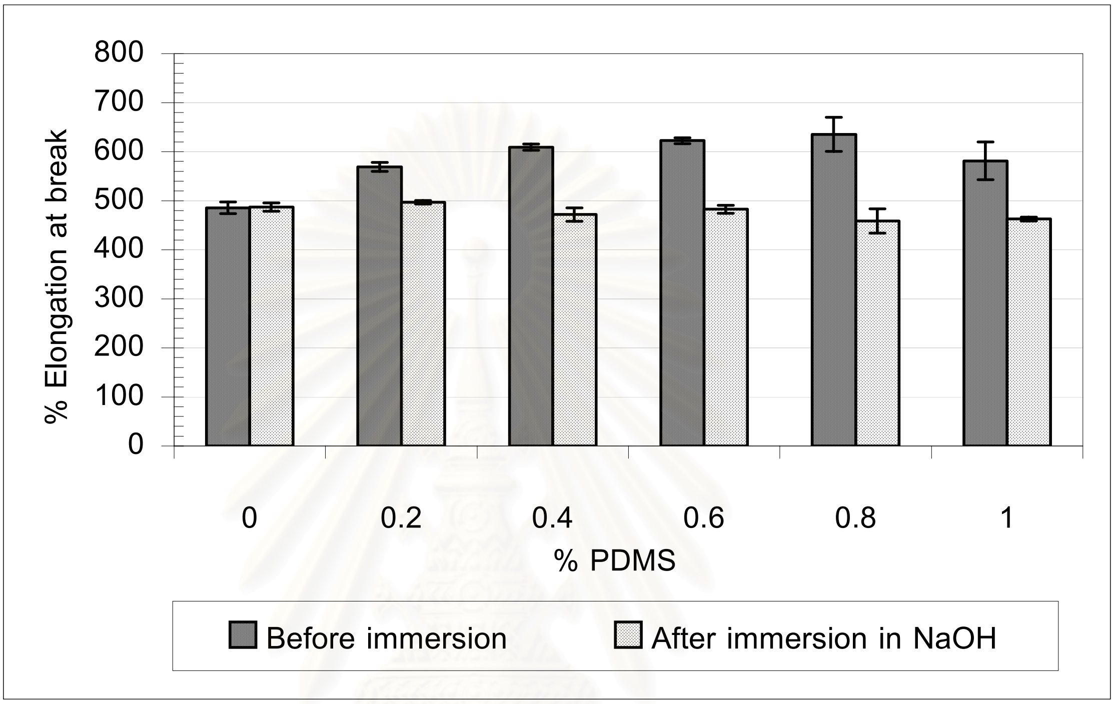


Figure 5.20 Comparison on elongation at break of virgin TPU and blended TPU at various PDMS contents before and after immersion in NaOH.

The results on Young's modulus of virgin TPU and blended TPU at various PDMS contents after base immersion are shown in Table 5.14 and Figure 5.21, comparing to results before base immersion.

Table 5.14 Young's modulus of TPU/PDMS blends before and after immersion in NaOH.

%PDMS	Young's modulus (MPa)	
	Before immersion	After immersion in NaOH
0	3.4	7.8
0.2	3.2	3.5
0.4	4.1	5.6
0.6	4.7	3.9
0.8	4.1	6.1
1.0	4.2	7.3

Young's modulus of blended TPU after base immersion is decreased from that of virgin TPU when TPU is blended with PDMS at all PDMS contents. After base immersion the values of Young's modulus of blended TPU with 0.2%, 0.4%, 0.6%, 0.8%, and 1% of PDMS are lower than that of virgin TPU about 55%, 28%, 50%, 22% and 6%, respectively. PDMS content at 0.2% strongly affects the young's modulus while higher PDMS contents have less effects on the Young's modulus of blended TPU.

Young's modulus of virgin TPU after base immersion is higher than that of before base immersion by almost 130% while those of blended TPU after base immersion at 0.4%, 0.8% and 1.0% are higher than those before immersion about 27% to 74%. Young's modulus of other blended TPU are more or less similar to those before base immersion. The results on virgin TPU and blended TPU with 1% of PDMS indicates that base immersion has a strong effect on increasing the Young's modulus of virgin TPU and blended TPU with 1% of PDMS.

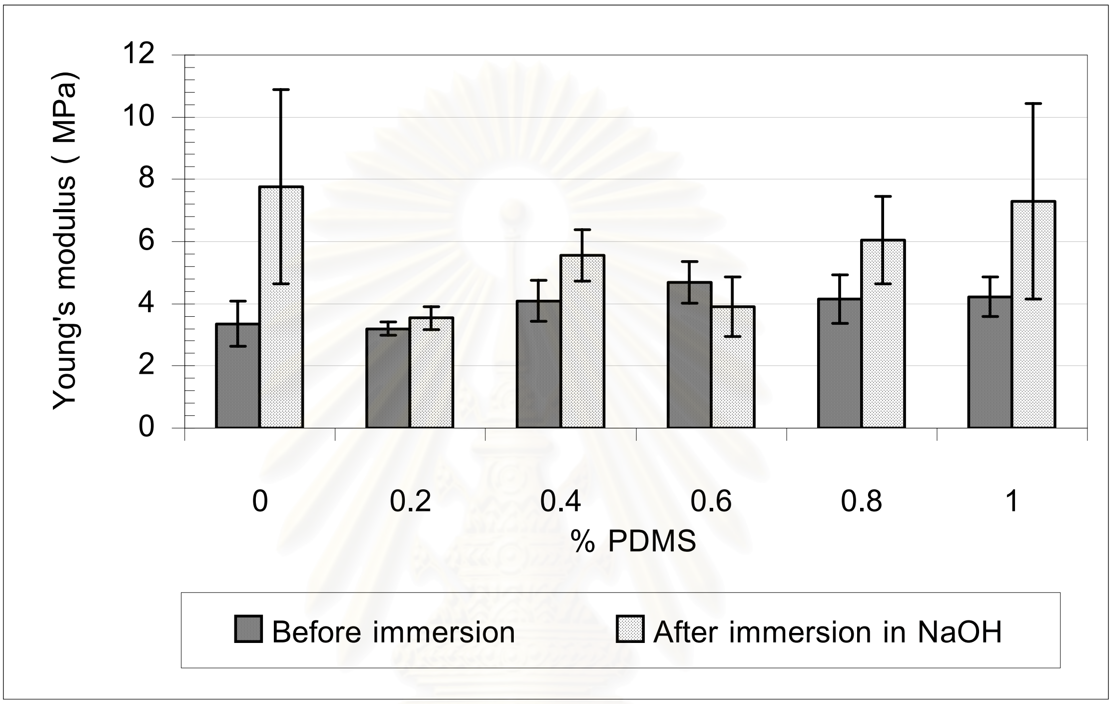


Figure 5.21 Comparison on Young's modulus of virgin TPU and blended TPU at various PDMS contents before and after immersion in NaOH.

The results on energy to break of virgin TPU and blended TPU at various PDMS contents after base immersion are shown in Table 5.15, comparing to results before base immersion.

Table 5.15 Energy to break of TPU/PDMS blends before and after immersion in NaOH.

%PDMS	Energy to break (N-mm)	
	Before immersion	After immersion in NaOH
0	5798	2590
0.2	5842	4235
0.4	5756	3184
0.6	5141	4116
0.8	5167	2909
1.0	5126	2306

The stress-strain curves of virgin TPU and blended TPU with 0.8% of PDMS before and after base immersion are shown in Figure 5.22. The energy to break of virgin TPU and blended TPU after base immersion, comparing to those before base immersion, indicates that the energy to break of virgin TPU after base immersion is noticeably lower than that before base immersion by 55% while the energy to break of all blended TPU after base immersion is lower from that before immersion around 20% - 55%. This could imply that base immersion has a strong effect on decreasing the toughness of samples, especially virgin TPU and blended TPU with 1% of PDMS.

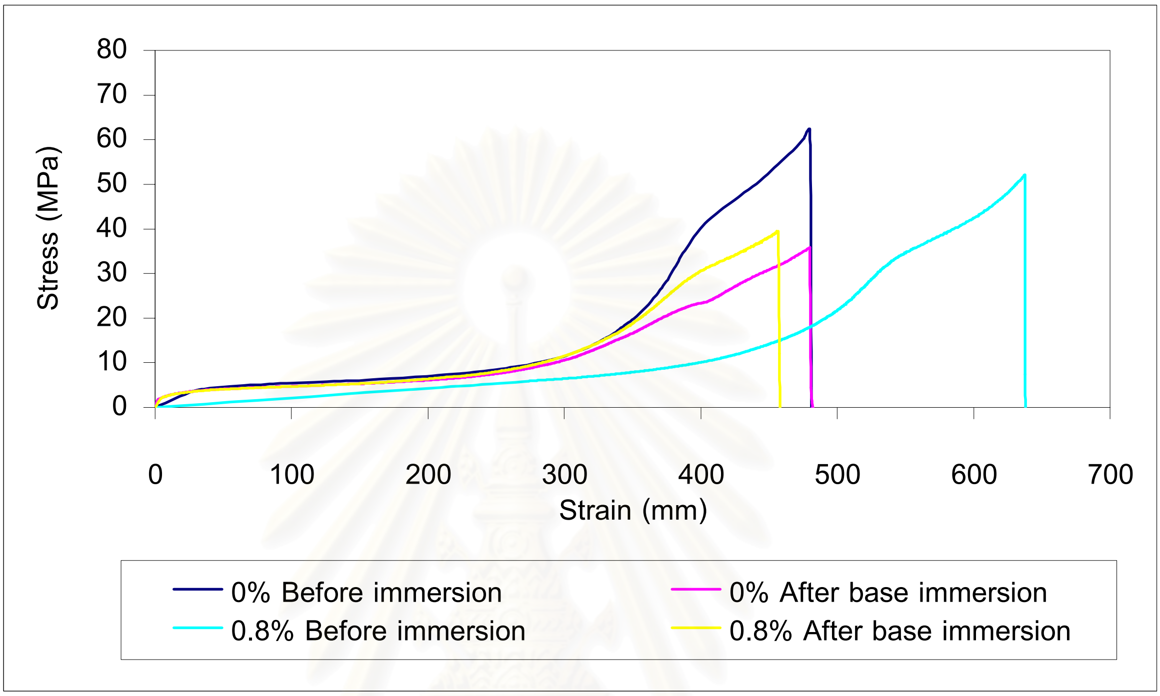


Figure 5.22 Stress-strain curves of virgin TPU and blended TPU at 0.8% of PDMS before and after base immersion.

5.3.5 Comparison of chemical resistance in various chemical reagents

Comparison of the ultimate tensile strength, the elongation at break, Young's modulus and the energy to break, of the blended TPU at all compositions before and after immersion in various chemical reagents are shown in Figure 5.24, Figure 5.25, Figure 5.26, and Figure 5.27, respectively. The results on the chemical resistance to tensile properties can be concluded as follows

The ultimate tensile strength, Young's modulus and the energy at break of the blends at all composition after immersion in water and acid (H_2SO_4 (3%)), comparing to those before immersion, are not significantly obvious. This could imply that the water immersion has no effect on the tensile properties of the blends. In the case of acid immersion, a slight effect of PDMS contents on the acid resistance to the tensile properties can be noticed. The results can be confirmed from the physical appearance in section 5.2.2 and section 5.2.3.

In the case of base immersion, the results on tensile properties can be concluded that base immersion has a strong effect on tensile properties. The effect of PDMS contents on the base resistance to the tensile properties is marked, i.e. the effective PDMS contents in blended TPU does, more or less, not exceed 0.8%. At 1% of PDMS content, the effects on each property is obviously less, i.e. the value of each property is closed to that of pure TPU. This is similar to the resulted found in the case of TPU/PDMS blends before immersion.

Comparing immersion in various types of chemical reagents, NaOH (10% w/v) has the strongest influence on the tensile properties of virgin TPU and blended TPU. For virgin TPU after base immersion comparing to before base immersion the ultimate tensile strength and energy at break is decreased, the Young's modulus is increased while the elongation at break is rather consistent. For blended TPU after base immersion comparing to before base immersion, similar trends for each property are noticed when PDMS content in the blend is not more than 0.8%.

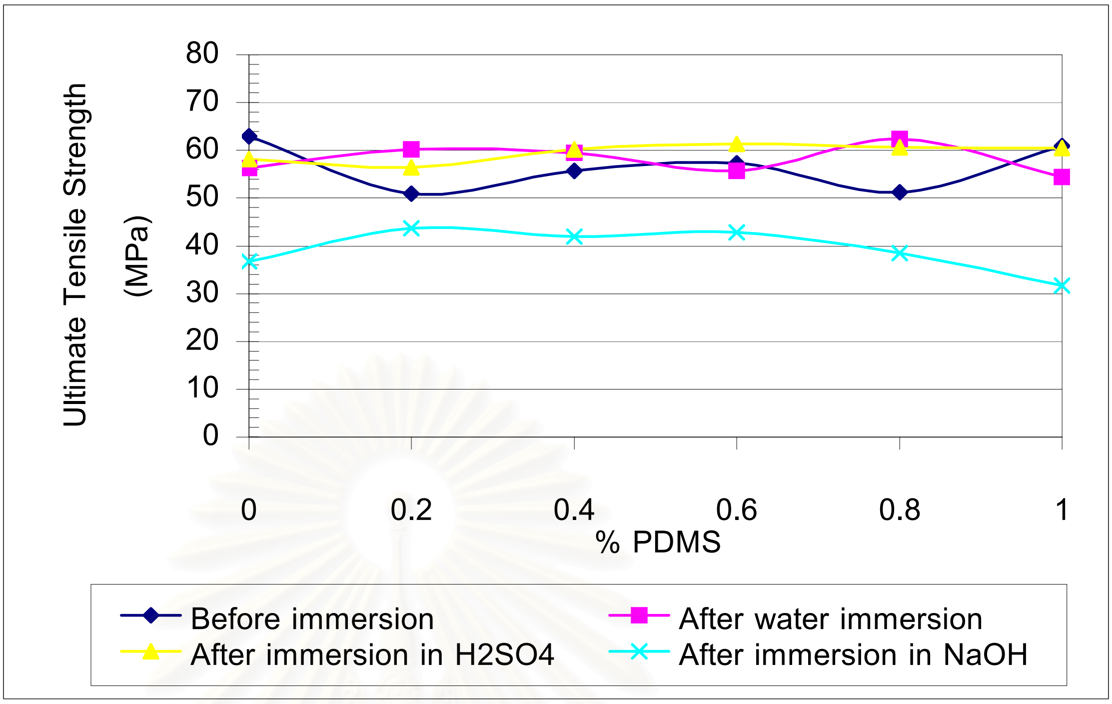


Figure 5.23 Comparison on the ultimate tensile strength of the virgin TPU and blended TPU before and after immersion in various chemical reagents.

