เยื่อแผ่นกราฟต์โคพอลิเมอร์ของยางธรรมชาติ/เมทิลเมทาคริเลต สำหรับการแยกน้ำมันหล่อลื่นใช้แล้ว

นางวรรณี อู่ไพบูรณ์

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หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
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NATURAL RUBBER/METHYL METHACRYLATE GRAFT COPOLYMER MEMBRANE FOR USED LUBRICATING OIL SEPARATION

Mrs. Wannee Aupaiboon

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for the Degree of Master of Science in Petrochemistry and Polymer Science
Program of Petrochemistry and Polymer Science
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By : Mrs. Wannee Aupaiboon
Field of Study : Petrochemistry and Polymer Science
Thesis Advisor : Associate Professor Amorn Petsom, Ph.D.

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

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วรรณี อู่ไพบูรณ์ : เยื่อแผ่นกราฟต์พอลิเมอร์ของยางธรรมชาติ/เมทิลเมทาคริเลตสำหรับ
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GRAFT COPOLYMER MEMBRANE FOR USED LUBRICATING OIL SEPARATION)
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วัตถุประสงค์ของงานวิจัยนี้คือ เตรียมเยื่อแผ่นกราฟต์โคพอลิเมอร์ของยางธรรมชาติ(NR)/เมทิลเมทาคริเลต(PMMA)สำหรับการแยกน้ำมันหล่อลื่นใช้แล้ว เตรียมเยื่อแผ่นโดยใช้กระบวนการพอลิเมอไรเซชันในภาวะอิมัลชัน พิสูจน์ผลิตภัณฑ์ที่ได้ด้วยฟูเรียทรานฟอร์มอินฟราเรดสเปกโทรสโกปี และการหาประสิทธิภาพของการกราฟต์ นำยางธรรมชาติกราฟต์ด้วยพอลิเมทิลเมทาคริเลตที่ได้วัลคา-ไนท์ด้วยซัลเฟอร์ทำเป็นแผ่นฟิล์มอบที่อุณหภูมิ 115 องศาเซลเซียส 10 นาที เตรียมฟิล์มที่อัตราส่วนต่างๆของ PMMA: NR เพื่อศึกษาอัตราส่วนPMMAต่างๆมีต่อสมบัติของฟิล์ม สมบัติที่ทำการศึกษาคือ การเกิดฟิล์มใช้การตรวจพินิจ ศึกษาลักษณะผิวหน้าของแผ่นฟิล์ม โดยวิธีSEM ศึกษาความคงทนต่อตัวทำละลายเฮกเซนและน้ำมันหล่อลื่น โดยวิธีวัดการบวมของเยื่อแผ่น ศึกษาความสามารถในการซึมผ่านของน้ำมันหล่อลื่นด้วยวิธีการดูดซับ แยกน้ำมันหล่อลื่นใช้แล้วด้วยวิธีไดอไลซิส ศึกษาผลของความเข้มข้นของน้ำมันที่ใช้แยกต่อปริมาณน้ำมันที่แยกได้ต่อปริมาณออสโมซิสและต่อปริมาณน้ำมันที่แยกได้เมื่อคิดเป็นเปอร์เซ็นต์ หลังจากนั้นนำน้ำมันที่ได้มาวิเคราะห์คุณสมบัติทางเคมีและทางฟิสิกส์ เปรียบเทียบสมบัติกับมาตรฐานผลิตภัณฑ์อุตสาห-กรรมสำหรับน้ำมันพื้นฐานแปรใช้ใหม่

จากการศึกษาพบว่าปริมาณ PMMA มีผลต่อสมบัติของฟิล์มคือ ที่ปริมาณ PMMA มากกว่า22.5 เปอร์เซ็นต์การเกิดฟิล์มจะยากขึ้นและเกิดการแตกได้ง่าย ปริมาณ PMMA ยิ่งมากยิ่งทำให้ผิวหน้าของฟิล์มเกิดรูพรุนมากขึ้น มีความคงทนต่อตัวทำละลายเฮกเซนและน้ำมันมากขึ้น ความสามารถในการซึมผ่านของน้ำมันผ่านเยื่อแผ่นแสดงด้วยค่าสัมประสิทธิ์การแพร่และสัมประสิทธิ์การซึมผ่าน ซึ่งมีค่ามากขึ้นตามความพรุนที่มากขึ้น กลไกการซึมผ่านเป็นแบบ anomalous เยื่อแผ่นที่มีสมบัติเหมาะสมนำไปใช้ในการแยกน้ำมันใช้แล้วคือที่ 31:69 PMMA:NR วัลคาไนท์ด้วยซัลเฟอร์จากกระบวนการ ไดอไลซิสพบว่าปริมาณน้ำมันที่ได้และปริมาณออสโมซิสแปรผันตามความเข้มข้นแต่ปริมาณน้ำมันที่ได้เมื่อคิดเป็นเปอร์เซนต์จะแปรผกผันกับความเข้มข้น เมื่อศึกษาสมบัติทางเคมีและทางฟิสิกส์ของน้ำมันที่ได้พบว่าสามารถกำจัดตะกอน สารแขวนลอย น้ำและสิ่งปนเปื้อนต่างๆได้ 70-80% สามารถนำน้ำมันกลับมาใช้ใหม่ได้ถึง75% เมื่อผ่านการกรองด้วยดินเคลือบด้วยด่าง และสารดูดซับกลิ่นและสี ได้น้ำมันหล่อลื่นที่มีสมบัติตามผลิตภัณฑ์มาตรฐานอุตสาหกรรม

ภาควิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....
สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา ....
ปีการศึกษา 2545

##4372392223 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD : USED LUBRICATING OIL/ MEMBRANE/NATURAL RUBBER GRAFTED PMMA/ RE-REFINED USED OIL/ DIALYSIS

WANNEE AUPAIBOON : NATURAL RUBBER/METHYL METHACRYLATE GRAFT COPOLYMER MEMBRANE FOR USED LUBRICATING OIL SEPARATION. THESIS ADVISOR : ASSOC. PROF. AMORN PETSOM, Ph.D., 78 pp. ISBN 974-17-3210-4

The objective of this research was to prepare natural rubber/ methyl methacrylate copolymer membrane for used in lubricating oil separation. The graft copolymerizations of Polymethyl methacrylate on NR (NR-g-PMMA) was prepared by emulsion polymerization process. Fourier transform infrared spectroscopy (FT-IR) and graft efficiency was used to verify the modified products. NR-g-PMMA latex was vulcanized with sulfur. Casting films of NR-g-PMMA were cured at 115°C for 10 min. NR-g-PMMA films were prepared with various ratios of the components. The effect of ratio of PMMA on the properties of film were studied *i. e*., film forming by specific appearance, surface of films by scanning electron microscope (SEM), durability in hexane and lubricating oil by swelling method, transportation properties by gravimetric sorption. The used lubricating oil was separated by dialysis process. The effect of concentration of initial oil to dialysate oil, osmosis volume, and percent dialysate oil were studied. Finally, the chemical and physical properties of the dialysate oil were compared with re-refined base oil standard of Thailand Industry Standard Institute.

The study showed that the amount of PMMA had affected on quality of films. It was found that at high ratio of PMMA to NR more than 22.5% of film exhibited the decrease of film forming ability. Increasing of the ratio of PMMA to NR induced the roughness surface of film. The durability in solvent was improved. The transportation properties showed in term of diffusion coefficient (D) and permeability coefficient (P) were higher and varied with the roughness of surface. The transport mechanism of film was anomalous-type diffusion. The ratio of PMMA: NR vulcanized with sulfur membrane that suitable for membrane separation process was at 31:69 The dialysis process indicated that the concentration was proportional to dialysate oil and osmosis volume, but inverse proportional with percentage of dialysate oil. The chemicals and physicals properties of dialysate oil showed that the contaminant could be reduced by 70-80%. The oil recovery was 75%. When percolation oil through caustic-treated clay and pass to absorption clay, the re-refined oil met the specification of re-refined base oil standard.

Program Petrochemistry and Polymer Science Student's signature…………….
Field of study Petrochemistry and Polymer Science Advisor's signature……………
Academic year…2002….

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Ultimately, I would like to praise to my family for their love, willpower and understanding.

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ABBREVIATIONS

NR	Natural rubber
NR(HA)	Natural rubber (high ammonia)
MMA	Methyl methacrylate
PMMA	Poly(methyl methacrylate)
d. r. c.	Dry rubber content
FT-IR	Fourior Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
GE	Grafting efficiency
TBHP	*tert*-Buthyl hydroperoxide
TEPA	Tetraethylene pentamine
ASTM	The American Society for Testing and Materials
TISI	Thai Industrial Standard Institute

CHAPTER I

INTRODUCTION

1.1 The purpose of the investigation

Used oil is referred to oil remain from internal combustion engines, gear box and differentials whose physicals and chemical properties have changed such that it cannot be used for its original purpose. Used oil can contain up to 15 to 20% of impurities such as water, sludge, carbonaceous particle and oxidation products.[1] Huge quantities of this oil, is actually contributing to the increased pollution of our waterways and land because indiscriminate dumping. There are basically two types of reclaiming facilities including reprocessors and re-refiners. Reprocessors use mild processing techniques to produce partially cleaned fuel oil. In general, the type of treatment employed by reprocessors does not remove all the contaminants found in used oil. Generally, the used oil contains 0.5 wt.% of ash residue after combustion. For reuse as fuel, this ash creates air pollution concerns. In comparison, the principle product of a re-refiner is clean oil, which used primarily as lubricating base oil. The crankcase fluid is possible to re-refined oil if the contaminants and/or the color are improved. The cleaned oil can then be reformulated with the required additives to meet specification. There are several processes available for the re-refining of the used oil such as an acid/clay treatment, membrane-based filtration, solvent extraction and distillation/ hydrotreatment but only a small volume of the used oil is cleaned for this purpose due to (1) the significant capital investment requirement, (2) potential secondary pollution, and/or (3) substantial operating cost for re-refining the used oil.

Acid/clay treatment is one of the most commonly used oil recovery process,[2] which used chemical treatment process. This process make used of sulfuric acid, they yield sulfuric mud which constitute a by product which cannot be easily treated or removed without introducing another source of pollution, the corrosion problems, and the maintenance costs. Membrane separation is an interesting process for replacement of conventional process because it used physical process which is sufficiently efficient to provide for the easy and non polluting regeneration. In term of energy, this process used less energy than other processes and the investment cost is lower than those of other processes. Generally, there are two kinds of industrial membrane *i.e.*, polymer and ceramic membrane. Their costs are very expensive and must imported from aboard. It is not suitable for re-refining because used oil is very dirty and easy to form gel, which resulted in the surface fouling of membrane. Therefore its lifetime is reduced and it does not appropriate with its cost. To reduce the production cost, it ought to use less expensive membrane. Natural rubber (NR) is an interesting material because it is low price and available in large quantity. NR is a resource of Thailand that has high potential of production each year. The two major requirements of membrane in re-refining process are durable in oil and process solvent and has molecular weight cut off suitable for impurity separation. But the disadvantage of NR is its little resistance to nonpolar solvent. So the improvement in oil resistant of NR by grafting with polar polymer such as polymethyl methacrylate (PMMA) is chosen which resulted in high hydrophilicity and its appropriate properties.

In this research, the property of NR was improved by grafting with PMMA. The synthesis, characterization and transportation properties of NR-g-PMMA membrane will be investigated. The suitable membrane will be used to re-refining used oil by dialysis process. The physical and chemical properties of re-refine oil were also investigated and compared with the re-refine base oil standard of Thailand (TISI standard).

1.2 Objectives

The objectives of this research are as the followings:

1. To prepare polymethyl methacrylate grafted natural rubber by emulsion polymerization method.
2. To study the degree of monomer conversion, grafting efficiency and properties of grafted natural rubber.
3. To develop the efficient method for re-refined waste lubricating oils using polymethylmethacrylate grafted natural rubber membrane in dialysis process.
4. To test the quality of re-refining base oil from dialysis process.

1.3 Scope of the investigation

1. Literature reviews
2. Experimental
3. Preparation of the NR-g-PMMA by emulsion polymerization method.
4. Suitable properties of membrane were determined by varying amount of monomer.
5. Durability of membrane was evaluated by swelling of the membrane in hexane and lubricating oil.
6. Porosity of membrane was investigated by SEM
7. Transport properties of membrane was investigated by sorption gravimetric method
8. Re-refining used oil was investigated by dialysis process
9. Analytical quality was investigated of re-refining oil
10. Data analysis and discussion

CHAPTER Ⅱ

THEORY AND LITERATURE REVIEW

2.1 Natural rubber latex

The natural rubber (NR) latex [3] is obtained in latex form produced by certain plants and trees (field latex). Generally it has a dry rubber content (d.r.c.) of about 30% to 40%. Although field latex can be preserved with ammonia or fixed alkali, its low rubber content and high non rubber solid content severely limit its usefulness. Hence it is necessary to increase the d.r.c. in NR latex to 60% or more to improve the economics of transportation. Concentrated latex tends to be more uniform in quality than do field latices. This due in part to the partial removal of non-rubber constituents in several concentration processes. Four methods are used for concentrating natural rubber latex; centrifugation, creaming, evaporation and eletrodecantation. Of these processes, centrifugation is the most widely used.

The commercial product is obtained exclusively from the tree Hevea brasiliensis. The hydrocarbon component of NR consists of over 99.9% of linear long chain *cis*-1,4-polyisoprene, $-CH_2-C(CH_3)=CH-CH_2-$. NR has molecular weight in the range of 10^4 to 10^7. There is one double bond for each isoprene unit. These double bonds and the 2-methylene groups are reactive groups for vulcanization reaction with sulfur. After vulcanization, the vulcanized rubber had better quality such as high impact strength, low T_g and flexibility. It also has many inferior properties, for example, low hardness, stiffness, abrasion tear resistance and little resistance to swelling in nonpolar solvents. Increasing the volume of NR vulcanizates several hundreds percent when contact with mineral oil. Consequently, these inferior properties have to be improved by adding fillers, graft or blend with polymer.

2.2 Polymethyl methacrylate (PMMA) [4]

PMMA is polymerized by solution, suspension, and emulsion processes. PMMA is completely amorphous but has high strength and excellent dimensional stability due to the rigid polymer chain (T_g =105^{O}C). The structure of PMMA is shown in Figure 2.1

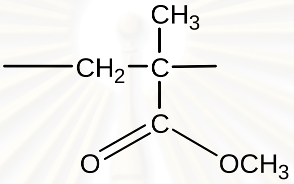


Figure 2.1 Structure of Polymethyl methacrylate (PMMA)

The best known and remarkable property of PMMA is probably its excellent transparency. PMMA is the most resistant of all transparent plastics to ultraviolet radiation and moisture. The outstanding transparency, light piping qualities, colorability, and dimensional stability of PMMA coupled with the retention of these properties in outdoor applications over long periods of time make this resin useful in many industries. The chemical resistance of PMMA, for example the effect of various environments upon the acrylics in general, it is essentially unaffected by weak solutions of oxidizing acids, but deteriorates rapidly in highly concentrated solutions of oxidizing acids.

PMMA is used for aviation parts, including pilot’s canopies and windows on commercial aircraft because it is free from optical distortion, resistance to light and weathering, resistance to shuttering and able to withstand high pressure and temperature differentials. Other uses include safety glass interlaying, glazing, dentures, contact lenses and various coatings and finishes.

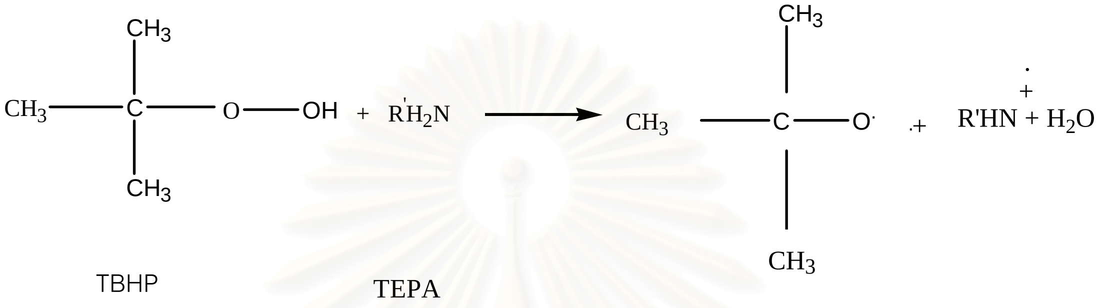
2.3 Polymeric modification[5]

Natural rubber graft-copolymerization with polymethyl methacrylate (NR-g-PMMA) is the process of "grafting" polymer side chains onto natural rubber. Polymerization of methyl methacrylate monomers can be carried out in the presence of solid rubber, rubber in solution, or in latex. One important motivation has been the desire to produce rubber which, when vulcanized, swells less when in contact with hydrocarbon oils than do vulcanizates from unmodified natural rubber. Natural rubber graft-copolymerization with polymethyl methacrylate is the most important product has been a self-reinforced rubber. This product finds used in applications which require a hard rubber with optimum properties such as tensile strength and impact strength, and where the use of reinforcing carbon black is undesirable. NR-g-PMMA is in a commercial product known as “Heavea Plus MG “ and it can be used in latex form or in solution as an adhesive or bonding agent for rubber to poly(vinyl chloride), textiles and leather. It blends readily with NR and can be processed on conventional rubber machinery and vulcanized in the usual way.

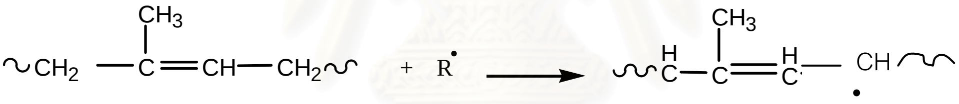
2.4 Emulsion polymerization[6]

The polymerization of PMMA on NR latex is carried out using *tert*-butyl hydroperoxide as an initiator, tretraethylenepentamine as coinitiator and oleic acid as emulsifier. In this process the monomer is first emulsified with a surfactant and then polymerized by free radicals polymerization reaction. The mechanism of this reaction is illustrated in equations 2.1 – 2.3.

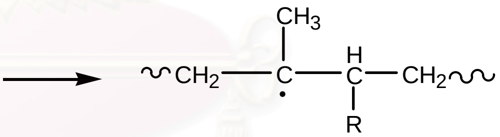
The initiators could decompose to yield the radicals, as shown in equation 2.1. The free initiator radicals (represented as $R^{\cdot}$ in the proceeding reaction) may promote grafting in two different ways. First the free initiator radicals reacted with MMA monomer and polyisoprene simultaneously. The latter reaction generated the free radicals intermediates involved MMA polymerization was highly reactive, both toward the double bond and alpha methylenic groups in NR, to form the graft copolymer. The end product of the polymerization process was a latex *i.e.*, PMMA grafted NR polymer particles disperse in a continuous aqueous phase. The latexes had a.) Initiation:



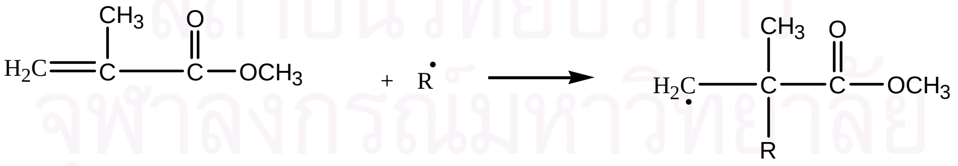
$$(CH_3)_3C{-}O{-}OH + R'H_2N \longrightarrow (CH_3)_3C{-}O^{\cdot} + R'H\overset{\cdot}{\overset{+}{N}} + H_2O$$ (2.1a)



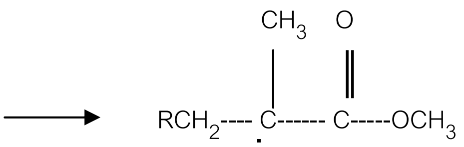
$$\sim CH_2{-}C(CH_3){=}CH{-}CH_2\sim + R^{\cdot} \longrightarrow \sim\overset{H}{C}{-}C(CH_3){=}\overset{H}{C}^{\cdot}{-}\dot{C}H\sim$$ (2.1b)



$$\longrightarrow \sim CH_2{-}\dot{C}(CH_3){-}\overset{H}{C}(R){-}CH_2\sim$$ (2.1c)

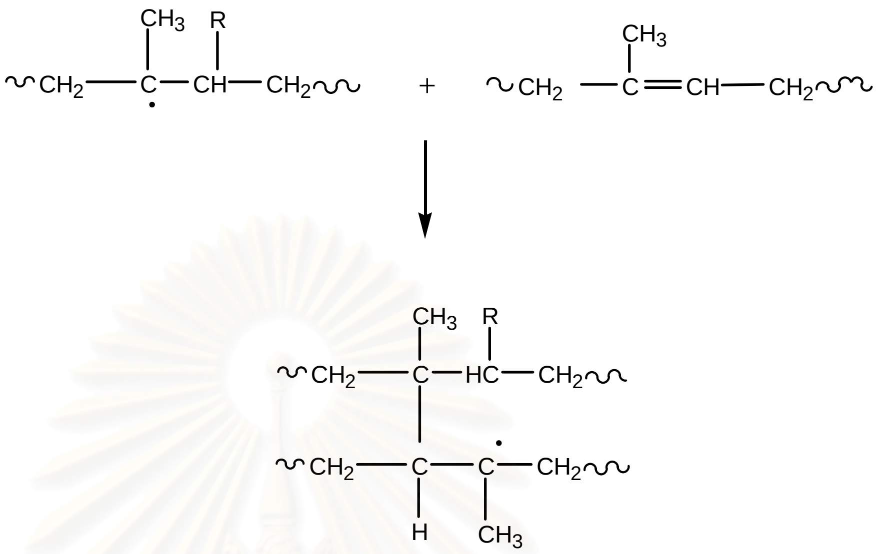


$$H_2C{=}C(CH_3){-}C({=}O){-}OCH_3 + R^{\cdot} \longrightarrow H_2\dot{C}{-}C(CH_3)(R){-}C({=}O){-}OCH_3$$ (2.1d)

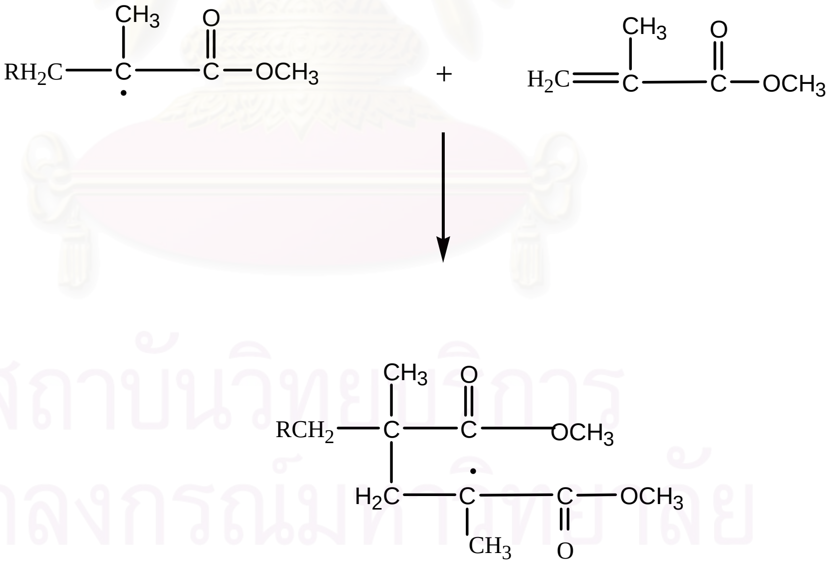


$$\longrightarrow RCH_2{-}\dot{C}(CH_3){-}C({=}O){-}OCH_3$$ (2.1e)