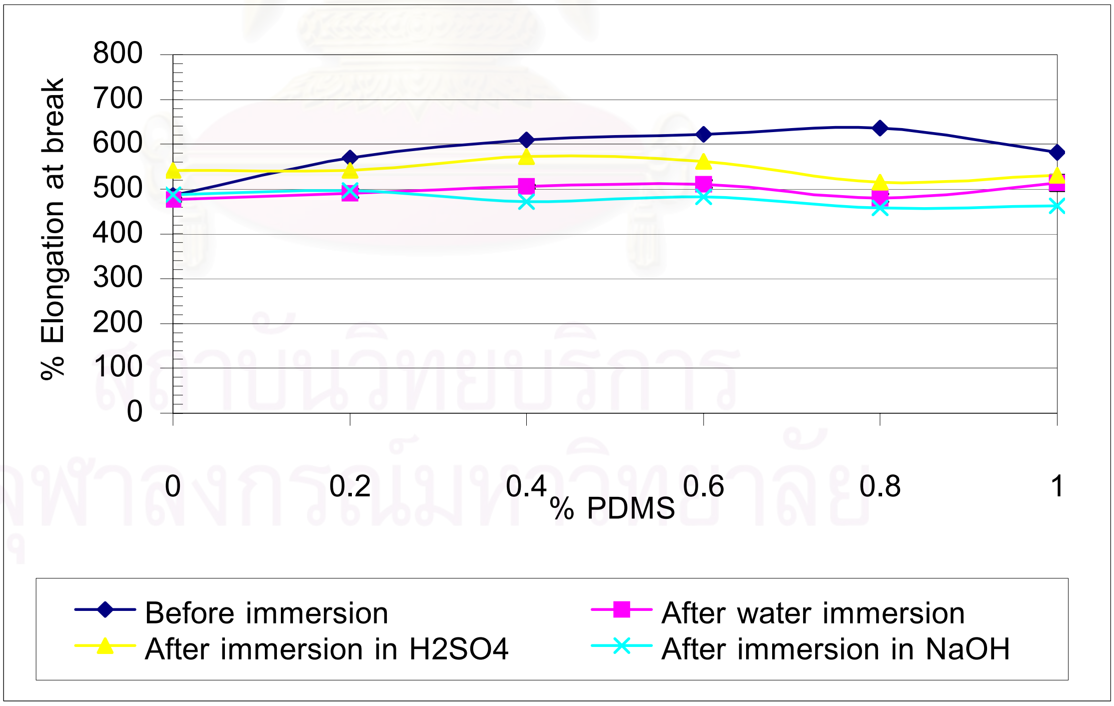


Figure 5.24 Comparison on the elongation at break of the virgin TPU and blended TPU before and after immersion in various chemical reagents.

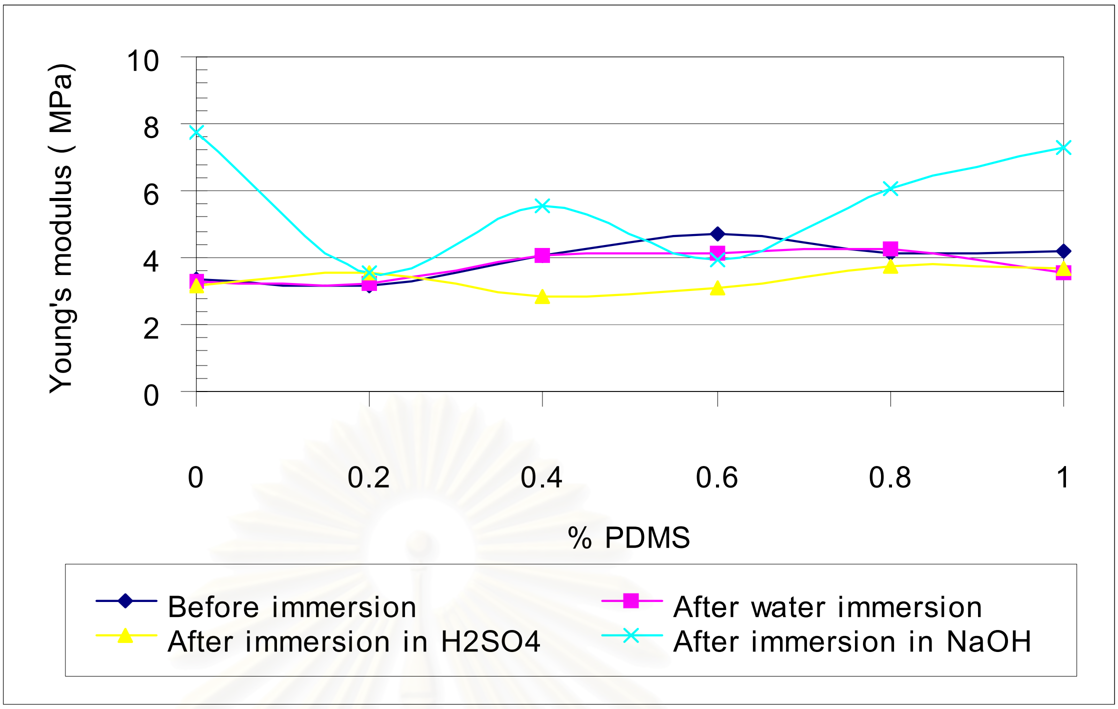


Figure 5.25 Comparison on Young's modulus of the virgin TPU and blended TPU before after immersion in various chemical reagents.

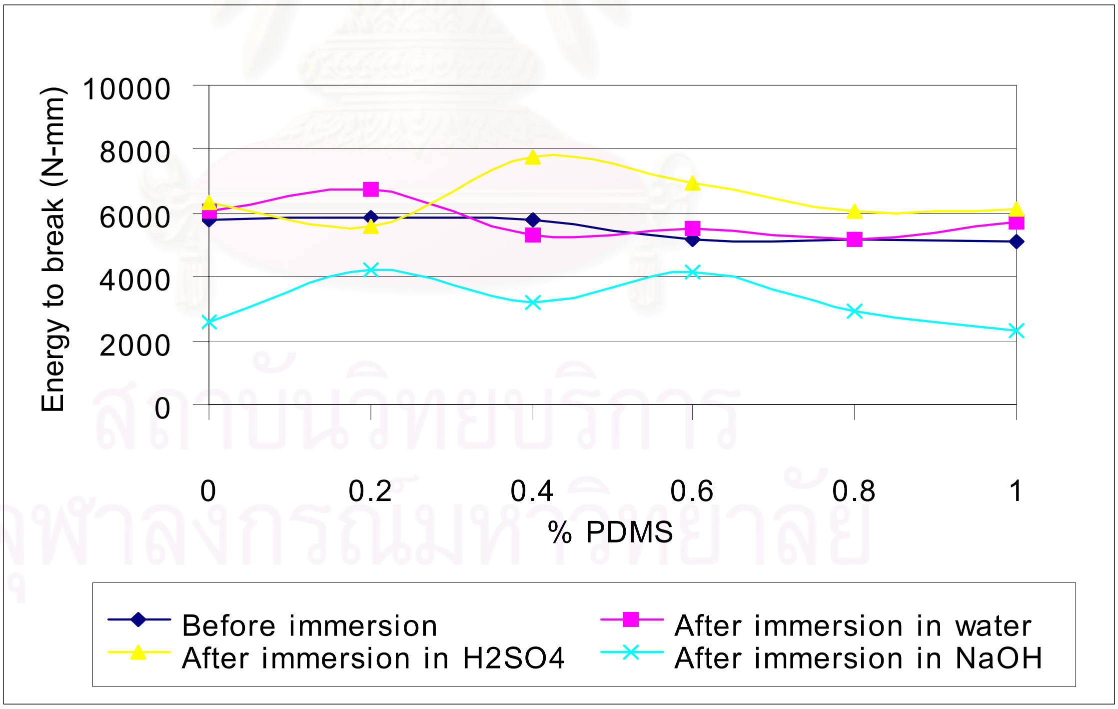


Figure 5.26 Comparison on the energy to break of the virgin TPU and blended TPU before and after immersion in various chemical reagents.

5.4 Morphology of TPU/PDMS blends by SEM

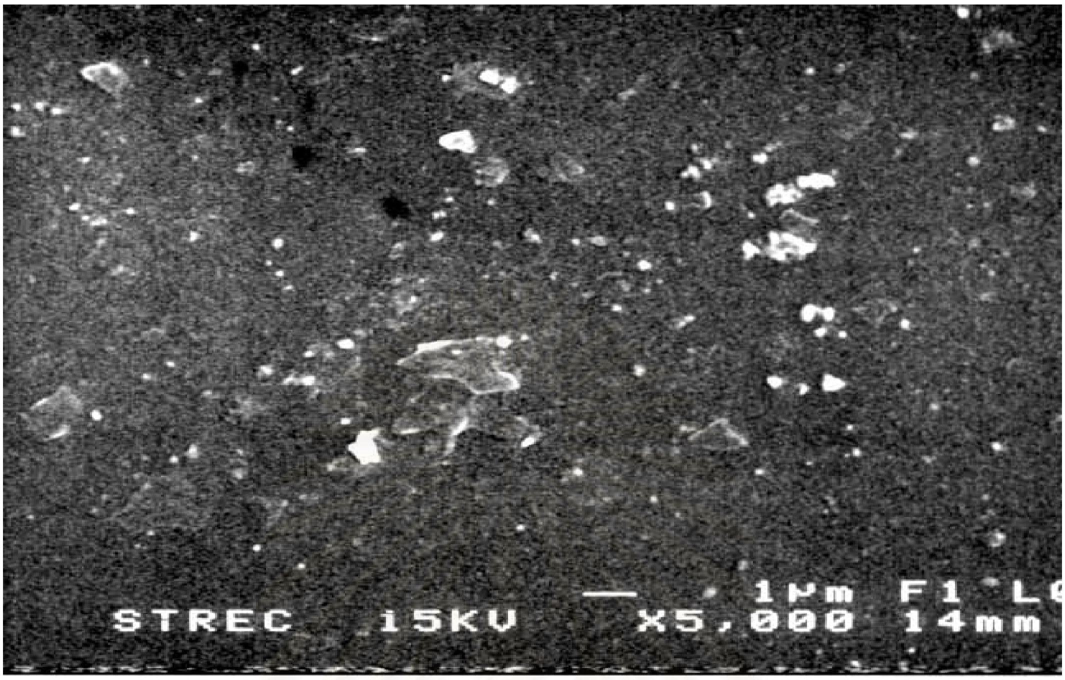
5.4.1 Morphology of TPU/PDMS blends

The properties of TPU are very dependent on the morphology of the polymer [Yue, 1996] that can be determined by electron microscopy technique. SEM photomicrograph of virgin TPU is presented in Figure 5.27. It can be seen that there are many particles at various sizes distributed on the surface of TPU. This could possibly be a part of the hard segment of TPU.

SEM photomicrographs of TPU/PDMS blends at 0.2%, 0.4% and 0.8% of PDMS prepared by melt mixing method from the twin screw extruder are presented in Figure 5.28, Figure 5.29, and Figure 5.30, respectively. Figure 5.28, Figure 5.29, and Figure 5.30 show that PDMS is evident as the dispersed phase in TPU matrix. The average domain size of PDMS at various contents can be indicated that domain size of PDMS at 0.2% concentration (about 0.6-0.7μm) is largest while those at 0.4% concentration (about 0.2-0.3 μm) is larger than those at 0.8% concentration (about 0.1-0.2 μm). This is an indication that the average domain size becomes smaller for higher PDMS concentration. It can also imply that TPU/PDMS blends at all concentration exhibit dispersed phase morphology.

SEM photomicrographs of the fractured surface of virgin TPU and TPU blends at 0.2%, 0.4% and 0.8% of PDMS after tension are presented in Figure 5.31, Figure 5.32, Figure 5.33, and Figure 5.34, respectively. In Figure 5.31, the fibrous characteristic of elongated chain segments of virgin TPU can be observed. It may indicate that this is the part of soft segment of TPU structure that shows ductility and toughness as evidenced from the stress-strain curve. This is consistent with the results on tensile test that exhibit high elongation at break, ultimate tensile strength and energy to break.

Fractured surface of blended TPU at 0.2% and 0.4% of PDMS contents, in Figure 5.32 and Figure 5.33, is different from that of virgin TPU, i.e. the less amount of fibrous characteristic in the blends is noticed and, moreover, there is a group of craze structure formed. In contrast, the fibrous characteristic and craze formation in blended TPU at 0.8% of PDMS content, shown in Figure 5.34, is not visible. The fractured structure in this case appears in a chunky crack form. This is evident that there are three different fractured mechanism occurred. The first mechanism of fibrous characteristic occurred with the virgin TPU. The second mechanism of craze formation with some fibrous characteristic can be observed in the blended TPU at 0.2% and 0.4% of PDMS. The third mechanism of chunky formation without any fibrous characteristic of TPU occurred in the blended TPU with 0.8% of PDMS. A change in the phase morphology of TPU blend at an optimum amount of PDMS concentration corresponds with the results on tensile properties that found the reduced effect of PDMS content on the tensile properties of TPU blends at around 0.6%-0.8% of PDMS content.

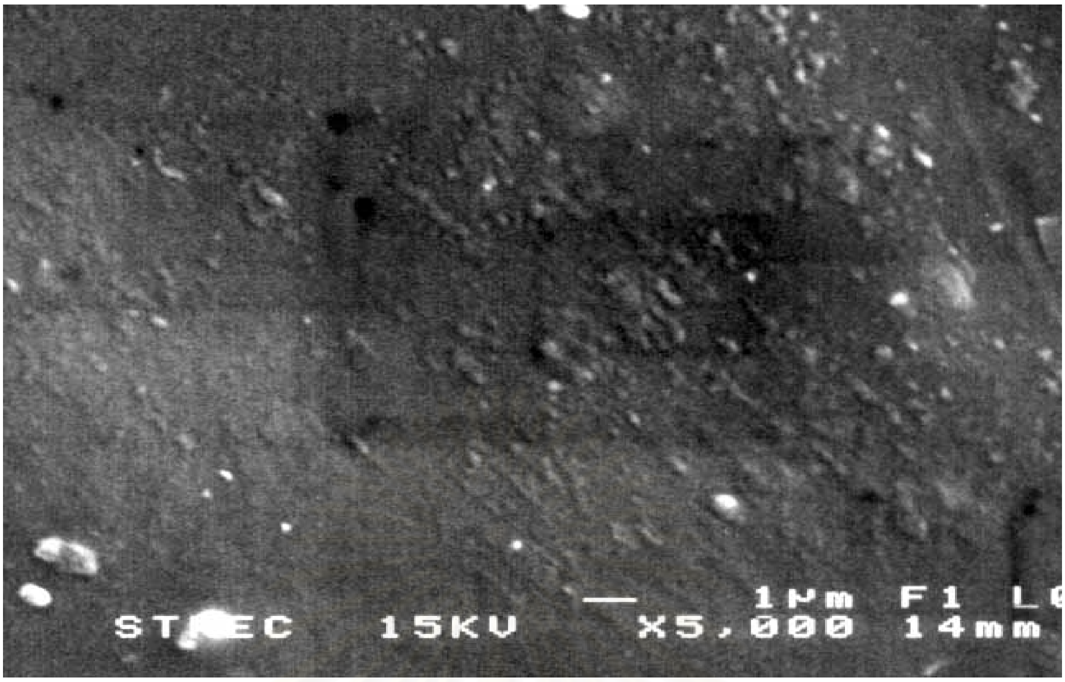


(a)

Figure 5.27 SEM photomicrographic of virgin TPU.