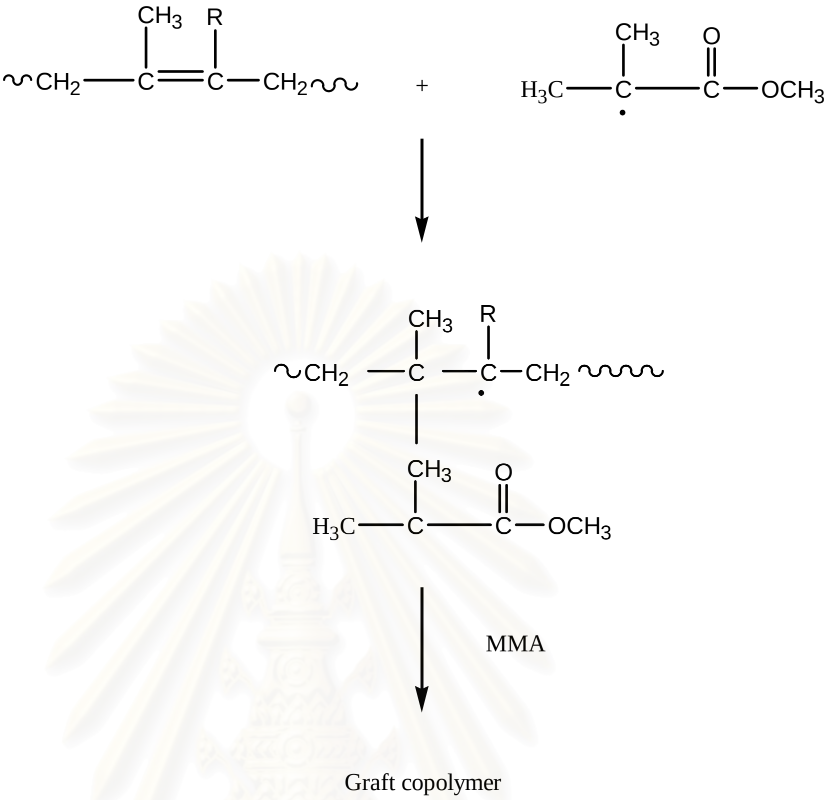
b.) Propagation



(2.2a)

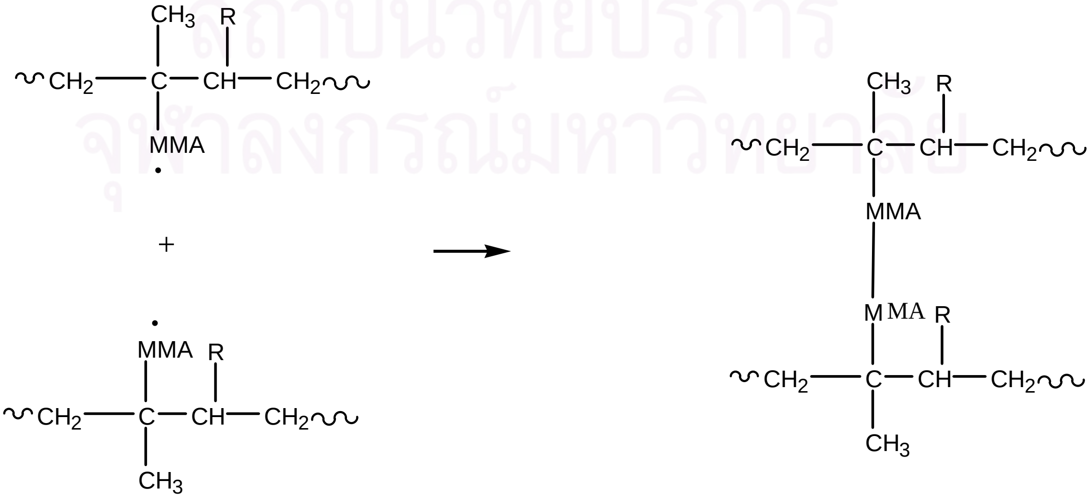


(2.2b)

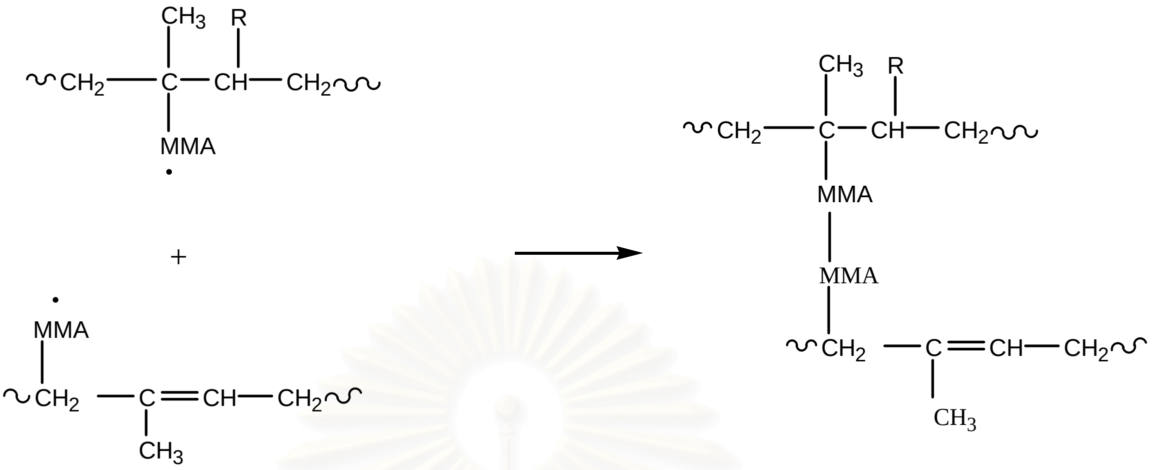


(2.2c)

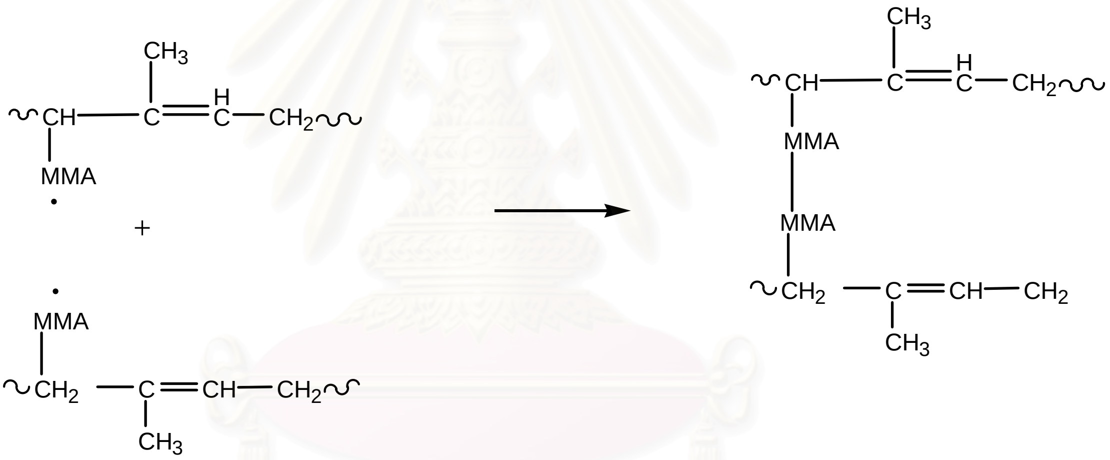
c. Termination



(2.3a)



(2.3b)



(2.3c)

good long-term stability. An exotherm causing a temperature to rise of around 10°C was observed during the first hour of the polymerization. There are various grades of this material had been produced, depended on the mass ratio of PMMA to NR, the amount of unmodified NR and homopolymer. NR-g-PMMA latex is cured in the same manner as natural rubber. It has significantly better resistance to swelling in hydrocarbon and shows self-reinforcement.

2.4.1 Core-shell mechanism

The redox initiator, TBHP/TEPA, could be used to prepare NR-based core/shell latex particles. Since the peroxide is soluble in both the monomer and the NR particle, whereas the activator TEPA is water soluble, the free radical are produced at the particle/water or monomer droplet/water interface. The MMA monomer absorbed at or near surface of NR latex particles where the redox partners met and the emulsion polymerization took place. The PMMA phase was, therefore, locked into a core-shell configuration. The core-shell mechanism is shown in Figure 2.2

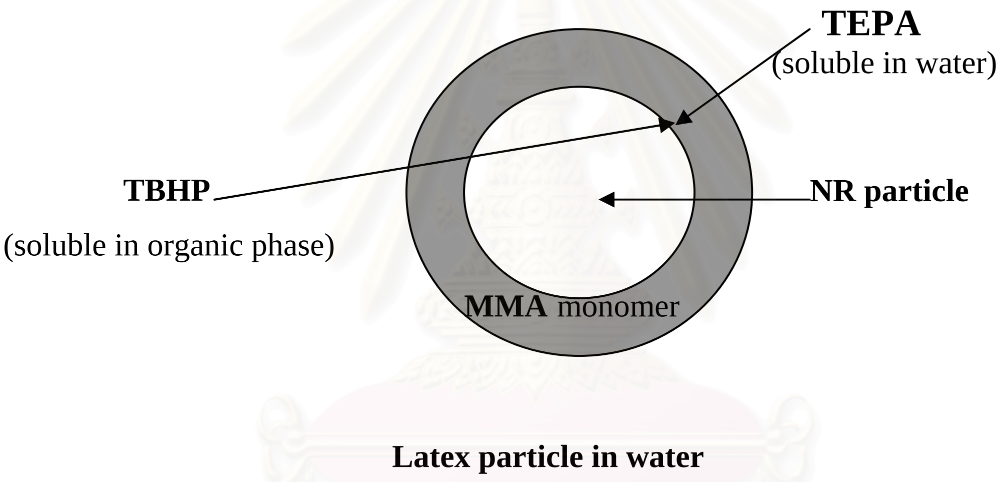


Figure 2.2 The polymerization of MMA in NR latex when using initiator system TBHP/TEPA

2.5 Latex film formation[7]

The "latex film" normally refers to a films formed from soft latex particles where the forces accompanying the evaporation of water are sufficient to compress and deform the particles into a transparent, void-free films. Latex film can also be obtained by compression molding of a dried latex powder composed of polymers such as PS or PMMA that its T_g is above room temperature.

2.5.1 Mechanisms of latex film formation

Three steps can be distinguished in the process of film formation from a latex considering only pure, unfilled polymeric films (Figure 2.3).

Step I

In the first step, water evaporates at a constant rate until the particles form dense packing of spheres. For monodispersed latex, the highest solids volume fraction is then to 0.74. An addition condition for high packing fraction is sufficient colloid stability.

Step II

At the beginning of the second step, particles appear at the surface of latex, and the rate of water evaporation decreases. Forces start to act and ensure the deformation of the particles in such a way that polymeric material fill all the space. The forces acting have to overcome the mechanical resistance of the particle to deformation. Later, the spherical particles are transformed into rhombic dodecahedral. At this stage, interfaces between particles still exist.

Step III

The final step corresponds to evolution of the interfaces between particles. They tend to disappear by inter diffusion of the macromolecular chains from one particle to its neighbors. It is sometimes call maturation. Film properties like mechanical strength and permeability are altered during this step.

2.6 Transport phenomena in polymer films

Membrane permeation is defined as the flow of a substance through a polymer membrane or film under a gradient of concentration of the permeating substance. Several factors determine the ability of a molecule to permeate through a membrane-size, shape and chemical nature of the polymer, and interaction between permeate and polymer. The study of transport of small molecule through polymer films is interesting because a number of important practical applications depend wholly or in part on such phenomena. These include protective coating such as paints and vanish, electronic devices and cable materials, packaging materials for food and vegetable. In order to properly design and use membrane separation procedure it is necessary to understand the basic nature of permeation and factors, which govern the flux, and perselectivity of polymer membrane system. These knowledge serves as a guide for the selection or modification of membrane materials to achieve optimum separation of desired multi component mixtures.

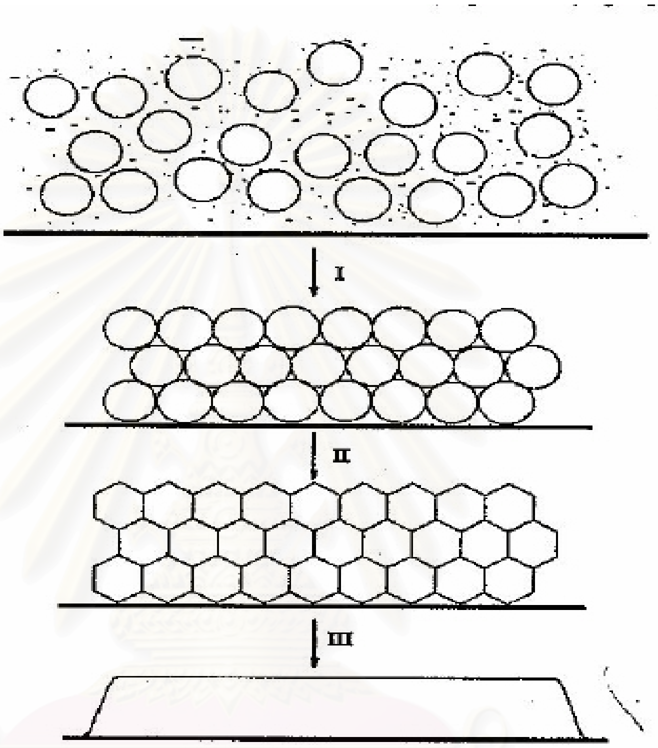


Figure2.3 Schematic of latex film-formation process showing the three main steps i) Concentration latex; ii) Deformation of particles; and iii) Interdiffusion of chain across particle boundaries

2.6.1 Transport parameters

Penetrant transport through a polymer matrix can be described in term of diffusion, permeation and sorption phenomena.

Diffusion coefficient [8-12]

Diffusion coefficient is one of fundamental properties of system. The diffusion coefficient can be thought of as the resistance to mass transfer through the film, analogous to the thermal conductivity in heat transfer, and viscosity in momentum transfer. In general, the diffusion coefficient can be dependent on the concentration of the diffusion species as well as time dependent. The unit of D is $(\text{length})^2$ /time, *e.g.*, cm^2/sec. The diffusion of molecule in a polymer occurs due to random motion of individual molecules. A net transport of penetrate occurs in the direction of decreasing concentration. This process can be described in term of Fick's first law of the diffusion according to which the flux (J) in the x-direction of flow is proportional to the concentration gradient ($\partial c/\partial x$) as

$$J = D (\partial c/\partial x) \qquad \text{----------} \ 2.4$$

where,

c = concentration
x = direction

Here, D is the diffusion coefficient. This equation is applicable to diffusion in steady state, *i.e.*, when the concentration does not vary with time. On the other hand, Fick' s second law of diffusion describes the non-steady state condition and for diffusion in one dimension, it may be written as

$$\partial c/\partial t = D\, \partial^2 c/\partial x^2 \qquad \text{-----------} \ 2.5$$

where t is the time and where D, the diffusion coefficient is assumed constant. However, in the case of liquid interacting with high polymers, the diffusion coefficient is usually a function of the concentration of penetrant. In such case, eq. 2.5 is usually rewritten as

$$\partial c/\partial t = \partial(D\partial c/\partial x)/\partial x \qquad \text{-----------} \ 2.6$$

The follow assumption have been made to calculate the diffusion coefficients of solvent molecules into membrane:

(i) Diffusion through thin-sheet membranes is assumed to be unidirectional.

(ii) Separation takes place under transient conditions with a constant diffustivity.

(iii) During sorption, when the membrane comes into contact with the solvent, the solvent concentration on the membrane surface reaches the equilibrium value soon after the sample is immersed in the solvent.

(iv) The time required for the polymer to establish thermal equilibrium is negligible when compared to the time of sorption.

(v) Changes in polymer dimensions are negligible during the immersion experiment.

The analytical solution of eq. (2.6) to determine the liquid sorbed by membrane of thickness, *h,* at a time, *t* and distance, *x* is given by

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2} \times \exp\left[-\frac{D(2n+1)^2\pi^2 t}{h^2}\right] \qquad \text{-------2.7}$$

M_t = cumulative mass of solvent sorbed or desorbed from polymer sample at time t

M_∞ = cumulative mass of solvent sorbed or desorbed from polymer sample at equilibrium

h = initial membrane thickness (cm)

For short time, this equation simplifies to

$$\frac{M_t}{M_\infty} = \frac{4}{h}\left[\frac{Dt}{\pi}\right]^{1/2} \qquad \text{-------- 2.8}$$

The diffusion coefficient can be obtained from the initial slope of the graph of M_t *versus* $t^{1/2}$

$$\text{Slope }(\theta) = \frac{4}{h} M_\infty (D/\pi)^{1/2} \qquad \text{--------2.9}$$

$$D = \frac{1}{\pi}\left[\frac{\theta h}{4M_\infty}\right]^2 \qquad \text{---------2.10}$$

D = diffusion coefficient

θ = initial slope of graph of M_t *versus* $t^{1/2}$

h = initial membrane thickness

M_∞ = cumulative mass of solvent sorbed or desorbed from polymer sample at equilibrium

Sorption coefficient[8]

Sorption is a general used to describe the permeation and dispersal of penetrate molecules in a polymer matrix. On the phenomenological level, sorption can be described as the distribution of penetrate between two or more phases to include absorption, filling of microvoids, cluster formation and other modes of mixing. Additionally, penetrate distribution depends on the concentration of sorption material, temperature, time of sorption to equilibrium, swelling – induced structural changes, and other factors. All diffusing species consider here will have a finite solubility in the polymer membrane. If liquid molecules have a solubility parameter close to that of membrane material will tend to be more soluble, possibly resulting in higher fluxes. Therefore, the sorption coefficient (S) can calculate using

$$S = \frac{M_\infty}{M_P} \qquad \text{------- 2.10}$$

where, M_∞ = mass of solvent taken up at equilibrium swelling

M_p = mass of polymer sample

Permeability coefficient[11]

Permeation, like diffusion, is also a transport property. Permeability, or the permeability coefficient (P), is a measure of the barrier protection or separation potential offered by the polymer membrane. It can be calculated as the product of the diffusion coefficient and solubility of the fluid in the membrane

$$P = D \times S \qquad \text{-------- } 2.11$$

Where,

D = diffusion coefficient
S = sorption coefficient

2.6.2 Prediction of type of transport mechanism[13]

In order to investigate type of diffusion mechanism, the sorption data of all polymer solvent system should be fitted to the following relation

$$\log (Q_t/Q_{eq}) = \log K + n \log t \qquad \text{-------- } 2.12$$

where,

Q_t = weight uptake of solvent at time *t* by 100g of the polymer
Q_{eq} = maximum weight equilibrium uptake of solvent by 100g of polymer

K is characteristic constant of polymer, *i.e*., the value of K depends on the structural characteristic of the polymer network in addition to its interaction with solvent molecule. n value gives an idea about the type of transport mechanism in Eq. 2.12. For the Fickian mode the value of n is 0.5 while n=1 indicates non-Fickian transport. However, the intermediate values of n from 0.5 to 1 suggest the occurrence of combined mechanism, *i.e.*, the anomalous mechanism.

2.7 Dialysis

Dialysis is a process that relies on concentration-driven transport for separation. The method is used for the separation of small solutes from synthetic of biological macromolecules, the membrane material serves to retain molecules large than the material-related cut-off of the membrane by hindering them from entering the membrane due to sterical reasons. The smaller solutes freely diffuse through the membranes, eventually leveling out concentration differences. If the osmotic pressure is different in the two membrane-contacting phases, solvent molecules will also diffuse though the membrane, stirring for equilibrium. Maximum efficiency occurs when the membrane is thin and the concentration differential is large. Dialysis membranes are normally regarded as dense membranes. The non - porous structure is, however, true only for a membranes in a dry state. A dialysis membrane will normally swell in the solvent used, and this introduces a certain separation of the polymer chains in the membranes, this swelling is reversible and introduces a porosity that accounts for the separation of molecules of different sizes.

2.7.1 Theory of dialysis[14-15]

Fick' s general law of diffusion, which can be expressed as, relates the rate at which a substance diffuses through a solution to a concentration gradient across the diffusing path

$$dS = - Dq(dc/dx)\, dt \qquad \text{----------} \; 2.12$$

S represents the amount of substance diffusing through a diffusion plane of thickness *x* and area *q* in time *t* under a concentration gradient *dc/dx*. D is the specific diffusion coefficient defined by amount of substance diffusing across unit area per unit time under concentration gradient of unity. The minus sign denotes that the substance diffuse in the direction of decrease concentration. The rate at which the concentrations of the two solutions are equalized will then be proportional to the diffusion coefficient. The driving force for the equalization of concentrations will be the concentration gradient across the membrane. For thin membrane of uniform thickness the equation can be rewritten as

$$dS = k_1A\,(C_1\text{-}C_2)dt \qquad \text{--------} \; 2.13$$

Where A = area of membrane

C_1 and C_2 = solute concentration on either side of membrane

k_1= constant

Integrated with respect to t, eq.2.13 becomes

$$S = kA(C_1\text{-}C_2)t \qquad \text{---------}2.14$$

Which rearrangement gives

$$k = S/At(C1-C2)$$

k is permeability coefficient and is considered a constant for a given membrane-solute combination, although it often varies with solute concentration. The permeability coefficient is reasonably constant for many nonelectrolyte solutes, where it is generally variable with electrolytes and, as expected for a diffusion process, increases with an increase in temperature.

2.8 Lubricating oil[16]

The basic functions of a lubricant are friction reduction, heat removal, suspension of contaminate. The lubricating oil usually consists of base fluid, generally of petroleum origin, combined with additive chemicals that enhance the various desirable properties of the base fluid. Base fluids are essentially obtained from two main sources: the refining of petroleum crude oil and synthesis of relatively pure compounds with properties that are suitable for lubricant purposes.

2.8.1 Petroleum lubricating oils

Petroleum lubricating oils are distinguished from other fractions of crude oil by their usually high (>400 ^{O}C) boiling point, as well as their high viscosity. Materials suitable for the production of lubricating oils are comprised principally of hydrocarbons containing from 25 to 35 or even 40 carbon atoms per molecule, where as residual stocks may contain hydrocarbons with 50-60 or more (up to 80) carbon atoms per molecules.[17]

2.8.2 Synthetic base oil

Many compounds have been investigated as possible base stocks for synthetic lubricants. Seven types are of major importance: polyalphaolefins, alkylated aromatics, polybutenes, aliphatic diesters, polyolesters, polyalkyleneglycols, phosphate esters other such as silicones, borate esters, perfluoroether and polyene ethers are also as importance, but there applications are restricted due either to high cost or to performance limitations.

2.8.3 Additives in automotive lubricating oil

The main types of additives used for formulating engine oil lubricants are: alkaline detergents, dispersants, antioxidants, corrosion inhibitors, anti-wear and extreme pressure additives, pour point depressants, as described as follows;

Viscosity index improvers.