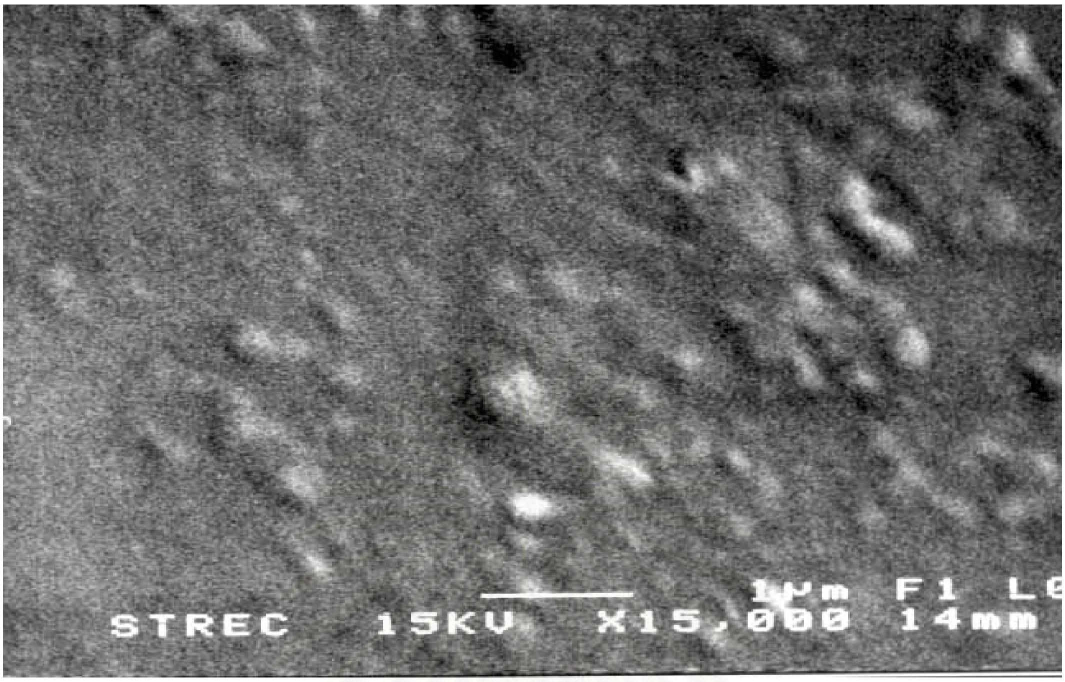
(b)

Figure 5.27 SEM photomicrographic of virgin TPU.



(a)

Figure 5.28 SEM photomicrographic of TPU/PDMS blends at 0.2% of PDMS.



(b)

Figure 5.28 SEM photomicrographic of TPU/PDMS blends at 0.2% of PDMS.

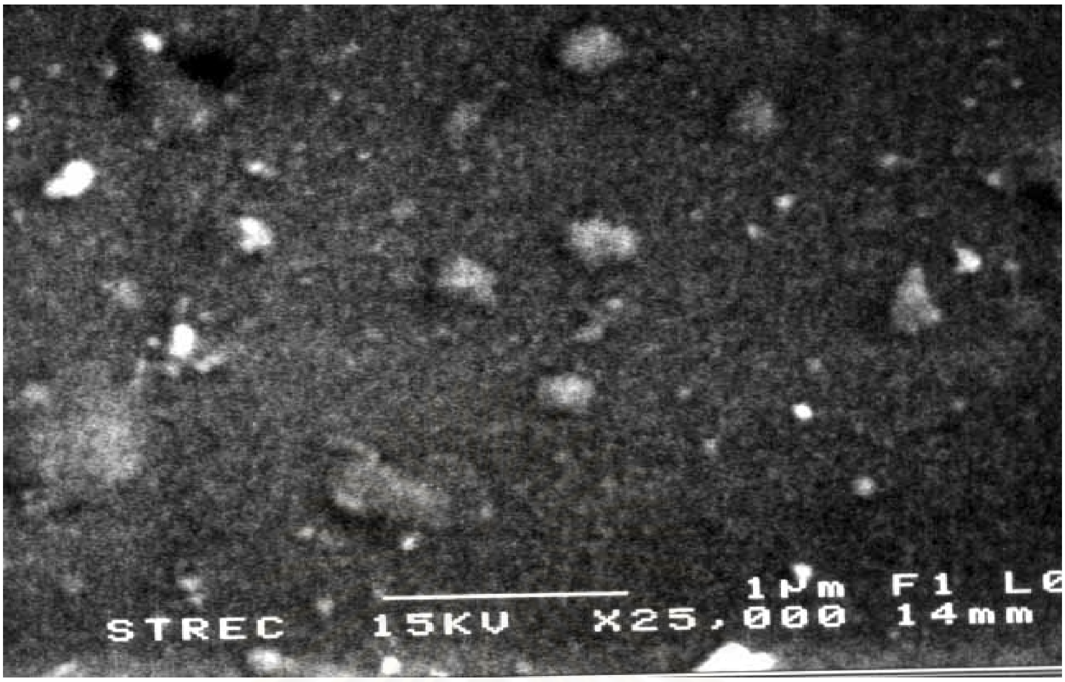


Figure5.29 SEM photomicrographic of TPU/PDMS blends at 0.4% of PDMS.

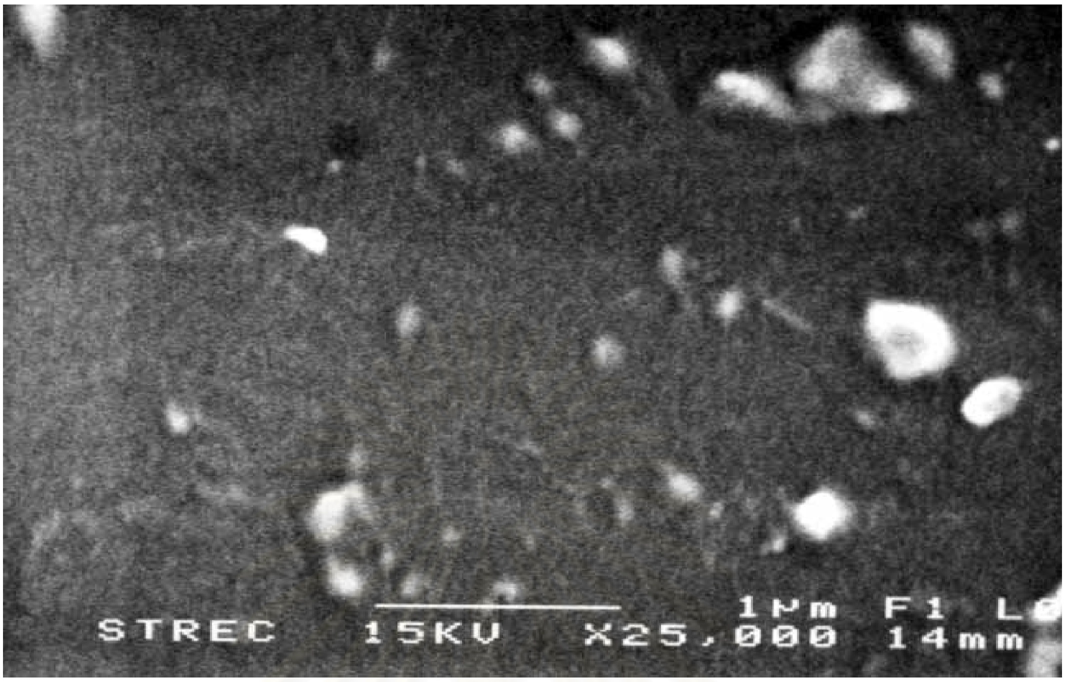


Figure 5.30 SEM photomicrographic of TPU/PDMS blends at 0.8% of PDMS.

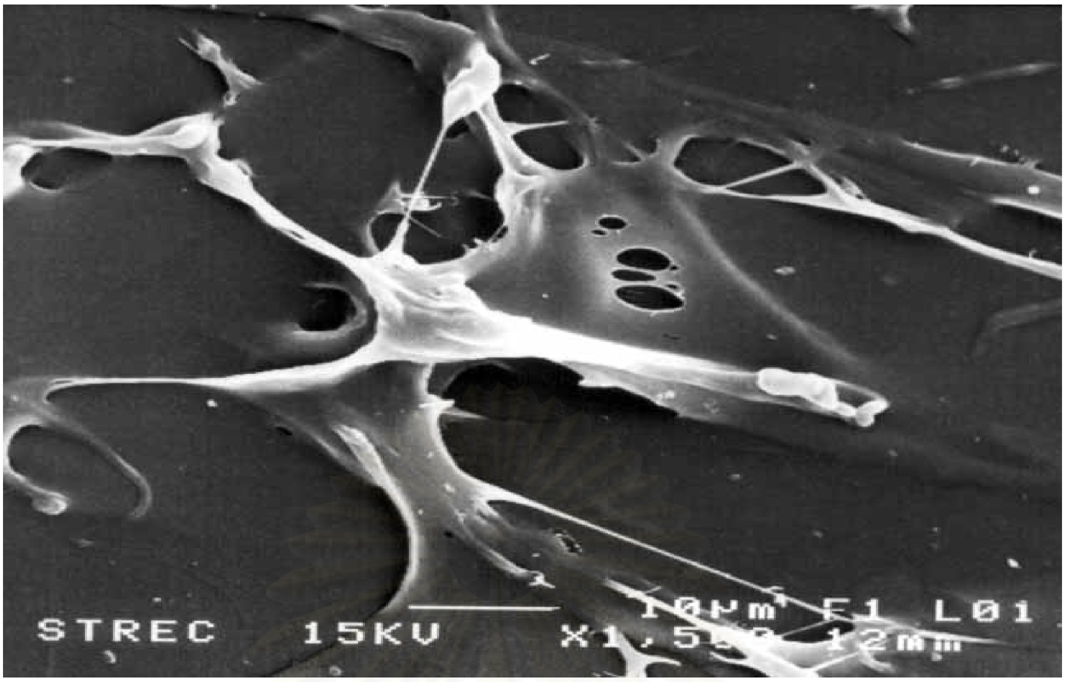


Figure 5.31 SEM photomicrographic of fractured surface of virgin TPU.

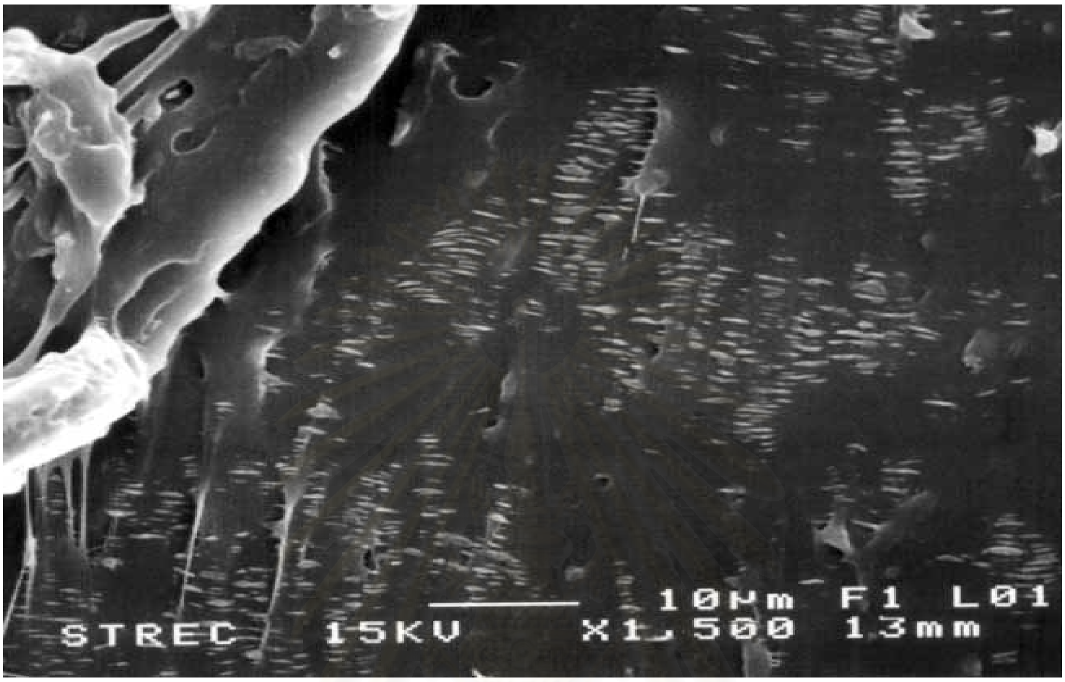


Figure 5.32 SEM photomicrographic of fractured surface of TPU/PDMS blends at 0.2% of PDMS.