Viscosity index (VI) improvers can alter the natural viscosity temperature relationship of oil. VI improvers are generally polymeric materials which tend to thicken the oil more at high temperatures than at low temperatures when cold the polymers are coiled up into small round particles and offer little resistance to the bulk oil flow. When the temperature rises, the polymers uncoil to form long string like fibers that restrict the free flow of the oil, giving rise to higher effective viscosity. VI improvers are polyisobutylenes, polyacrylates, polymethacrylates and ethylene-propylene copolymers.

Pour point depressants.

Lubricating oils containing straight chain paraffinic hydrocarbons tend to form wax crystals at low temperatures and these crystals form lattice structures, which impede the flow of the oil. Pour point depressants are structurally similar to VI improvers but are usually of a much lower MW. These materials are believed to function by interfering with the lattice like structure of the wax crystals. Typical examples are polymethacrylates, wax, alkylated naphthalenes, wax alkylated phenols and poly (alkyl phenol) ethers.

Extreme-pressure agent

These chemicals contain sulfur, phosphorous, chlorine and heavy or transition metals. They react with sliding metal surfaces under the influence of heat and pressure to form compounds of the metal and these compounds exist as a film on the metal surface which reduces frictional heat and prevents welding and scoring. Some of the materials are sulfurized olefins, sulfurized esters, phosphate and thiophosphate esters, zinc dialkyl dithiophosphates and chlorinated paraffin.

Dispersants

These compounds have been described in the literature as “detergent”. Since their function appears to be one of affecting a dispersion of particulate matter rather than one of “cleaning up” any existing dirt and debris, it is more appropriate to categorize them as dispersants.

2.9 Literature reviews

Pare[18] invented a new process for regenerating of used lubricating oil. This process used ultrafiltation membrane having a cut zone 10,000-100,000 e.g. cellulose, cellulose ester, polytetrafluoroethylene, sulfonated polystyrene, vulcanized natural rubber. Pressure difference between two sides of the membrane was not more than 10-15 atmosphere. The temperature was not higher than 70-80 °C, thickness of membrane ranges from 0.5 to 5 mm and operated with solution of the oil in solvent such as light hydrocarbon, pentane, hexane, heptane. Membrane can also be operated by dialysis. Treated oil showed reduction of the amount of most additives by comparing the content of sulfate ash of used oil and the treated oil. Quality of the treated oil from dialysis was color ASTM at 5, 0.1% sulfate ash, 74.5% yield. This process could remove additive better than ultrafiltration process.

Molone[19] disclosed the method which involved the isolation, analysis and characterization of dispersants present in motor oils. The method involved separating away other additives present in motor oil by treatment with the iodine. After treating with iodine followed by the isolation of the dispersant from oil by dialysis. The dialysis residue contained higher molecular weight components including dispersants and detergents. The membrane used for dialysis was Rames® # 19, 0.03 inch thickness. Extraction solvent was petroleum ether.

Bitter[20] invented a process for separation of solvents from hydrocarbons dissolved in the solvent by membrane separation. The hydrocarbon is from dewax oil treatment. The solvents were toluene and methyl ethyl ketone. The membrane comprised a layer of a halogen substituted silicone compounds e.g. 3,3,3-trifluoro propyl methyl siloxane, supported on porous polypropylene. The process recovered the solvent from one side of membrane and recovered hydrocarbon from the other side.

Ciora[1] refined used oil by membrane filtration processes to remove contaminant such as ash at the first step and follow by adsorption process to remove color and odor. The oil recovered from this process can be recycled to reused for fuel application. Membrane used was porous inorganic membrane *e.g.* stainless steel or ceramic. The membrane had a pore size in the range of 50 ^{o}A to 10 μm the temperature was in the range of 50-250 ° C, the pressure was in the range of 10-250 psi. This step can remove at least 50% of the ash from used oil. Metal content in recycle oil was below 0.2 ppm. In the second step, adsorbent consisted of activated alumina, zeolite, silica gel and anionic clay. The permeate oil contacted with adsorbent at 25 to 150 ° C, this step can improve the color and odor of treated oil.

Angier[21] prepared rubber/ polymer compounds by cold mastification of rubber under oxygen free conditions. Examples of monomer compounds include acrylic acid, ethyl acrylate, n-butylacrylate, methyl methacrylate, acrylonitrile, and acrylamide. Acetone extracted deprotein crepe gave more rapid polymerization than unextracted crepe. The physical properties of the product obtained on original rubber and the nature and proportion of polymerisable olifinic compounds. The obtained materials have high tensile strength and improve resistance to swelling by certain important solvent, e.g. fuel oil.

Pendle[22] compared the MG49 with PVAC and PSC additive in latex vulcanizates. The results showed that MG49 latex gave the highest tensile strength and aging resistance at 100 ° C whereas PVAC and PS appeared to have lower aging resistance. MG49 gave a reduction of vulcanizate swelling in hydrocarbon solvents. Disadvantages of MG lattices were their poor firm forming characteristics.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Natural rubber latex (high ammonia grade) and prevulcanized rubber : were supplied by Revertex (Thailand) Co., Ltd.,
2. Methyl methacrylate monomer, Commercial grade: Siam Chemical Industry Co., Ltd., Thailand.
3. *tert*-Butyl hydroperoxide, Analytical grade: Fluka, Steinheim, Switzerland.
4. Oleic acid, Analytical grade: Merck, Honenbrunn, Germany.
5. Potassium hydroxide, Analytical grade: BDH, Poole, England.
6. Light petroleum ether, Analytical grade: Lab Scan Asia Co., Ltd., Bangkok, Thailand.
7. Acetone, Commercial grade: J.P.M. & Scientific, Bangkok, Thailand.
8. Ammonium hydroxide, Analytical grade: BDH, Poole, England.
9. Zinc oxide, Merck, Honenbrunn, Germany.
10. Dioctyl phathalate, Merck, Honenbrunn, Germany.
11. Hexane Commercial grade: J.P.M. & Scientific, Bangkok, Thailand.

3.2 Glasswares

1. Viscometer tube
2. Pour point tube
3. Soxhlet
4. Other general laboratory glassware

3.3 Equipments

1. Viscometer: Cannon: CT-1000
2. Automatic titration: Mettler DL70 Titrator
3. Automatic flash point: ISL CLEVELAND ASTM D92

4. Scanning Electron Microscopy: JEOL model JSM-S800LV
5. Fourier Transform Infrared Spectroscopy: FTIR-Impact 410 Nicolet

3.4 Experimental procedure

3.4.1 Purification of monomer

Methyl methacrylate monomer (MMA) was washed with 10 wt% aqueous sodium hydroxide solution followed by water washes until neutral, and then dried using anhydrous sodium sulfate, and passed through an activated aluminum oxide column to remove the residual inhibitor. The purified MMA was stored in the refrigerator.

3.4.2 Polymerization of MMA on natural rubber[23]

PMMA grafted NR was prepared by emulsion polymerization method, using formulary in Table 3.1. Natural rubber latex with high ammonia preservative (60% rubber content) was added and placed in a 1000 cm^3 conical flask reactor. The aqueous ammonia solution was added to the latex and the mixture stirred thoroughly. The *tert*-Butyl hydroperoxide (as an initiator) and oleic acid were mixed with the methylmethacrylate monomer. This solution was then added to the latex slowly with moderately vigorous stirring, after which the mixture was agitated slowly for 15 minutes. The tretraethylenepentamine (TEPA) solution was then added slowly to the mixture and stirring continued for a further 10 minutes. The mixture was left for at least 18 hours to permit completion of polymerization. During polymerization the latex should be stirred as gently and as little as possible in order to preventing localized overheating.

3.4.3 Preparation of sulfur vulcanized polymerization PMMA on natural rubber

The ingredients in Table 3.2 should be added to the NR-g-PMMA latex in the correct order.[24] The mixture was stirred at slow speed for 12 hours at room temperature. After that the mixture was filtered to separate the suspended solid. The latex was then ready to produce membrane.

Table 3.1 The formulation of the PMMA grafted natural rubber

Ingredients	Amount of PMMA			
	20%	30%	40%	50%
60% Natural rubber latex (HA)	1000	1000	1000	1000
2% ammonia solution	252	282	700	735
Methyl methacrylate monomer	240	270	400	610
tert-Butyl hydroperoxide	1.7	1.8	2.0	2.0
Oleic acid	3.0	3.0	3.0	3.0
10% Tetraethylene pentamine solution	7.0	7.0	8.0	8.5
Plasticizer	← varies →			

Table 3.2 Formulation of sulfur vulcanized membrane

Ingredients	Weight(g)
1. NR-g-PMMA latex(50%solid)	100
2. Sulfur	1.5
3. Stearic acid	0.5
4. Zinc oxide	2.5
5. ZDEC	0.23

* Cure time115^{O}C, 10min

3.4.4 Preparation of PMMA grafted natural rubber membrane

The PMMA grafted NR (3.4.2, 3.4.3) was casted on ∅ 9 cm. glass plate to form membrane sheet which allowed to completely dry at room temperature. The membrane was leached in cold water for 24 hours, during this period the water was changed several times. The sheets was then dried in oven at 70 °C for thoroughly dry. The dried membrane was supported on fabric which pore size very much larger than pore size of membrane and cured by compression molding at 115 °C for 10 min. The thickness of membrane was measured at several points by using a micrometer screw gauge with an accuracy of ± 0.01 mm.

3.4.5 Determination of the properties of PMMA grafted natural rubber

3.4.5.1 Determination of the conversion of graft copolymerization

The conversion of graft copolymerization was determined by the percentage increase of rubber weight. The calculations were as in equation 3.1.

$$\text{Total conversion} = \frac{\text{Total weight of polymer formed x100}}{\text{Weight of monomer charged}} \qquad \text{-------- 3.1}$$

3.4.5.2 Determination of the percentage of grafted natural rubber and grafting efficiency

The amount of grafted natural rubber, free natural rubber, free PMMA in the product could be determined by soxhlet extraction. The free natural rubber was extracted by light petroleum (60-80 ^{o}C) for 24 hours. The grafted natural rubber content was determined by the residual weight after extraction of homopolymer. The grafting efficiency is defined as the mass of NR-g-PMMA divided by the total PMMA produced. All of calculations are as in equations 3.2 and 3.3

$$\text{\% Grafted Natural rubber} = (b/\ a+b+c)\ \text{x100} \qquad \text{--------- 3.2}$$

where,

a is the weight of free rubber determined by soxhlet extraction with light petroleum ether for 24 hours.

b is the weight of Grafted copolymer determined from the residual weight after extraction of free homopolymers.

c is the weight of free PMMA determined by soxhlet extraction with acetone for 24 hours.

$$\%\text{Grafting efficiency} = \frac{\text{the weight of polymer as grafted copolymer x100}}{\text{the total weight polymer formed}} \quad \text{--3.3}$$

3.4.6 Rubber property change in length during liquid immersion[25]

This test method covers a technique to measure the effect of immersion liquid on rubber vulcanized or rubbery materials change in specimen geometry and dimensions are observed through the transparent walls of the tube containing the specimen immersed in the liquid. This test method differs from Test Method D 471 in that volume changes are approximated from observed dimensional changes rather than being calculated directly.

The method is carried out by placing the specimen (l x w x h, 100x1.6x2.0 mm.) in glass tube, 10 mm in outside diameter and 250 mm long, sealed at one end. Measure the original length of the specimen, L_1 by means of reading table. Add 10 cm^3 of test liquid, and stopper or seal. After conditioning for the desired time at room temperature the test sample was placed on the reading table and read the immersed length, L_2. The percentage increase in length was calculated as follows:

$$\text{Increase in length, \%} = [(L_2 - L_1)/L_1] \times 100 \qquad \text{----------------3.4}$$

3.4.7 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy (SEM) was used to investigate the fraction surface of the NR-g-PMMA. Samples for SEM were mounted on a SEM stub using a double side tape and the fracture specimens were coated with gold. The SEM (JEOL model JSM-S800LV) was operated at 15 KV.