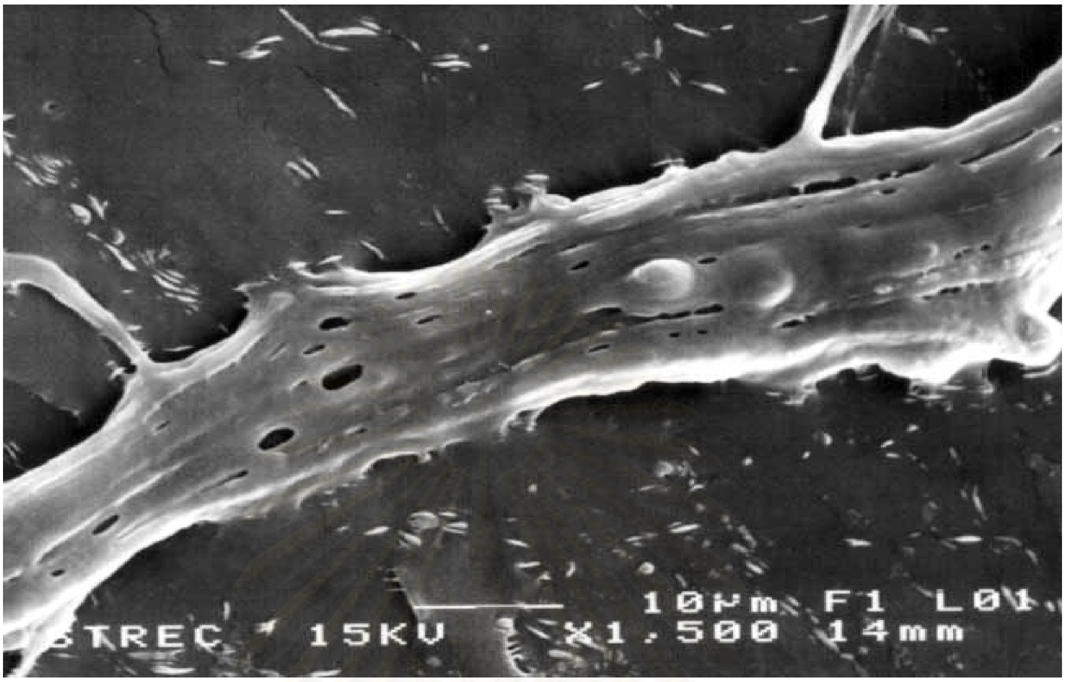
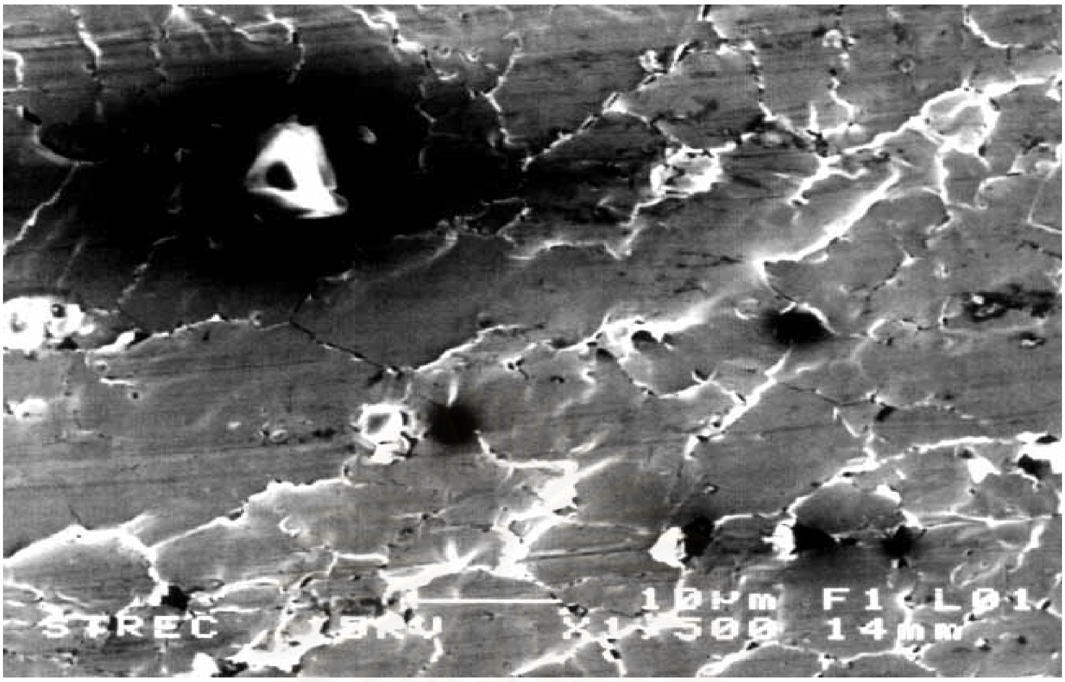
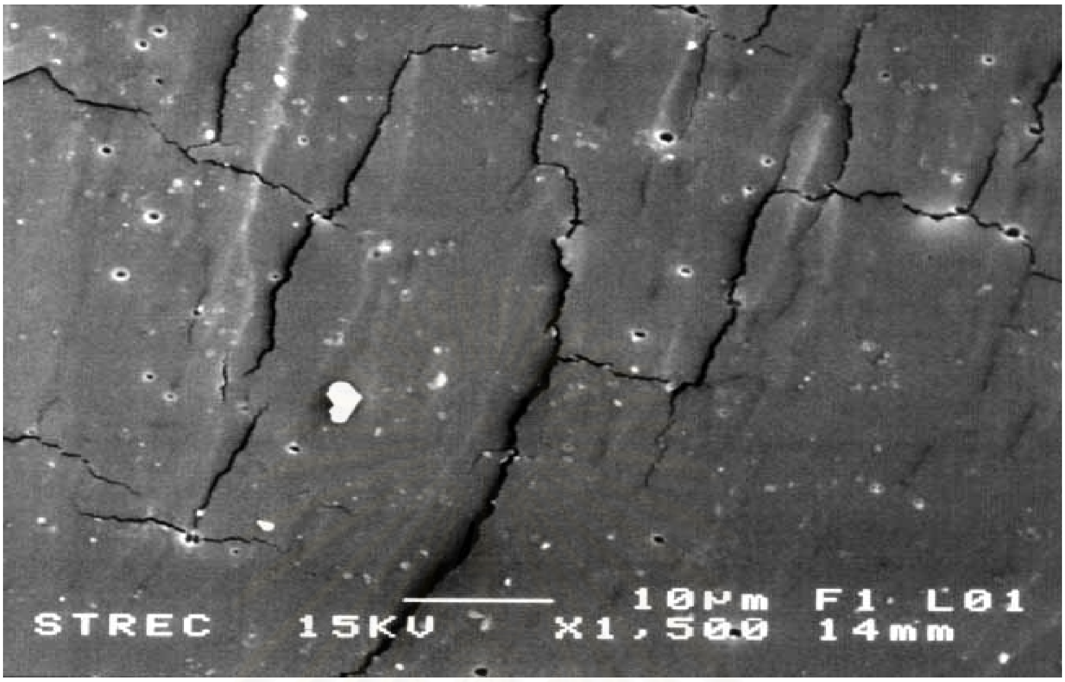


Figure 5.33 SEM photomicrographic of fractured surface of TPU/PDMS blends at 0.4% of PDMS.



(a)

Figure 5.34 SEM photomicrographic of fractured surface of TPU/PDMS blends at 0.8% of PDMS.



(b)

Figure 5.34 SEM photomicrographic of fractured surface of TPU/PDMS blends at 0.8% of PDMS.

5.4.2 Morphology of TPU/PDMS blends after immersion in H_2SO_4 (3%v/v)

SEM photomicrographs of the fractured surface from tensile test of virgin TPU and blended TPU at 0.2%, 0.4% and 0.8% of PDMS after acid immersion are presented in Figure 5.35, Figure 5.36, Figure 5.37, and Figure 5.38, respectively. The fractured structure of virgin TPU after acid immersion (Figure 5.35) exhibits fibrous characteristic similar to that of virgin TPU before immersion (Figure 5.31). The fractured structures of blended TPU at all PDMS compositions after acid immersion (Figure 5.36-5.38) still show fibrous characteristic of TPU of which the amount seems to be little less than that seen in virgin TPU. Craze formation can be noticed in all blended TPU. Comparing to blended TPU before immersion, it is noticed that the morphology of fractured TPU blends at 0.2% and 0.4% of PDMS before immersion (Figure 5.32-5.33) and after acid immersion (Figure 5.36-5.37) is similar. But the fractured surface of blended TPU at 0.8% of PDMS before immersion (Figure 5.34) is obviously different from that after acid immersion (Figure 5.38), i.e. that before immersion cracks in a chunky from with out any signs of fibrous characteristic and craze formation as seen from that after acid immersion. Thus, difference of morphology before and after acid immersion of blended TPU at 0.8% of PDMS content may support that acid immersion has changed the fractured mechanism of the sample. This indicates that acid immersion has an effect on the morphology of blended TPU at some particular PDMS content.

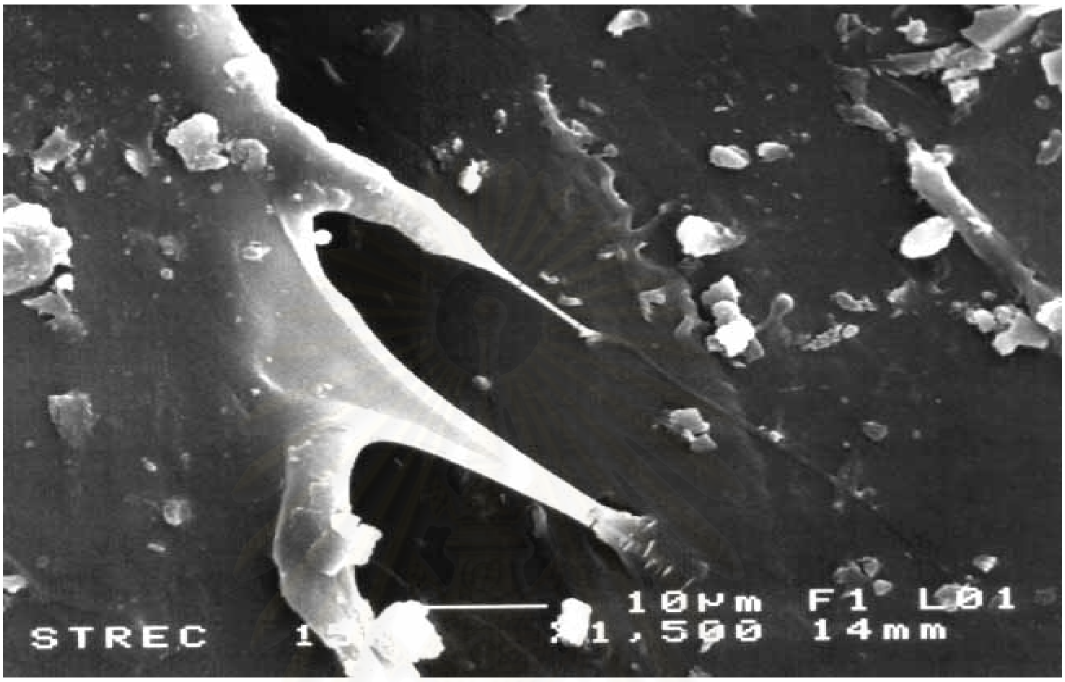


Figure 5.35 SEM photomicrographic of fractured surface of virgin TPU after acid immersion.

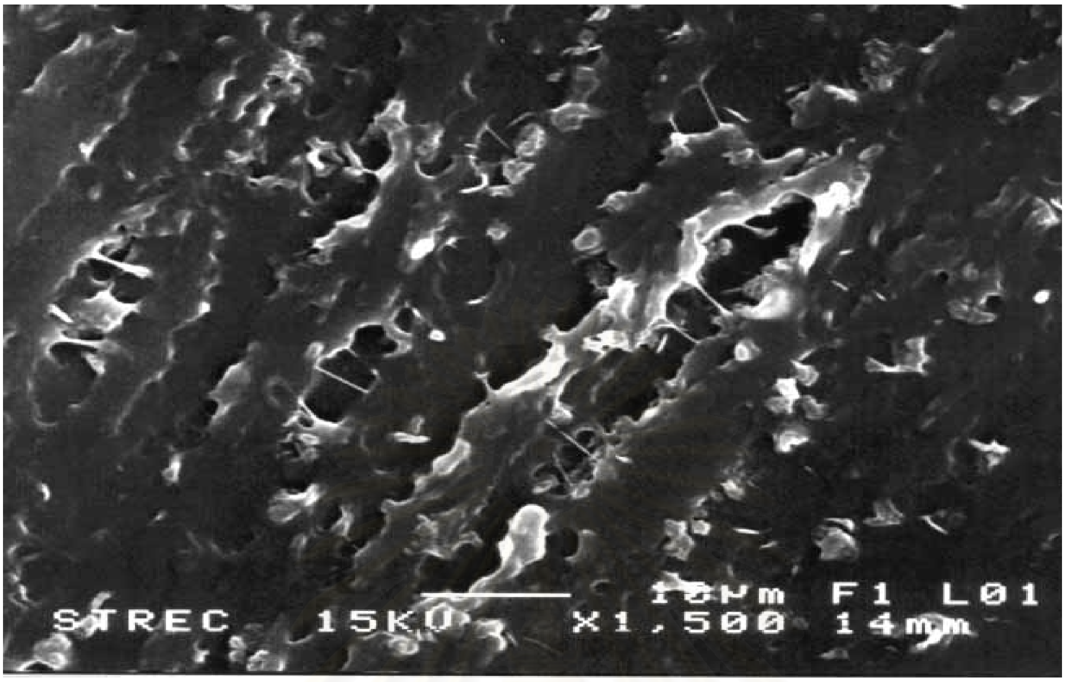


Figure 5.36 SEM photomicrographic of fractured surface of TPU/PDMS blends at 0.2% of PDMS after acid immersion.

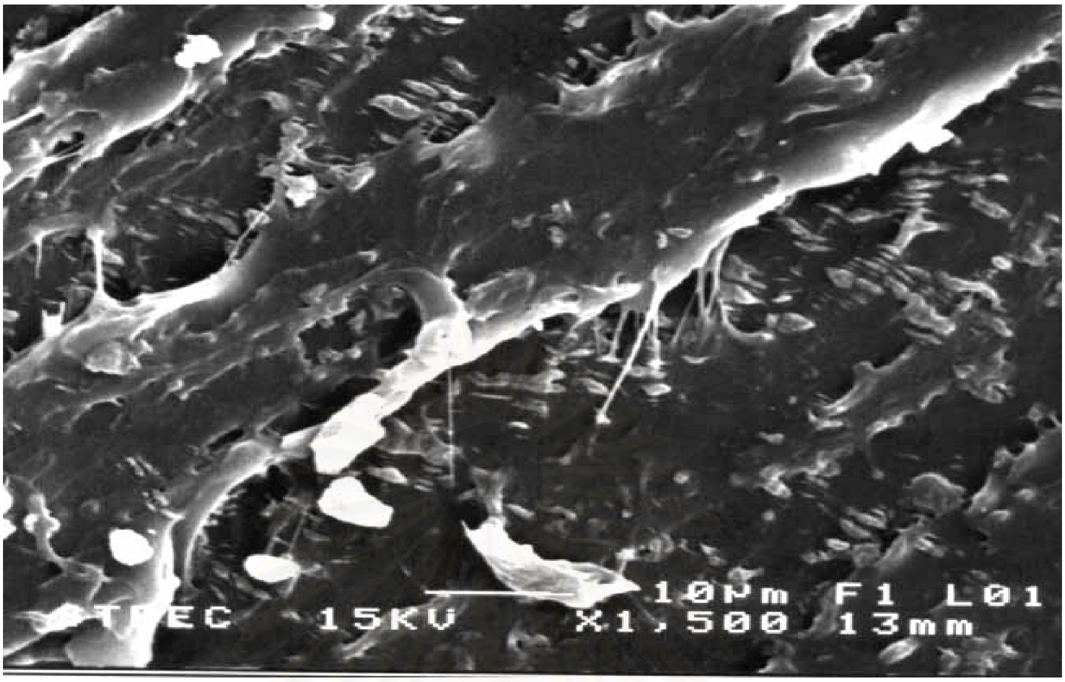


Figure 5.37 SEM photomicrographic of fractured surface of TPU/PDMS blends at 0.4% of PDMS after acid immersion.

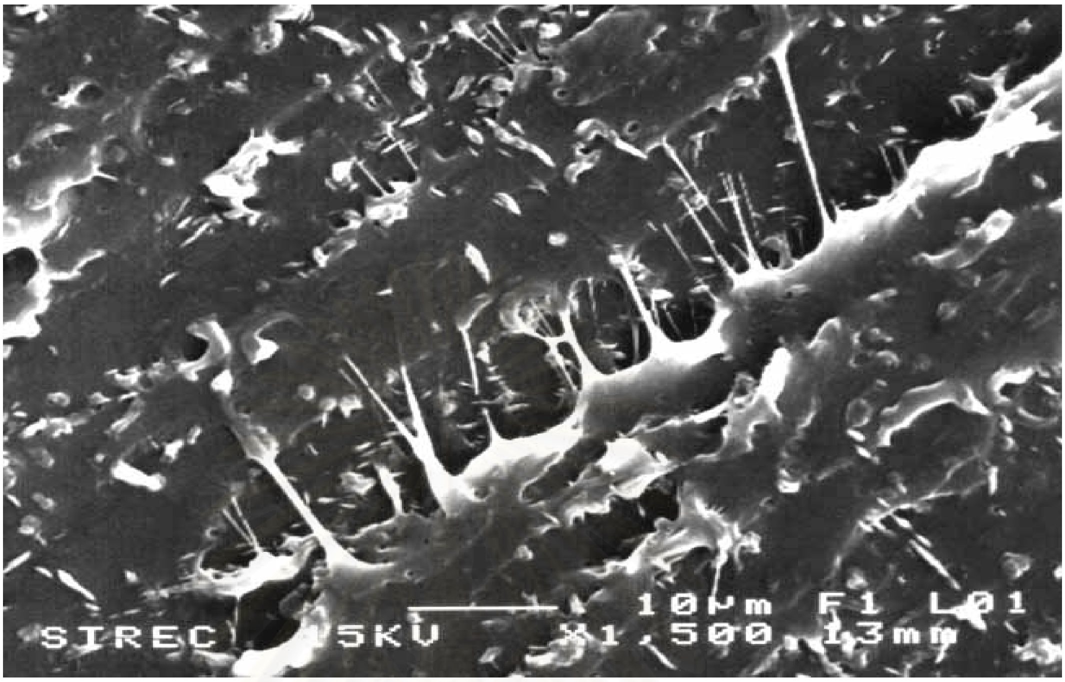


Figure 5.38 SEM photomicrographic of fractured surface of TPU/PDMS blends at 0.8% of PDMS after acid immersion.

5.4.3 Morphology of TPU/PDMS blends after immersion in NaOH (10%w/v)

SEM photomicrographs of the fractured surface from tensile test of virgin TPU and blended TPU at 0.2%, 0.4% and 0.8% of PDMS after base immersion are presented in Figure 5.39, Figure 5.40, Figure 5.41, and Figure 5.42, respectively. The fractured surface of virgin TPU after base immersion (Figure 5.39) exhibits very small amount of fibrous characteristic and there are some small particles detached at the surface. In case of the blended TPU with 0.2% and 0.4% of PDMS after base immersion (Figure 5.40-5.41), it can be obviously seen that a lot of particles with various sizes seem to come off and detach on the fractured surface while some fibrous characteristic and craze can still be observed. In case of the blended TPU with 0.8% of PDMS (Figure 5.42), a difference in fractured surface is remarkably noticed, i.e. there are a lot of hollows occurred and less amount of particles detached at the surface. The hollows seem to be the result of the particles that come off and separate from the surface. A formation of craze can still be seen.

From the morphology observed and the results on the weight loss and the surface appearance of virgin TPU and blended TPU after base immersion, one can imagine an occurrence of a corrosive reaction between the sample surface and NaOH solution (10% w/v). The corrosive reaction seems to be stronger when PDMS contents in the blended TPU is increased. Furthermore, the fibrous characteristic on fracture surface of virgin TPU and blended TPU after base immersion, is obviously decreased comparing to those before immersion, as shown in Figure 5.31 to Figure 5.34. This is consistent with the results of tensile test after base immersion that show the lowest ultimate tensile strength, the elongation at break and the energy to break, comparing to those before immersion and after immersion in other reagents. This indicates that base immersion, as well as the PDMS contents, has a strong effect on changing the morphology and tensile properties of virgin TPU and blended TPU after tensile testing.

Nevertheless, which parts of TPU and blended TPU that react with NaOH solution in corrosive reactive is still a question that needs further investigation.

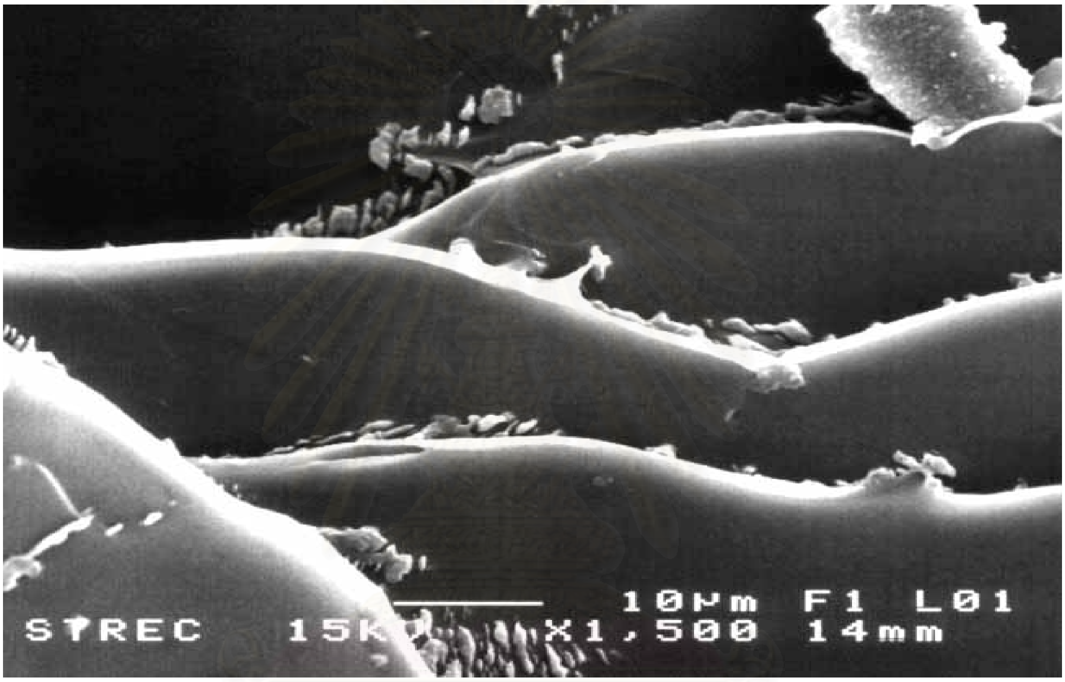
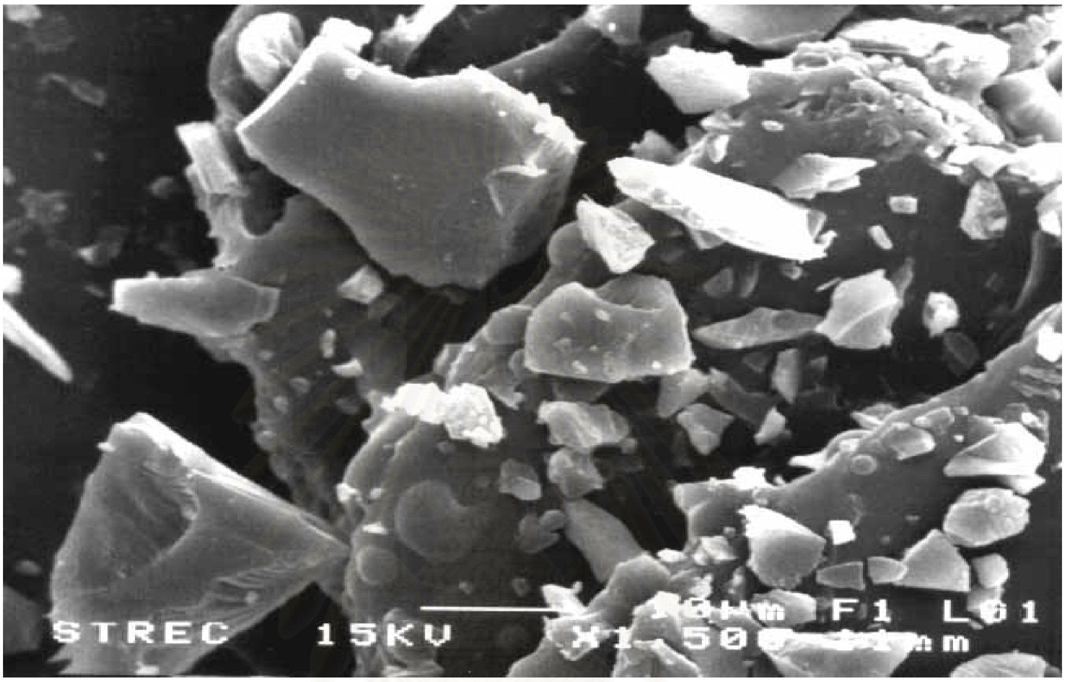
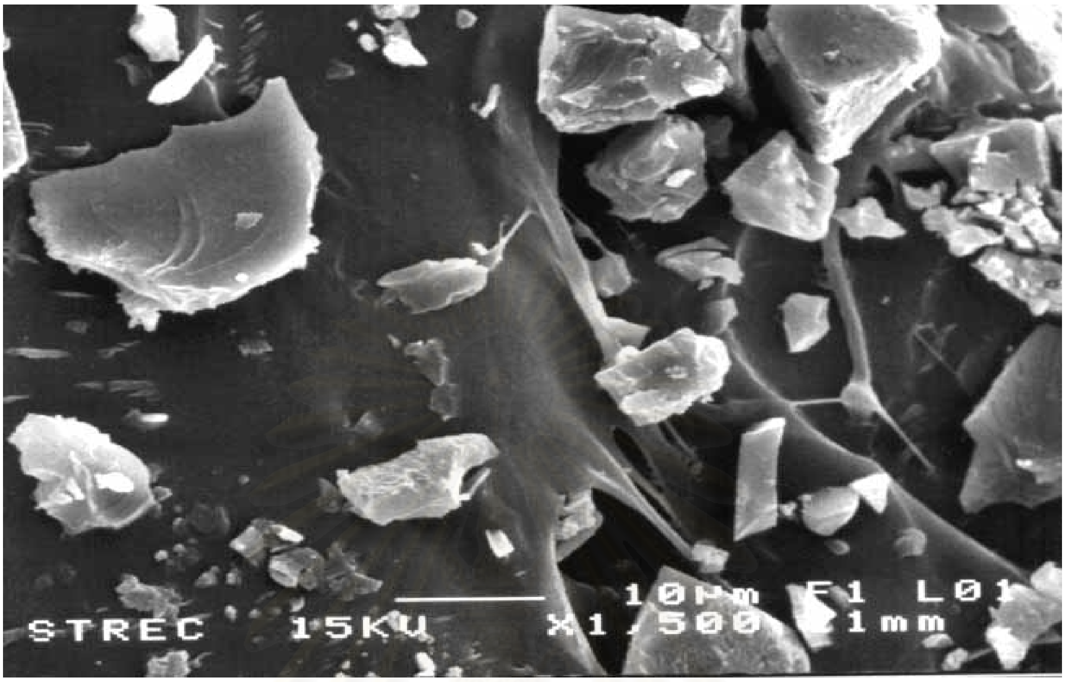


Figure 5.39 SEM photomicrographic of fractured surface of virgin TPU after base immersion.



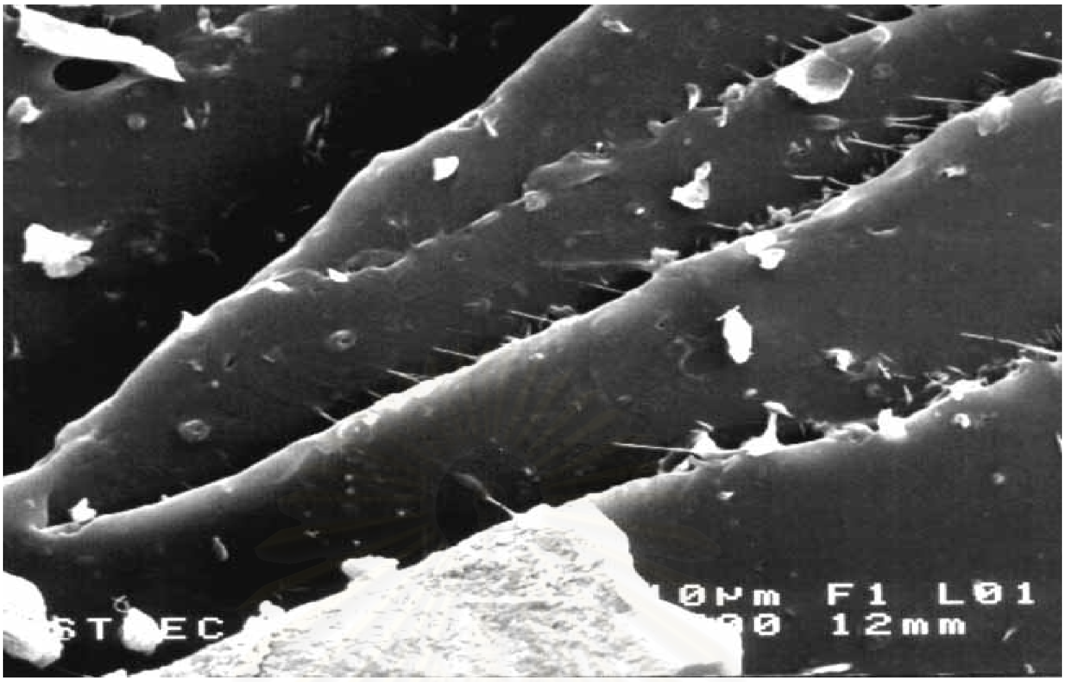
(a)

Figure 5.40 SEM photomicrographic of fractured surface of TPU/PDMS blends at 0.2% of PDMS after base immersion.



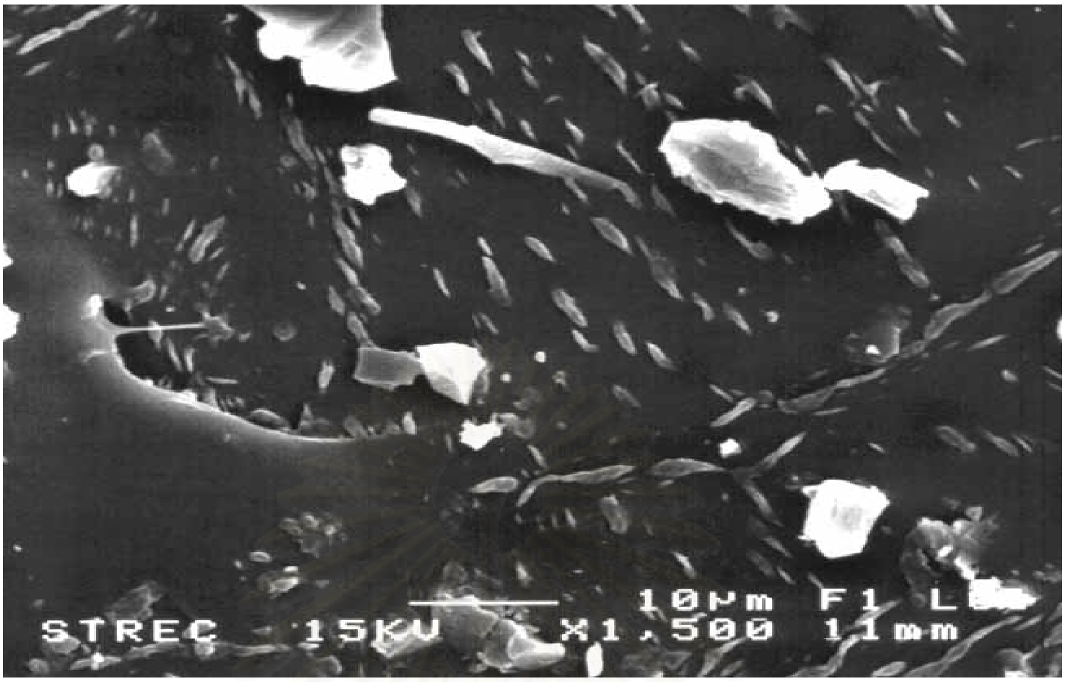
(b)

Figure 5.40 SEM photomicrographic of fractured surface of TPU/PDMS blends at 0.2% of PDMS after base immersion.