3.4.8 Permeation behavior of film prepared from NR-based latex particle

The membranes which prepared in section 3.4.4 were cut into uniform size. The thickness of sample, *h*, was measured at several points by using a micrometer screw gauge with an accuracy of ± 0.01mm. In the sorption experiment, the known weight of membrane from 100 to 500 mg were then immersed into 80 ml of lubricating oil at room temperature. The samples were periodically removed from the test bottle and weight (with accuracy of ± 0.01g) after blotting their surfaces with filter papers. The time each weighing was kept to a minimum of 30-40 sec in order to eliminate the error due to the evaporation of solvent from the samples. After weighing, the samples were re-immersed into the test bottles. This procedure was repeated until no more liquid uptake by the polymer was observed, *i.e.*, equilibrium swelling was attained. The results obtained were expressed as weight of liquid sorbed at time t by 100 g of the polymer sample (Q_t)

$$\text{weight \% uptake } (Q_t) = \frac{\text{weight of solvent at time t x100g of membrane}}{\text{initial weight of membrane}} \quad \text{-------- (3.4)}$$

From sorption experiment of the membrane diffusion, sorption and permeation coefficient were calculated for difference polymer-solvent systems to explore type of transport mechanism.

3.4.8.1 Calculation of diffusion coefficient (D)

The sorption curves, expressed as weight % uptake (Q_t) of a liquid by 100 g of the polymer (equation 3.5) *versus* square root of time ($t^{1/2}$) were plotted. From the initial linear portion of the curves, the diffusion coefficient (D) of the membrane-solvent systems was calculated using the following equation.

$$D = \pi(h\theta / 4Q_{eq})^2 \quad \text{---------- 3.5}$$

where

Q_{eq} = maximum weight equilibrium uptake of solvent by 100 g of membrane sample

h = initial membrane thickness (cm)

θ = slope of linear portion of sorption curves before attainment of 50% equilibrium

3.4.8.2 Calculation of sorption coefficient (S)

The sorption coefficient (S) which is maximum saturation value, was calculated using the following equation

$$S = M_\infty / M_p \qquad \text{---------} \; 3.6$$

where

M_∞ = weight of solvent at equilibrium swelling (g)

M_p = weight of membrane sample(g)

3.4.8.3 Prediction of type of transport mechanism

Plot log Q_t/Qeq value from sorption experiment in 3.4.9 *versus t* from a least-squares analysis, the value of K and n have been obtained. The intercept of this line at log Q_t/Qeq axis is equal to log K and slope is equal to type of transport, n.

3.4.9 Dialysis experiment

Used lubricating oil was re-refined by dialysis method. The apparatus was shown in Figure 3.1. The device consisted of two 120 ml cells filled with lubricating oil solution (A) and hexane (B), respectively. These two cells were connected by 3.75 cm. radius polymer membrane. The mass transport will occur at the polymer membrane interface only. Cell A was filled with 100 gram of lubricating oil solution, while 100 gram of hexane was used in the other cell. The membranes were immersed in hexane for at least 15 minutes prior to the experiments. The change in the lubricating oil concentration in cell B as function of time was determined by sampling oil to evaporate solvent in order to calculate %oil. The amount of oil obtained from weighting total oil in cell B. Each experiment was prepared with different concentration of oil in cell A (100,50,25,15% w/w). Data were recorded since the first hour to steady-state condition. A straight line was plotted as permeates *vs.* time.

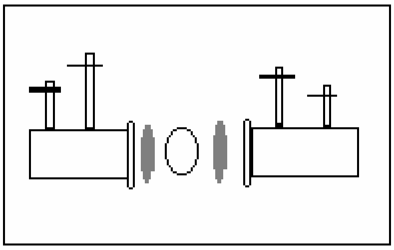


Figure 3.1 Dialysis Apparatus

3.4.10 Percolation through caustic-treated clay

Commercial bentonite clay (30-60 mesh) was mixed with an aqueous solution of sodium hydroxide so that the caustic was 10 weight – percent of the clay. The mixture was poured into the trays and dried for 48 hours at 100 ^{O}C. The treated clay was then packed into the column that was 1 cm. in diameter. The clay-oil ratio was 3:1. The lubricating oil was poured into the column. The treated oil was passed to the absorption clay.

3.4.11 Analytical properties of lubricating oil

See Appendix A.

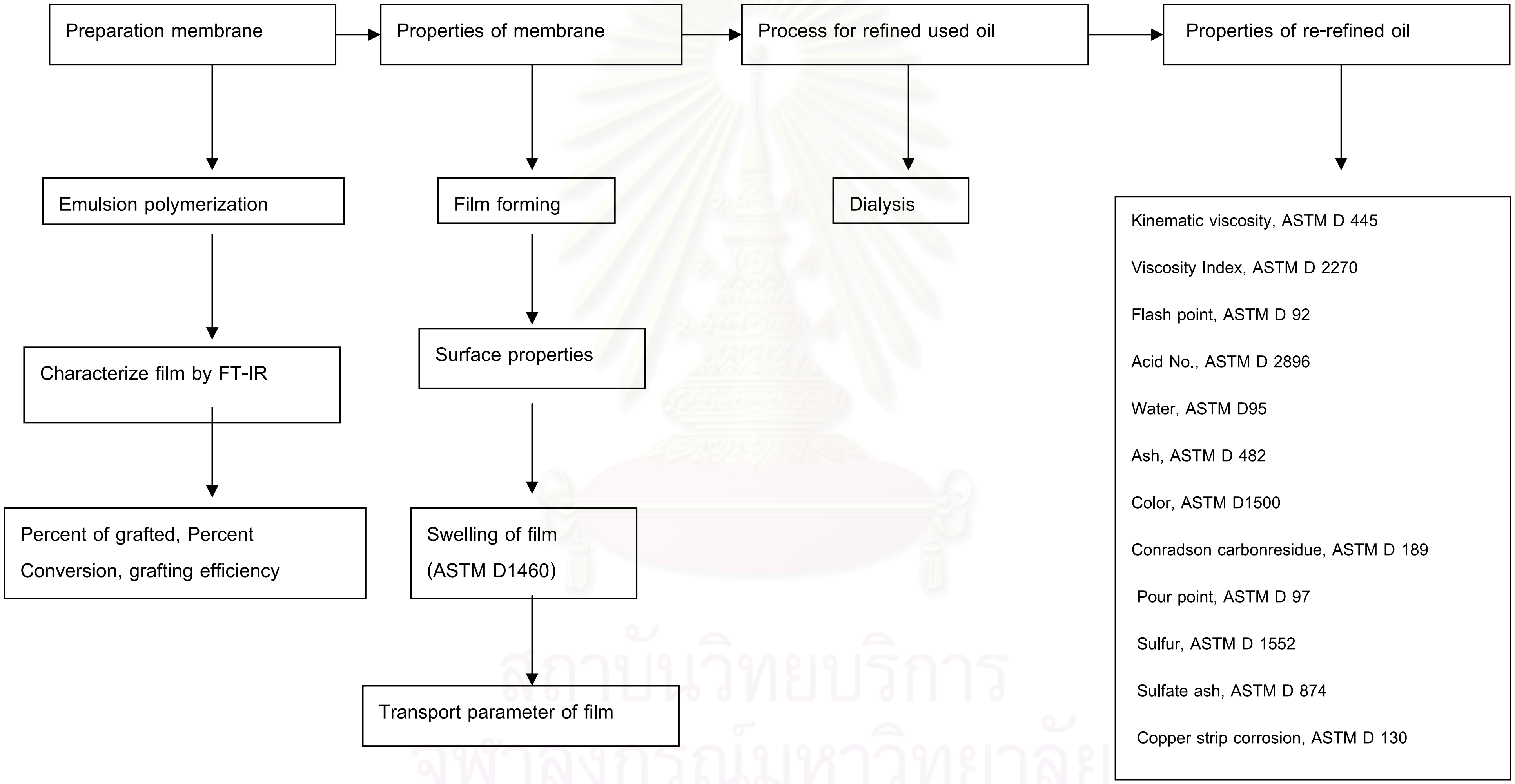


Figure 3.2 Experiment scheme of NR-g-PMMA membrane for used lubricating oil separation

CHAPTER IV

RESULTS AND DISCUSSION

The object of this research was to improve the property of natural rubber in making polymer membrane by grafting with polymer and used to refine used oil. The obtaining membrane should be semipermeable, that was, it should allow the low molecular weight solutes diffuse through the membrane and retain contaminants on the other side of membrane such as ash, sludge, metal, color. It must be durable in processing solvent and in lubricating oil. PMMA was the polymer which used to modify NR by emulsion polymerization method. This research was investigated the possibility of using this graft polymer as a membrane. The resistance of NR-g-PMMA membrane to the action of process solvent was evaluated by measuring changes in length of the membrane before and after immersion in solvent. Method for refining used oil was dialysis, when hexane was used as solvent. The quality of re-refined oil was tested by the ASTM methods and the quality was compared with TIST standard for re-refined base oil.

4.1Preparation of NR-g-PMMA

4.1.1 Characterization of latex film by FT-IR spectroscopy

The NR-g-PMMA was extracted as in method 3.4.6. The free PMMA and free NR were removed using acetone and petroleum ether. The purified NR-g-PMMA was dried in oven and confirmed by FT-IR spectroscopy. The FT-IR spectra in the region of 4000 - 400 cm^{-1} for natural rubber and the purified grafted NR are shown in Appendix B. The assignments are given in Table 4.1. The FT-IR spectra of NR exhibited the characteristic absorption bands of the C-H stretching vibration in aliphatic C-H bond at 1376 cm^{-1}, the C=C stretching vibration at 837 cm^{-1} and the C-C stretching vibration at 1243 cm^{-1}. The new peaks in FT-IR spectrum of the grafted natural rubber showed an intense absorption at 1733 and 1148 cm^{-1} corresponding to the C=O and C-O-C groups in methylmethacrylate chain along with characteristic absorption of the NR group. This confirmed the occurrence of grafting.

Table 4.1 The important characteristic peaks of FT-IR spectra of natural rubber and the grafted natural rubber

Natural Rubber		NR-g-PMMA	
Wave number cm^{-1}	Assignment	Wave number cm^{-1}	Assignment
837 1243 1376	C=C stretching C-C stretching C-H stretching	837 1149-1150 1242-1246 1376 1728-1730	C=C stretching C-O-C stretching C-C stretching C-H stretching C=O stretching

4.1.2 The percentage of grafted natural rubber

The extent of polymerization could be checked by extraction method, following in 3.4.6. The result is shown in Table 4.2.

The grafting properties of NR-g-PMMA which presented in Table 4.2 showed that the homopolymer of PMMA was increased but grafted efficiency and the % monomer conversion were decreased when increased the percentage of PMMA. Extraction of sulfur vulcanized grafted NR indicated the reduction of free NR. It showed that the grafted NR was better resistance in petroleum ether due to the procession of sulfur crosslinking in the molecule of grafted NR. The result was confirmed by early report[26] on the effect of both monomer and initiator concentration on the extent of grafting, the number of grafts per molecule, and the lengths of the grafted polymer chains. The vulcanization of the grafted copolymer showed improvements in tensile strength, shear strength, and abrasion resistant compared to vulcanized NR.

Table 4.2 The grafting properties of grafted natural rubber

Formulation	PMMA in the copolymer (%)	Grafted NR (%)	Free homopolymer (%)		Monomer conversion (%)	Grafting Efficiency (%)
			NR	PMMA		
1. 20% PMMA grafted NR	22.5	90.0	8.4	1.6	90.1	93.10
2. 30% PMMA grafted NR	24.8	75.8	18.2	6.0	88.0	75.7
3. 40% PMMA grafted NR	31.3	79.0	13.5	7.5	85.3	78.8
4. 50% PMMA grafted NR	36.0	60.7	17.3	22.0	86.8	47.0
5. Sulfur vulcanized 20% PMMA grafted NR	-	-	3.6	1.5	-	-
6. Sulfur vulcanized 30% NR/PMMA	-	-	4.3	3.5	-	-
7. Sulfur vulcanized 40% PMMA grafted NR	-	-	3.8	5.5	-	-
8. Sulfur vulcanized 50% PMMA grafted NR	-	-	4.3	22.9	-	-

4.2 Properties of latex films

In this section, the four properties of casting film were studied. First, the film forming and appearance of film. Then the surface property was studied by scanning electron microscope and resistant of film in processing solvent and lubricating oil was evaluated by using swelling method following the ASTM D1460. The transportation and mechanism of transport of latex film were investigated by sorption technique.

4.2.1 Properties of film forming

The film was prepared by casting method according to 3.4.9. The properties and appearance of films are shown in Table 4.3. The cast films were transparent and similar to NR films in appearance. However, they were stiffer and tackier than NR film. The results of film forming are shown in Table 4.4. The results indicated that when the PMMA content was more than 22.5%, the film forming ability of NR-g-PMMA decreased and had tendency to crack on drying. Film cracking using similar initiator systems had been reported by Bloomfield and Swiff[27] pointing out that the PMMA was a hard plastic and has a tendency to form a shell around the latex particles. These core shall reduce inter-particle adhesion. After vulcanization with sulfur the vulcanized showed less film forming, due to the increase of chain crosslink. The other factors of film cracking were the extent on the conditions of drying (temperature, drying rate, film thickness). The film-forming characteristic was improved if the PMMA was partially replaced by butyl metharylate[28] in the grafting reaction. Moreover, it could be improved by the addition of plasticizer such as di-octylphathalate.

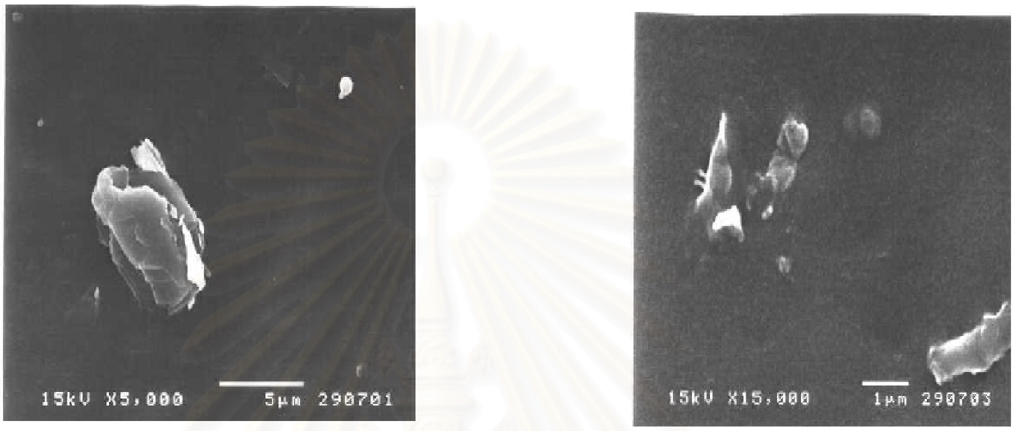
Table 4.3 Film forming properties of grafted natural rubber

Membrane type	Film forming	Appearance
NR(HA)	good	Elastic, transparent film
Prevulcanized NR	good	Elastic, transparent film
22.5%PMMA grafted NR	good	Elastic, transparent film
24.8% PMMA grafted NR	fair	Crack, transparent film
31.3% PMMA grafted NR	poor	Crack, transparent film
36.0% PMMA grafted NR	poor	Crack, transparent film
Sulfur vulcanized		
22.5%PMMA grafted NR	poor	Elastic, transparent film
24.8% PMMA grafted NR	poor	Crack, transparent film
31.3% PMMA grafted NR	poor	Crack, transparent film
36.0% PMMA grafted NR	poor	Crack, transparent film

4.2.2 Surface property by SEM

The morphology of surface of the films was studied under scanning electron microscope (SEM), and the micrographs are shown in Figures 4.1- 4.3.

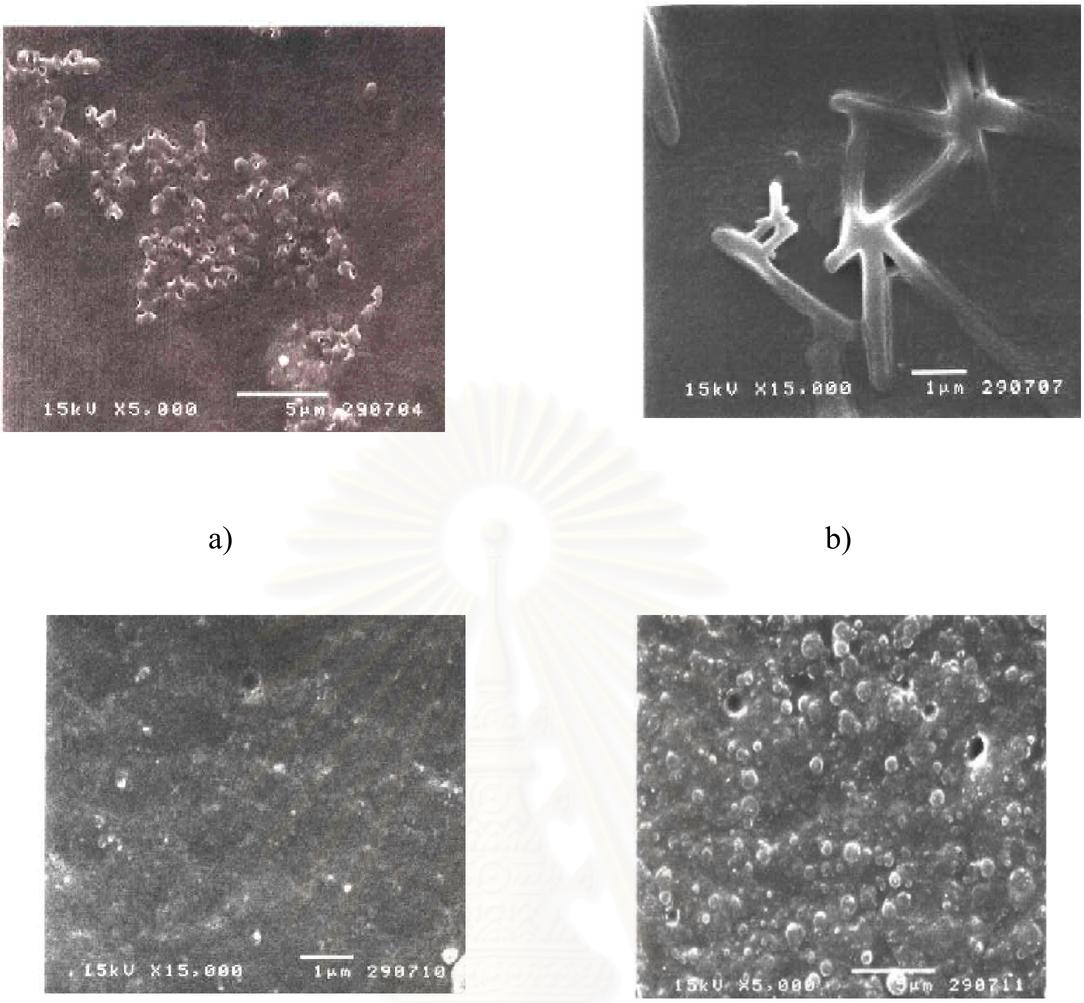
Figure 4.1 (a) showed SEM micrographs of film casted form the NR (HA), while Figure 4.1 (b) showed SEM micrographs of film casted form the prevulcanized NR. They showed that the latex film formed smooth structure.



a) b)

Figure 4.1 SEM micrographs of NR membrane, a) NR (HA) membrane, b) prevulcanized NR membrane

Figure 4.2 (a-d), showed the SEM micrographs of film casted form PMMA grafted NR, while Figure 4.2 (a, b) showed SEM micrographs of film casted form the 22.5% and 24.8% of PMMA on NR. They showed the heterogeneous morphology. Figure 4.2 (c, d) showed SEM micrographs of film casted form 31.3% and 36.0% PMMA grafted NR. The surface of film seemed to be rough and distributed randomly. The surface of film seemed to be rough proportional with the amount of PMMA, because PMMA could form core shell around NR particle exhibiting the formation of a coherent film. The different of polarity of NR and PMMA cause the PMMA to be preferentially concentrated at the surface of film. Whereas the rigid part of PMMA provoking incompletness of smooth film.

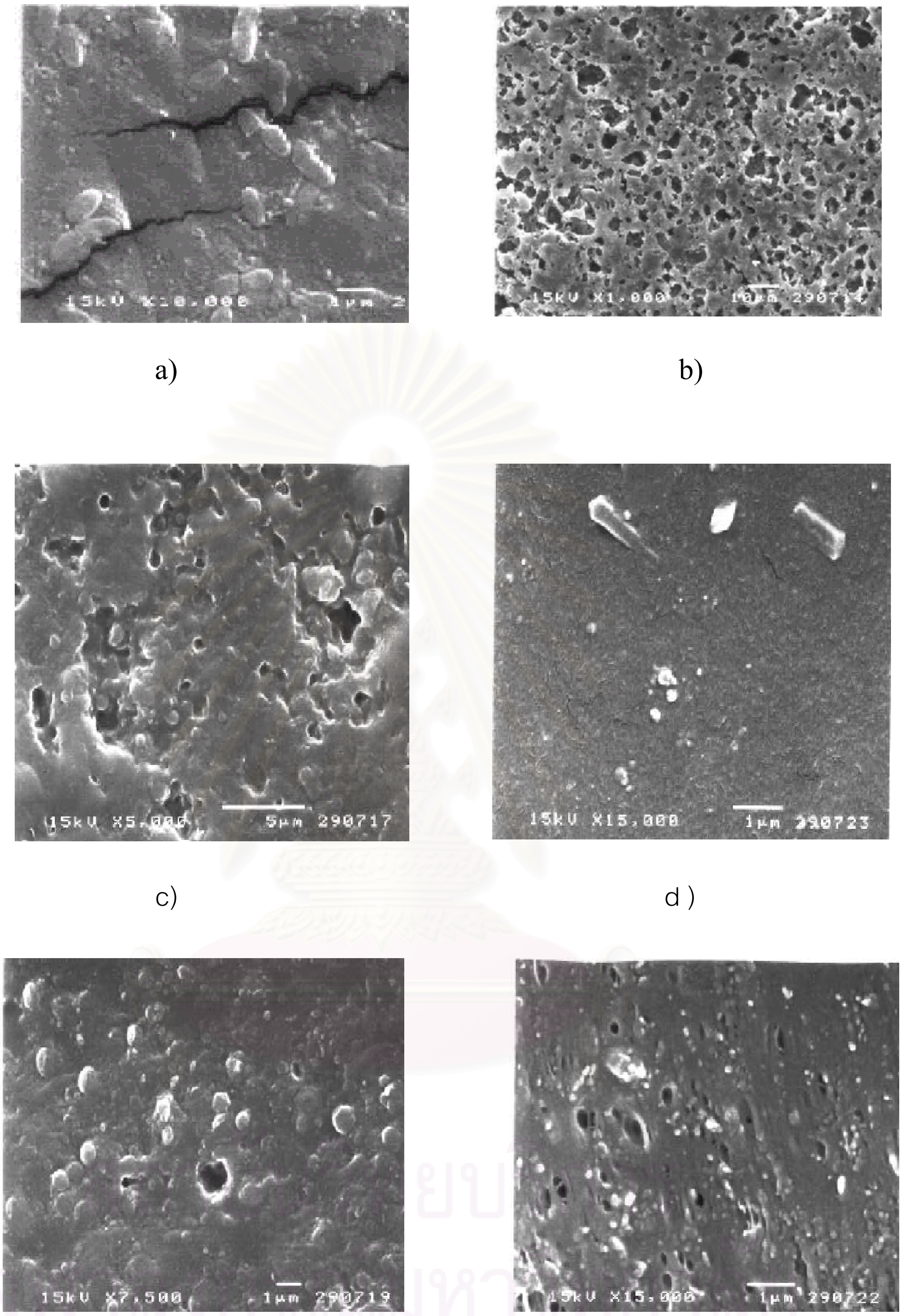


a) b)

c) d)