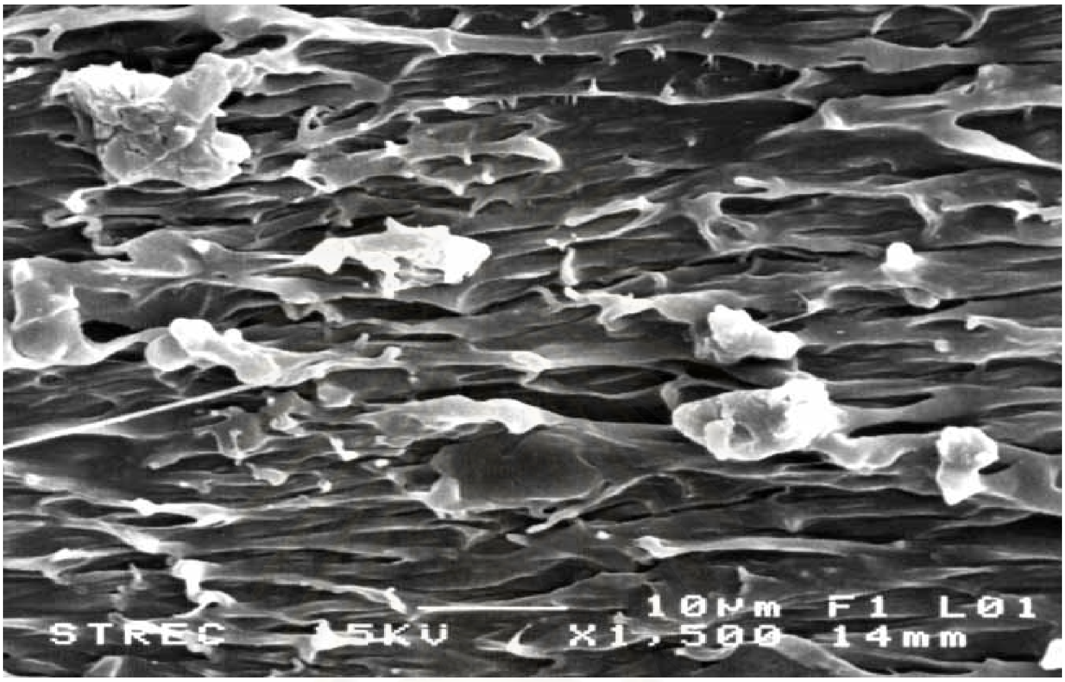
(a)

Figure 5.41 SEM photomicrographic of fractured surface of TPU/PDMS blends at 0.4% of PDMS after base immersion.



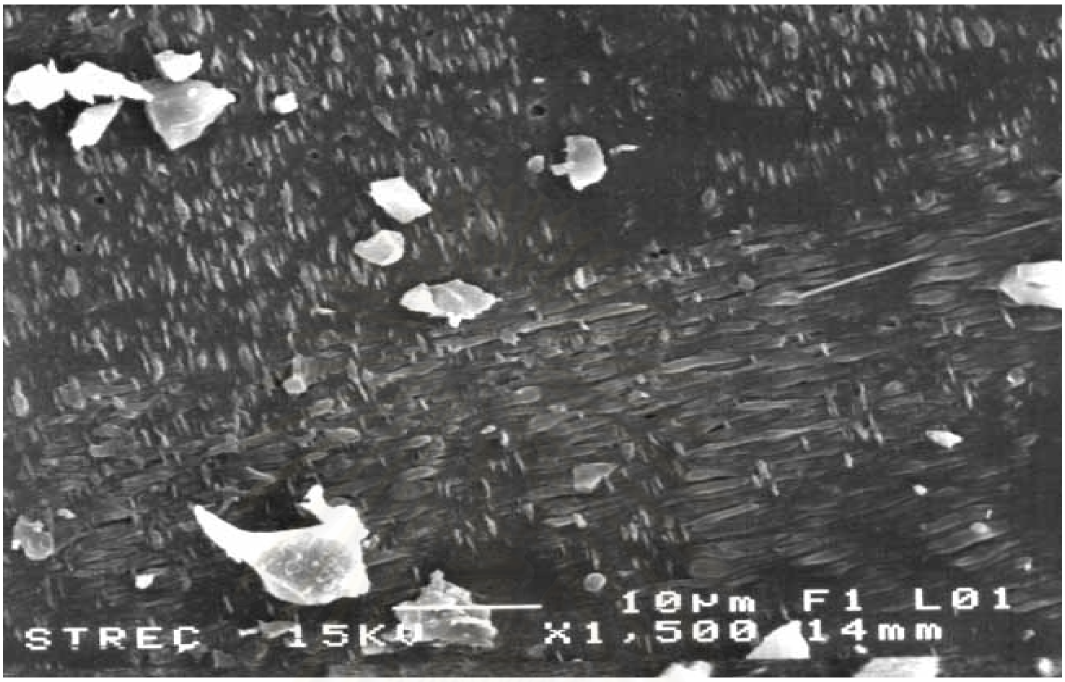
(b)

Figure 5.41 SEM photomicrographic of fractured surface of TPU/PDMS blends at 0.4% of PDMS after base immersion.



(a)

Figure 5.42 SEM photomicrographic of fractured surface of TPU/PDMS blends at 0.8% of PDMS after base immersion.



(b)

Figure 5.44 SEM photomicrographic of fractured surface of TPU/PDMS blends at 0.8% of PDMS after base immersion.

CHAPTER VI

CONCLUSIONS

6.1 TPU/PDMS blends

From the results of the tensile properties of blended TPU, it can be concluded that the ultimate tensile strength of the blended TPU is decreased about 20% while the elongation at break of blended TPU is gradually increased about 30% with increasing PDMS content in the blends from 0.2%-0.8%. Young's modulus of the blended TPU is increased about 40% with increasing PDMS content up to about 0.6% of PDMS. Energy to break of virgin TPU and blended TPU with 0.2% to 0.4% of PDMS is consistent but those with 0.6% to 1.0% of PDMS tend to decrease about 10%.

The resulting phase morphology of the blends shows that TPU/PDMS blends exhibit dispersed phase morphology. PDMS is evident as the dispersed phase in TPU matrix with the average domain size of PDMS at around 0.1-0.7 μm. The domain size of PDMS in the blends becomes smaller for higher PDMS concentration. In case of the fractured surface, there are three different fractured mechanism ocuured. The first mechanism of fibrous characteristic occurred with the virgin TPU. The second mechanism of craze formation with some fibrous characteristic can be observed in the blended TPU at 0.2% and 0.4% of PDMS. The third mechanism of chunky formation without any fibrous characteristic of TPU occurred in the blended TPU with 0.8% of PDMS. It can be concluded that there is an optimum PDMS contents at around 0.6% to 0.8% that has an effect on the tensile properties and a change in the phase morphology of TPU/PDMS blends.

6.2 TPU/PDMS blends after immersion in water and H_2SO_4 solution (3% v/v).

In the study of tensile properties and morphology after immersion in water and acid of TPU/PDMS blends, it can be concluded the water immersion has no effect on the tensile properties of the virgin TPU and blended TPU. In the case of acid immersion, a slight effect of PDMS contents on the acid resistance to the tensile properties can be noticed

The resulting phase morphology of the blends after immersion in H_2SO_4, it can be concluded that acid immersion has an effect on the morphology of blended TPU at some particular PDMS content. Since the fractured structures of blended TPU at all PDMS compositions after acid immersion show fibrous characteristic and craze formation similar to before acid immersion. While the fractured surface of blended TPU at 0.8% of PDMS after acid immersion does not show the mechanism of chunky formation. Thus, difference of morphology before and after acid immersion of blended TPU at 0.8% of PDMS content may support that acid immersion has changed the fractured mechanism of the sample.

6.3 TPU/PDMS blends after immersion in NaOH solution (10% w/v)

In the study of tensile properties and morphology of TPU/PDMS blends after base immersion, it can be concluded that the base immersion, as well as the PDMS contents, has a strong effect on changing the morphology and tensile properties of virgin TPU and blended TPU after tensile testing.

The results of the tensile properties of virgin TPU after base immersion comparing to before base immersion can be concluded that the ultimate tensile strength and energy at break is decreased, the Young’s modulus is increased while the elongation at break is rather consistent. For blended TPU after base immersion comparing to before base immersion, similar trends for each property are noticed when PDMS content in the blend is not more than 0.8%.

The resulting phase morphology of the all blends after immersion in NaOH exhibits very small amount of fibrous characteristic and a large amount of craze formation while there are some small particles detached at the surface. In case of the blended TPU with 0.8% of PDMS, there are a lot of hollows occurred too. The hollows seem to be the result of the particles that come off and separate from the surface.

From the morphology observed and the results on the weight loss and the surface appearance of virgin TPU and blended TPU after base immersion, it is suggested that there is an occurrence of a corrosive reaction between the sample surface and NaOH solution. The corrosive reaction seems to be stronger when PDMS contents in the blended TPU is increased.

6.4 Recommendation

Further study should be focused on:

- The details of the corrosive reaction of TPU and blended TPU with NaOH solution.
- The effect of chemical resistance to tensile properties and morphology of the blends in various time period of immersion.
- It is also of interest to study morphology of the blends by Transmission electron microscopy.

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APPENDICES

APPENDIX A

Raw data on experimental results of virgin TPU and blended TPU

Table A-1 Weight of virgin TPU and blended TPU before and after water immersion.

% PDMS	Weight (g)	
	Before immersion	After immersion in water
0	20.95	21.01
0.2	21.61	21.69
0.4	19.10	19.90
0.6	20.19	20.27
0.8	20.73	20.86
1.0	21.47	21.54

Table A-2 Weight of virgin TPU and blended TPU before and after immersion in H_2SO_4 (3% v/v).

% PDMS	Weight (g)	
	Before immersion	After immersion in H_2SO_4
0	19.72	19.78
0.2	17.53	17.59
0.4	20.22	20.29
0.6	20.32	20.37
0.8	18.69	18.78
1.0	20.24	20.32

Table A-3 Weight of virgin TPU and blended TPU before and after immersion in NaOH (10% w/v)

% PDMS	Weight (g)	
	Before immersion	After immersion in NaOH
0	18.67	15.78
0.2	20.17	18.25
0.4	19.82	17.07
0.6	18.73	16.29
0.8	20.52	17.58
1.0	19.16	16.66

Table A-4 Weight of virgin TPU and blended TPU before and after immersion in H_2SO_4 (30% v/v)

% PDMS	Weight (g)	
	Before immersion	After immersion in H_2SO_4
0	19.19	18.96
0.2	20.35	20.08
0.4	18.82	18.75
0.6	20.18	20.00
0.8	19.43	19.28
1.0	18.81	18.64

Table A-5 Tensile properties of virgin TPU

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	58.7	478.9	2.779	6446
2	61.45	477	2.886	6692
3	66.01	497.4	3.308	5992
4	65.84	494.9	3.567	5438
5	62.34	480.1	4.226	4422
average	62.87	485.7	3.353	5798
S.D.	3.10	9.68	0.583	905.5

Table A-6 Tensile properties of TPU/PDMS blends at 0.2% PDMS

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	56.37	574.8	2.95	6731
2	56.04	556.2	3.176	6334
3	52.66	571.5	3.154	6171
4	45.61	573.9	3.253	5490
5	43.59	568.1	3.424	4484
average	50.85	568.9	3.191	5842
S.D.	5.93	7.56	0.172	881.57

Table A-7 Tensile properties of TPU/PDMS blends at 0.4% PDMS

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	48.16	607	3.454	6105
2	53.09	602.7	3.595	6144
3	59.78	608	4.285	5954
4	60.5	613.4	4.42	5492
5	56.88	614.7	4.671	5084
average	55.68	609.2	4.085	5756
S.D.	5.12	4.91	0.532	456.3

Table A-8 Tensile properties of TPU/PDMS blends at 0.6% PDMS

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	52.09	624.4	4.144	5665
2	62.21	619.1	4.112	6135
3	55.15	630.2	4.993	4641
4	52.48	618.2	5.336	3958
5	64.76	619.8	4.859	5308
average	57.34	622.3	4.689	5141
S.D.	5.80	5.00	0.541	857.3

Table A-9 Tensile properties of TPU/PDMS blends at 0.8% PDMS

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	52.09	637.7	3.807	5322
2	48.96	681.7	3.346	6636
3	47.57	615.6	4.022	4695
4	54.32	613.1	4.927	4297
5	53.39	628.8	4.591	4888
average	51.26	635.4	4.1386	5167.6
S.D.	2.89	27.76	0.628	899.93

Table A-10 Tensile properties of TPU/PDMS blends at 1.0% PDMS

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	60	626.3	4.233	5551
2	64.15	601.1	4.685	5193
3	56.54	560.9	4.76	4427
4	61.98	561.4	3.619	5195
5	62.2	556.1	3.793	5266
average	60.974	581.16	4.218	5126.4
S.D.	2.88	31.08	0.513	417.75

Table A-11 Tensile properties of virgin TPU after water immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	57.91	472.3	3.373	5771
2	64.2	475.4	3.55	5719
3	56.17	482.7	2.941	6988
4	56.92	476.2	3.392	5852
5	61.46	474.8	3.23	5965
Average	59.33	476.3	3.297	6059
S.D.	3.39	3.87	0.229	527.6

Table A-12 Tensile properties of TPU/PDMS blends at 0.2% PDMS after water immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	62.62	502.8	3.086	7074
2	56.87	485.8	3.073	7130
3	59.22	486.9	3.217	6549
4	59.89	486.9	3.087	7000
5	62.22	489.2	3.542	5850
Average	60.164	490.32	3.201	6720.6
S.D.	2.3	7.09	0.200	538

Table A-13 Tensile properties of TPU/PDMS blends at 0.4% PDMS after water immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	58.51	507.8	3.997	5248
2	56.88	501.5	4.412	4968
3	61.82	503.2	4.51	4948
4	58.65	507.2	3.481	6133
5	61.35	507.2	4.013	5286
Average	59.44	505.4	4.083	5316
S.D.	2.08	2.84	0.41	482.1

Table A-14 Tensile properties of TPU/PDMS blends at 0.6% PDMS after water immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	56.1	514.1	3.743	5526
2	51.8	508.9	3.572	6407
3	56.93	518.9	4.249	5103
4	61	511.6	3.748	6119
5	70.44	531.8	8.704	4459
Average	59.254	517.06	4.8032	5522.8
S.D.	7.05	9.03	2.20	781.9

Table A-15 Tensile properties of TPU/PDMS blends at 0.8% PDMS after water immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	61.89	490.8	3.999	5485
2	70.03	471.6	4.741	4854
3	60.83	484.1	3.923	5591
4	57.95	476	4.45	4528
5	61.41	479.5	4.145	5499
Average	62.422	480.4	4.2516	5191.4
S.D.	4.52	7.41	0.34	472.9

Table A-16 Tensile properties of TPU/PDMS blends at 1.0% PDMS after water immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	52.93	527.3	3.326	5870
2	61.54	503.2	4.501	4720
3	50.9	509.5	3.213	6155
4	49.03	500.8	3.115	6083
5	57.41	529.2	3.662	5633
Average	54.362	514	3.5634	5692.2
S.D.	5.08	13.41	0.563	580.4

Table A-17 Tensile properties of virgin TPU after acid immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	55.71	555.9	2.974	6653
2	60.94	533.5	3.678	5337
3	64.64	544.7	3.455	6260
4	46.39	531	2.729	6088
5	62.77	541.1	2.92	7196
Average	58.09	541.2	3.15	6306.8
S.D.	7.34	9.90	0.4	689.40

Table A-18 Tensile properties of TPU/PDMS blends at 0.2% PDMS after acid immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	55.11	557.3	3.686	5250
2	50.72	529.1	2.973	6002
3	66.72	549.8	4.506	5174
4	55.99	535.2	3.29	5727
5	53.56	535.3	3.132	5695
Average	56.42	541.3	3.52	5569.6
S.D.	6.10	11.73	0.613	348.6

Table A-19 Tensile properties of TPU/PDMS blends at 0.4% PDMS after acid immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	61.37	573.2	3.094	6670
2	57.65	580.7	5.665	7951
3	62.55	560.5	2.887	7587
4	57.84	561	2.853	7839
5	61.59	583.6	2.76	8602
Average	60.20	571.8	3.45	7729.8
S.D.	2.29	10.78	0.161	700.9

Table A-20 Tensile properties of TPU/PDMS blends at 0.6% PDMS after acid immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	63.18	583	2.827	7948
2	58.19	575.5	2.749	7583
3	60.39	568.3	2.935	7102
4	62.87	555.1	3.2	6640
5	61.92	529.8	3.739	5447
Average	61.31	562.3	3.09	6944
S.D.	2.05	20.90	0.401	971.4

Table A-21 Tensile properties of TPU/PDMS blends at 0.8% PDMS after acid immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	59.78	493.2	5.02	4408
2	61.54	516.3	3.147	6971
3	67.96	538	4.088	6019
4	62.32	527.4	3.373	6414
5	51.77	498.1	3.016	6601
Average	60.67	514.60	3.73	6082.60
S.D.	5.84	19.0	0.832	997.0

Table A-22 Tensile properties of TPU/PDMS blends at 1.0% PDMS after acid immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	59.83	536.7	4.285	5523
2	66.3	538	3.927	6070
3	62.52	534.9	3.223	6871
4	58.04	525.4	3.451	6333
5	55.93	516	3.476	5804
Average	60.52	530.20	3.67	6120.2
S.D.	4.03	9.35	0.427	516.8

Table A-23 Tensile properties of virgin TPU after base immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	33.66	479.5	10.95	1815
2	40.3	492.3	8.083	2652
3	35.84	480	5.887	2803
4	35.96	494.6	9.199	2400
5	38.04	488.8	4.709	3279
Average	36.76	487.04	7.766	2590
S.D.	2.51	6.97	2.51	538.7

Table A-24 Tensile properties of TPU/PDMS blends at 0.2% PDMS after base immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	41.28	494.7	3.778	3819
2	42.75	499.3	3.737	4079
3	44.85	495.5	3.734	4208
4	44.56	494.2	3.284	4568
5	44.69	500.9	3.158	4502
Average	43.626	496.92	3.5382	4235
S.D.	1.56	2.99	0.29	308.3

Table A-25 Tensile properties of TPU/PDMS blends at 0.4% PDMS after base immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	40.94	476.2	6.174	2960
2	40.45	471.4	6.297	3091
3	43.72	478.2	5.022	3384
4	39.38	453.1	4.856	3171
5	44.92	481	5.428	3315
Average	41.88	471.98	5.555	3184
S.D.	2.33	11.12	0.66	170.41

Table A-26 Tensile properties of TPU/PDMS blends at 0.6% PDMS after base immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	44.93	488.4	3.33	4870
2	39.86	482.5	3.514	4151
3	44.31	476.2	4.816	3568
4	40.23	476	4.682	3372
5	44.77	489.7	3.209	4620
Average	42.82	482.56	3.91	4116.2
S.D.	2.55	6.49	0.77	647.6

Table A-27 Tensile properties of TPU/PDMS blends at 0.8% PDMS after base immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	35.34	439.4	5.373	2762
2	39.51	456.9	5.277	3004
3	42.22	478.8	5.621	3251
4	35.64	439.4	5.983	2655
5	39.94	479.3	8.010	2873
Average	38.53	458.8	6.053	2909
S.D.	2.96	19.85	1.13	230.98

Table A-28 Tensile properties of TPU/PDMS blends at 1.0% PDMS after base immersion

No. of sample	Ultimate tensile strength (MPa)	% Elongation at break (%)	Young's modulus (MPa)	Energy to break (N-mm)
1	30.87	459.7	8.892	1961
2	29.08	449.6	8.219	2264
3	35.29	478.8	4.677	2694
4	30.49	460.6	9.06	2033
5	32.99	464.7	5.478	2579
Average	31.74	462.68	7.265	2306
S.D.	2.43	10.59	2.04	324.2

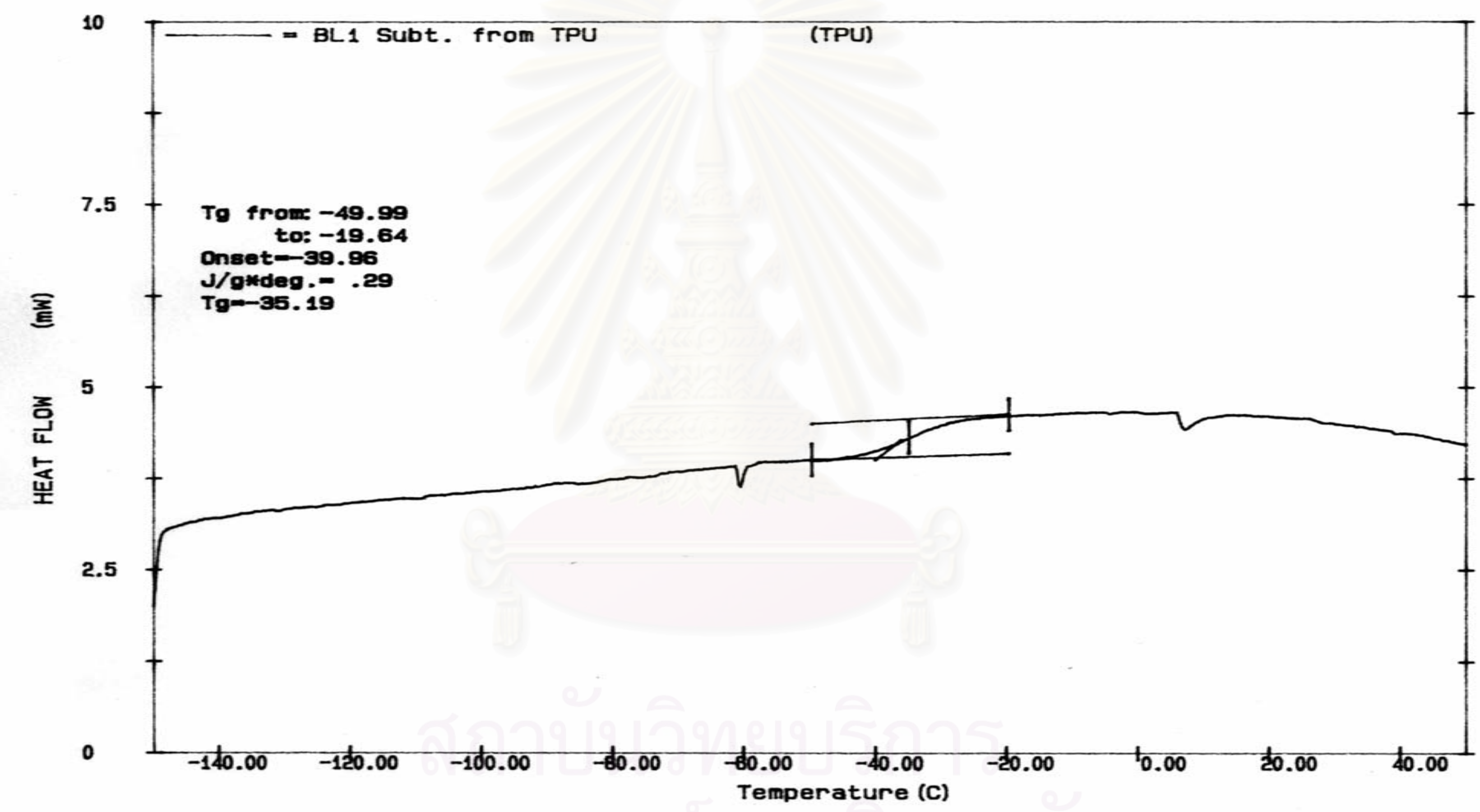


Figure A-1 DSC thermogram of thermoplastic polyurethane from the first heating cycle.

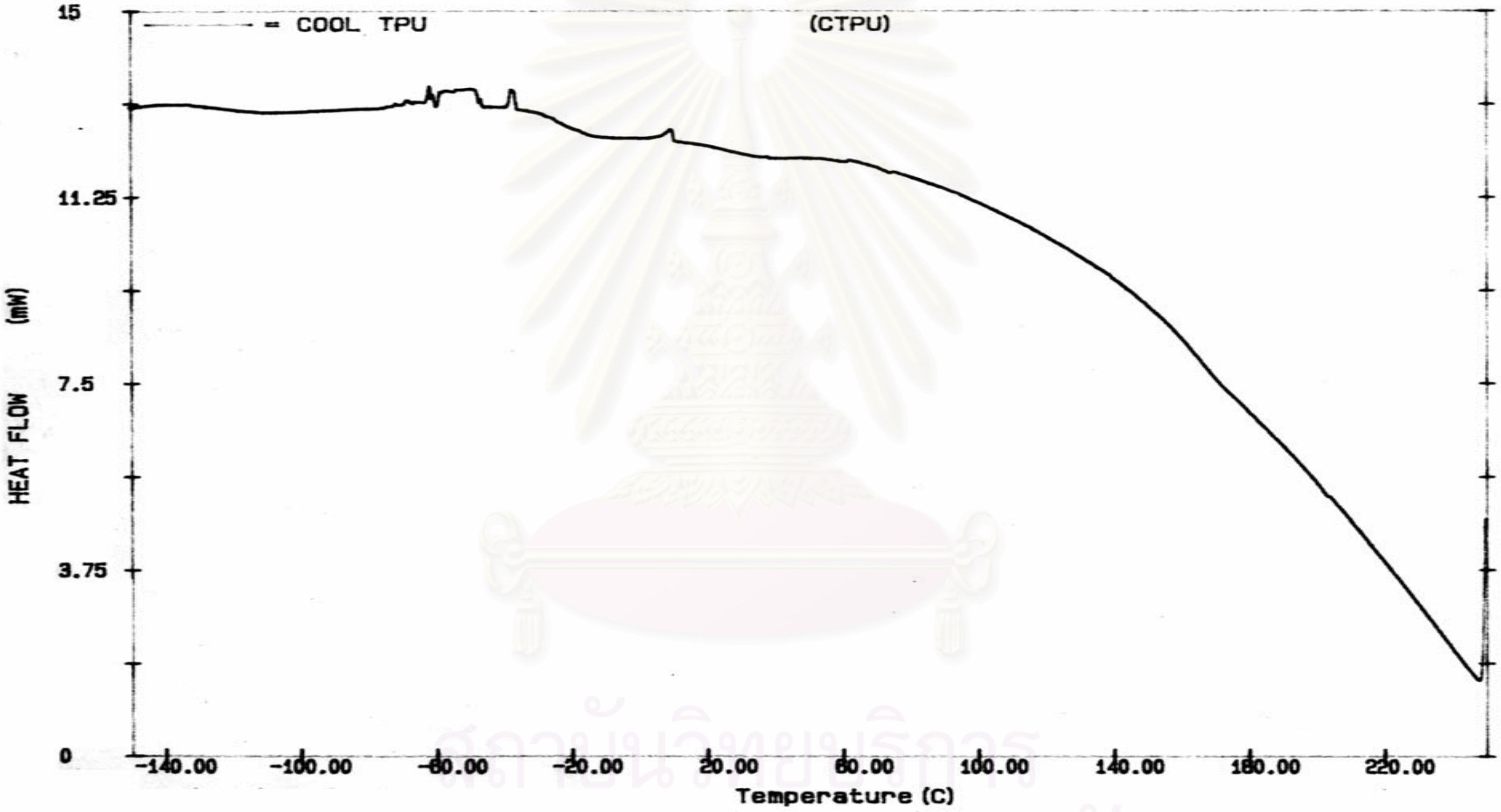


Figure A-2 DSC thermogram of thermoplastic polyurethane from the cooling cycle.

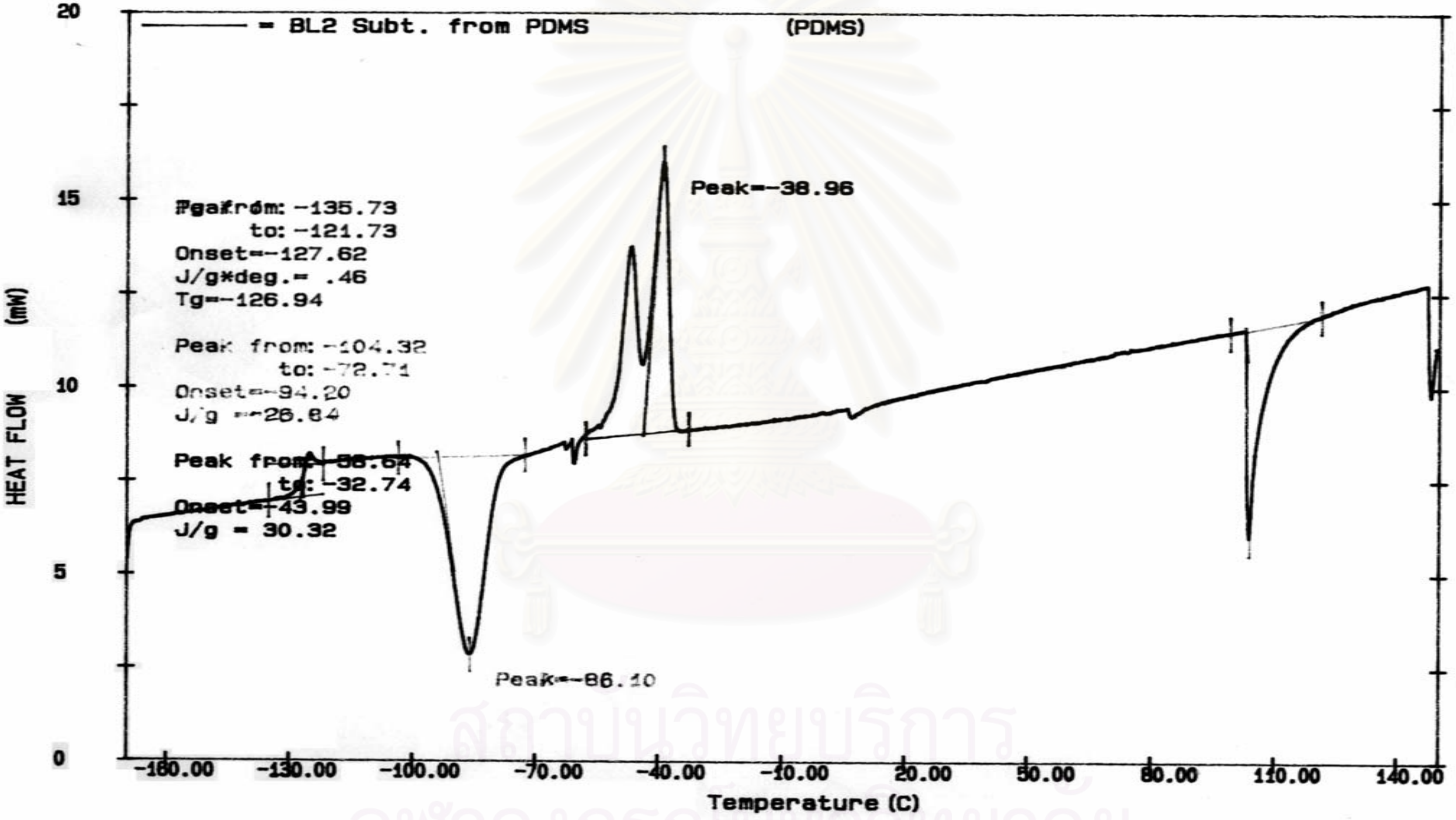


Figure A-3 DSC thermogram of polydimethylsiloxane from the first heating cycle.

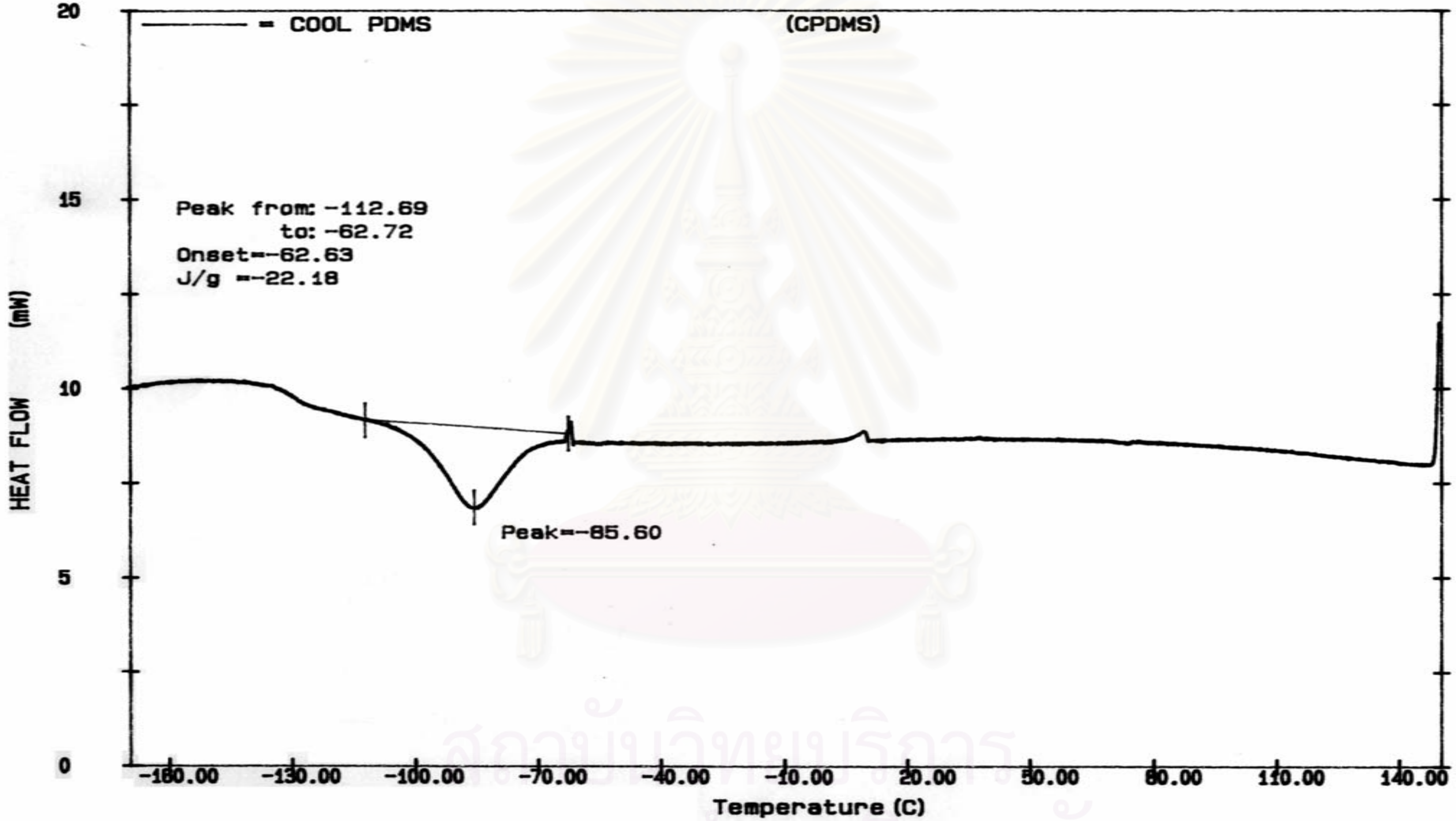


Figure A-4 DSC thermogram of polydimethylsiloxane from the cooling cycle.

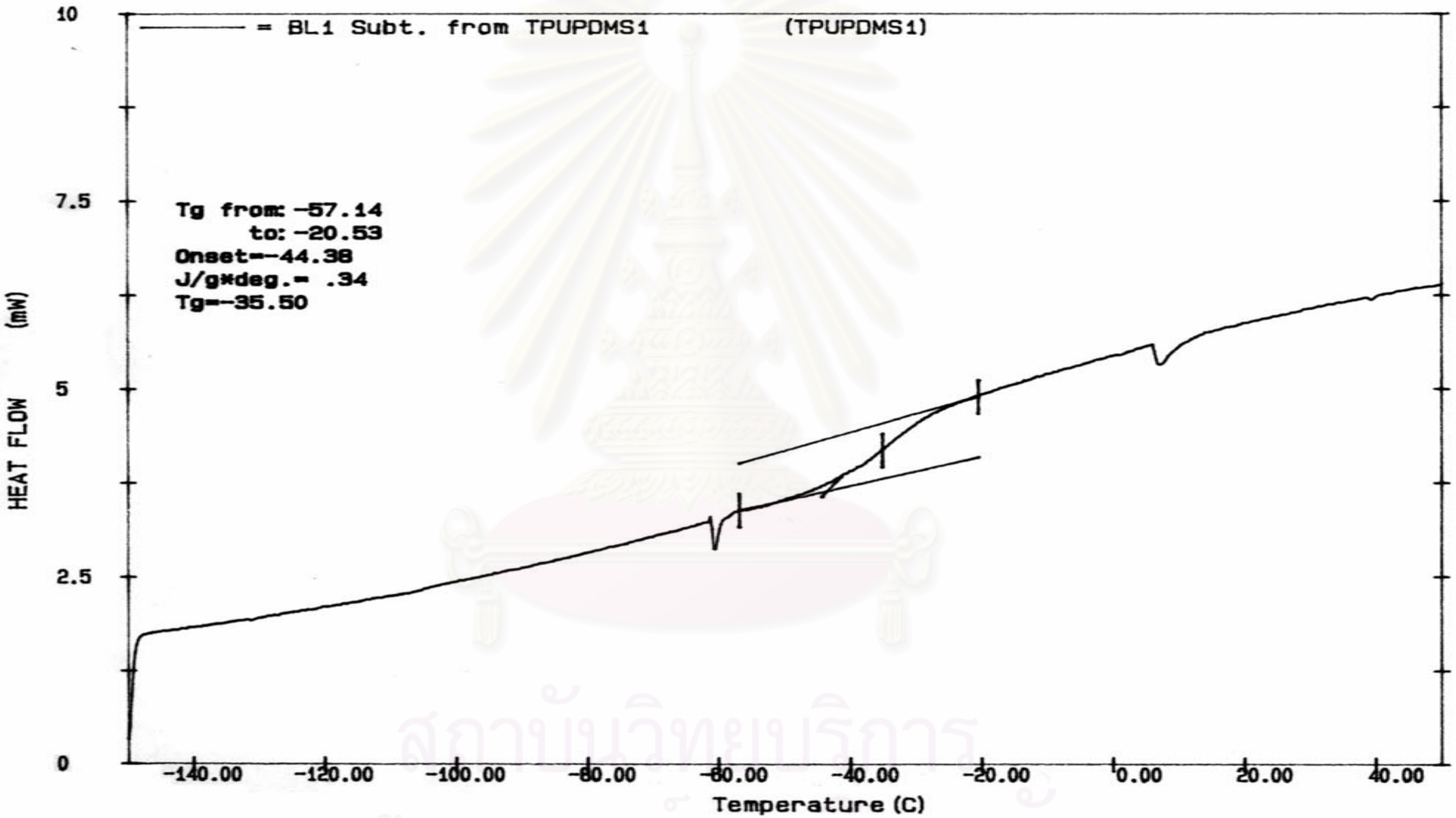


Figure A-5 DSC thermogram of TPU/PDMS blends at 1% of PDMS from the first heating cycle.

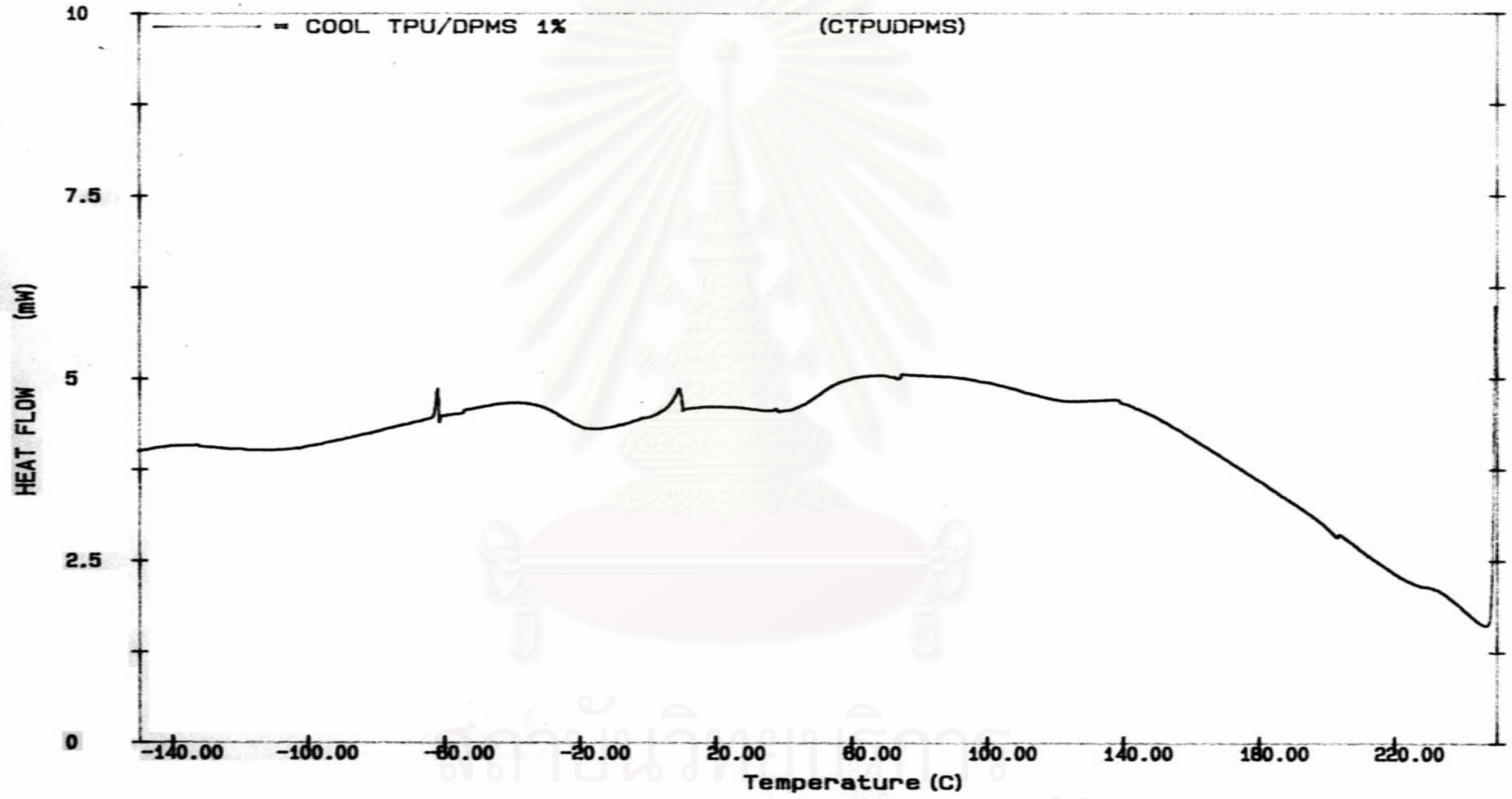


Figure A-6 DSC thermogram of TPU/PDMS blends at 1% of PDMS from the cooling cycle.

Appendix B

Error analyses

Most experimental data in this thesis are reported with the error bar of 95 % confidence. It should be noted that the 95% confidence interval or 0.95 confidence coefficient in fact means if it is assumed that the distribution is the normal probability distribution, 95% of data fall within this region. The value can be defined as;

$$t_{.025}\left(\frac{\sigma}{\sqrt{n}}\right) \qquad \text{(A-1)}$$

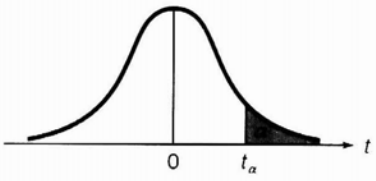
where $t_{.025}$ is the standard normal value of t.025 at the degree of freedom of (n-1), as can be seen in figure A-1.

σ is standard deviation

n is number of data

For example

From tensile test, it appears that the standard deviation of the ultimate tensile strength of virgin TPU is 3.097 and the number of specimen is five. At the column of $t_{.025}$ and the degree of freedom of 4 in figure A-1, it gives 2.776. The value of 95% confidence therefore is 3.845.



ν	$t_{.100}$	$t_{.050}$	$t_{.025}$	$t_{.010}$	$t_{.005}$	$t_{.001}$	$t_{.0005}$
1	3.078	6.314	12.706	31.821	63.657	318.31	636.62
2	1.886	2.920	4.303	6.965	9.925	22.326	31.598
3	1.638	2.353	3.182	4.541	5.841	10.213	12.924
4	1.533	2.132	2.776	3.747	4.604	7.173	8.610
5	1.476	2.015	2.571	3.365	4.032	5.893	6.869
6	1.440	1.943	2.447	3.143	3.707	5.208	5.959
7	1.415	1.895	2.365	2.998	3.499	4.785	5.408
8	1.397	1.860	2.306	2.896	3.355	4.501	5.041
9	1.383	1.833	2.262	2.821	3.250	4.297	4.781
10	1.372	1.812	2.228	2.764	3.169	4.144	4.587
11	1.363	1.796	2.201	2.718	3.106	4.025	4.437
12	1.356	1.782	2.179	2.681	3.055	3.930	4.318
13	1.350	1.771	2.160	2.650	3.012	3.852	4.221
14	1.345	1.761	2.145	2.624	2.977	3.787	4.140
15	1.341	1.753	2.131	2.602	2.947	3.733	4.073
16	1.337	1.746	2.120	2.583	2.921	3.686	4.015
17	1.333	1.740	2.110	2.567	2.898	3.646	3.965
18	1.330	1.734	2.101	2.552	2.878	3.610	3.922
19	1.328	1.729	2.093	2.539	2.861	3.579	3.883
20	1.325	1.725	2.086	2.528	2.845	3.552	3.850
21	1.323	1.721	2.080	2.518	2.831	3.527	3.819
22	1.321	1.717	2.074	2.508	2.819	3.505	3.792
23	1.319	1.714	2.069	2.500	2.807	3.485	3.767
24	1.318	1.711	2.064	2.492	2.797	3.467	3.745
25	1.316	1.708	2.060	2.485	2.787	3.450	3.725
26	1.315	1.706	2.056	2.479	2.779	3.435	3.707
27	1.314	1.703	2.052	2.473	2.771	3.421	3.690
28	1.313	1.701	2.048	2.467	2.763	3.408	3.674
29	1.311	1.699	2.045	2.462	2.756	3.396	3.659
30	1.310	1.697	2.042	2.457	2.750	3.385	3.646
40	1.303	1.684	2.021	2.423	2.704	3.307	3.551
60	1.296	1.671	2.000	2.390	2.660	3.232	3.460
120	1.289	1.658	1.980	2.358	2.617	3.160	3.373
∞	1.282	1.645	1.960	2.326	2.576	3.090	3.291

From Mendenhall, W. and Sincich, T., " A Second Course in Statistics: Regression Analysis", 5th edition, Prentice-Hall International, New Jersey, 1996.

Figure B-1 Critical value for student's t

CURRICULUM VITAE

Miss Ratirat Sinweeruthai was born in Samutsakhon, Thainland on July 2, 1975. She graduated the secondary school from Samutsakhonburana School in Bangkok and received the Bachelor degree of Chemical Engineering, Kasetsart University, Thailand in 1997. She entered the Master of Engineering in Chemical Engineering Program at Chulalongkorn University in 1998.