Figure 4.2 SEM micrographs of PMMA grafted NR membrane
a) 22.5%PMMA, b) 24.8%PMMA, c) 31.3%PMMA,
d) 36.0% PMMA

Figure 4.3 (a-f) showed SEM micrographs of film sulfur vulcanized 22.5-31.3% PMMA grafted NR casted form. Figure 4.3 (a) showed SEM micrograph of sulfur vulcanized of 22.5% PMMA grafted NR indicating that the surface appeared as crack surface. Figure 4.3 (b, c) showed SEM micrographs of sulfur vulcanized 24.8-31.3 % PMMA grafted NR. The surface appeared to be highly reticulated with an extensive pore structure which gave a sponge-like structure. The pore seemed to be distributed randomly. The cross-section 31.3% PMMA grafted NR shown in Figure 4.3 (d), indicated that the porosity was largely restricted to the surface and did not penetrate



a) b)

c) d)

e) f)

Figure 4.3 SEM micrographs of sulfur vulcanized PMMA grafted NR membrane a) 22.5%PMMA, b) 24.8%PMMA , c) 31.3%PMMA, d) 31.3% PMMA(cross-section), e) 36.0%PMMA, f) 36.0%PMMA (cross-section)

into the interior. When study the SEM micrograph of sulfur vulcanized 36.0 % NR-g-PMMA in Figure 4.3(e, f), it was found that the surfaces appeared to have some porous structure and cross section of the film showed that porous were spread into the interior of film. The pore size ranged from 0.2-1.5 μm in diameter. This indicated that sulfur vulcanized 36.0% PMMA grafted NR was not suitable for used as a membrane because the pores were too large that some additives such as phenate, overbase sulfonate and ashless dispersants could pass through. The phenate is approximately 60^{o}A in size, overbase sulfonate 150 ^{o}A and ashless dispersant 65 ^{o}A.[29]

4.2.3 Swelling of membrane in hexane and lubricating oil.

The swelling test of membrane was carried out in commercial grade hexane and lubricating oil, following the ASTM D1460-86. The results are shown in Table 4.4 and in Figure 4.4-4.5. The trends showed in Table 4.4 could be predicted by the swelling behavior of the polymers. The resistance to hexane and lubricating oil was proportional to the amount of PMMA grafted on NR. In hexane, the % swelling of NR (HA) latex was about >700%. The % swelling of prevulcanized NR was about 300%. The resistance of membrane samples varied in the order of 36.0% PMMA grafted copolymer>31.3%> prevulcanized >24.8%>22.5%> NR (HA). The sulfur vulcanized of the PMMA grafted NR gave better resistant to swelling in the same order, due to the effect of increasing the PMMA content in grafted NR might increase the polarity of the polymer. Then, the grafted NR exhibits the resistance to oil absorption (non-polar oil). In lubricating oil, the same orders of swelling were obtained but the values were lower than those in hexane.

Table 4.4 Solvent swelling of membrane

Membrane	Hexane		Lubricating oil	
	Length change %	Volume change %	Length change %	Volume change %
1.NR(HA)	>300	>700	228.5	>700
2. Prevulcanized	60	309.6	46.3	213.1
3. 22.5%PMMA grafted NR	93	618.9	48.7	228.7
4. Sulfur vulcanized 22.5%PMMA grafted NR	85	533.2	27.6	107.7
5.24.8%PMMA grafted NR	77	454.5	40.4	176.7
6. Sulfur vulcanized 24.8%PMMA grafted NR	60	309.6	25.4	97.1
7. 31.3%PMMA grafted NR	44	198.6	32.9	134.8
8. Sulfur vulcanized 31.3%PMMA grafted NR	31	124.8	18.1	64.7
9. 36.0%PMMA grafted NR	28	109.7	16.4	57.7
10. Sulfur vulcanized 36.0%PMMA grafted NR	13	44.3	12.7	41.9

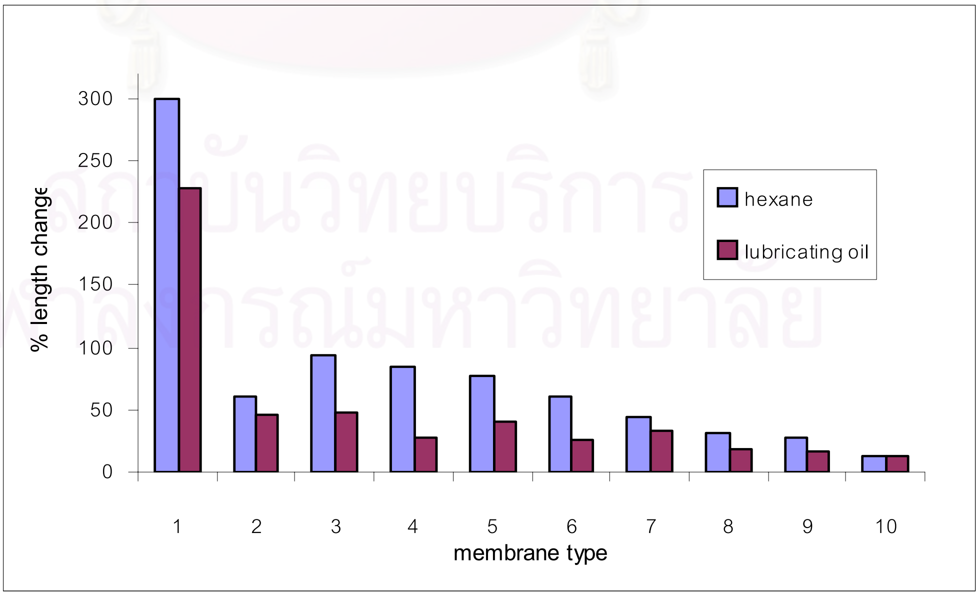


Figure 4.4 Change in length of membrane during immersion in solvent

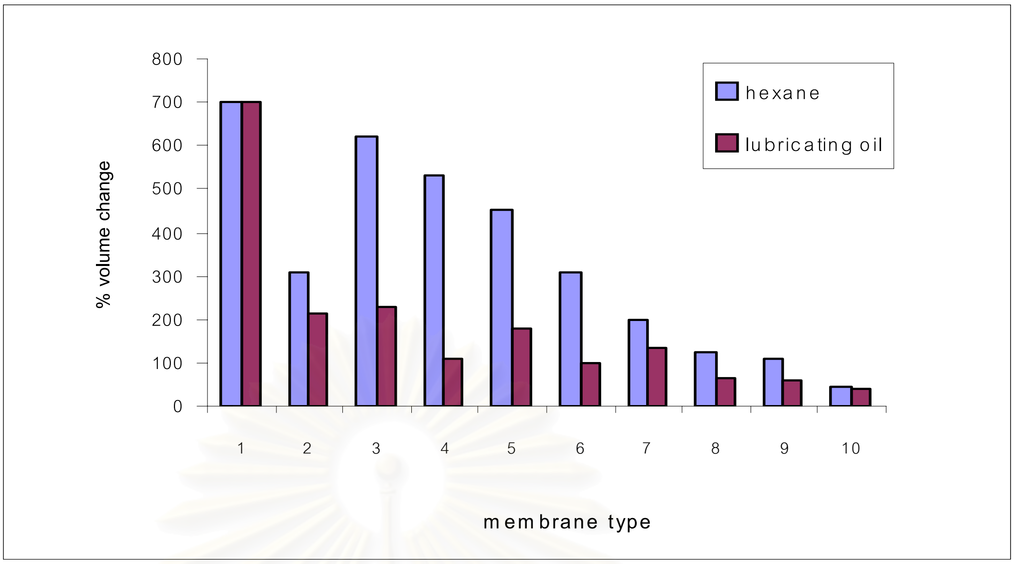


Figure 4.5 Change in volume of membrane during immersion in solvent

4.2.4 Determination of transport parameters of latex films

The study in transport parameters of polymer membrane was important in application of polymeric material in separation process. Transportation into the polymer could be described by transport parameter *i.e.*, D, S, P, n, K. The diffusion coefficient (D) characterizes the ability of the solvent molecule to move among the polymer segment, the sorption coefficient (S) is related to the equilibrium sorption of the penetrant. A large value of S shows a tendency of solvent to dissolve into the polymer. The permeability coefficient (P) implies the net effect of sorption and diffusion. The object of this work was to measure the sorption and transport characteristics of NR and grafted NR from gravimetric sorption.

Diffusion coefficient (D), sorption coefficients (S) and permeation coefficients (P)

The sorption data and graph of sorption of membranes and lubricating oil are shown in Appendix B. The sorption graphs were interpreted in terms of percent weight (%Q_t) increasing versus square root of time ($t^{1/2}$). Weight percent of oil was defined as weight of oil absorbed by 100 g of polymer membrane. The initial slope (θ) of this study, *i.e.*, before the attainment of 50-55% equilibrium sorption was calculated from linear regression of curve. The calculation was carried out using the equation 3.5 to calculate value of diffusion coefficient and equation 3.6 to calculate the sorption coefficient. The results of the permeability coefficient (P) calculated from equation 2.11. All results are shown in Table 4.5.

Table 4.5 Values of diffusion coefficient (D), sorption coefficient (S) and permeation coefficient (P) of synthetic latex films at 30^{o}C by using hexane and lubricating oil as a solvent.

Latex films	Dx10^{-9} (cm^2/sec)		S (g/g)		Px10^{-8} (cm/sec)
	D_{Avg}	SD	S_{Avg}	SD	
Prevulcanized	5.51	0	3.38	0.16	1.86
31.3% PMMA grafted NR	9.18	0.04	2.83	.04	2.60
Sulfur vulcanized 31.3% PMMA grafted NR	19.10	0.01	2.74	0.10	5.23

The calculated values of diffusion coefficient, sorption coefficient, permeation coefficient were also included in Table 4.5. It was found that sulfur vulcanized of 31.3% PMMA grafted NR membrane exhibited the highest D values of 19.1x10^{-9} and varied in order of sulfur vulcanized of 31.3% PMMA grafted NR >31.3%PMMA> prevulcanized NR while S values showed the opposite trend. The sulfur vulcanized of 31.3% PMMA grafted NR membrane had the higher D and lower S values that meant that the lubricant oil could rapidly enter in the film but could not dissolve. This could be explained by considering Figure 4.3(c) that the higher roughness of surface might allow the solvent to penetrate easier than the other membrane. Since PMMA tended to form a shell around NR core, the solubility of the membranes might be decreased. The prevulcanized NR showed a tendency to dissolve in the solvent. Furthermore, a high diffusion coefficient did not necessarily mean that a lot of liquid was being transported since the latter was governed by the permeability, which was the product of the diffusion coefficient and the solubility of the liquid in the material. The results obtained showed that the higher P value was obtained in the same order of diffusion coefficient. This meant that the lubricating oil could greatly penetrate through the film casted from sulfur vulcanized of 31.3% PMMA grafted NR rather than that casted from 31.3%PMMA and prevulcanized NR.

4.2.5 Transport mechanism of latex films

To study the type of transport mechanism for all solvent-polymer systems, the dynamic swelling results should be fitted to the following equation:

$$\mathrm{Log}\ (Q_t/Q_{eq}) \quad = \quad \log K + n \log t$$

Graphs of log (Q_t/Q_{eq}) *versus* log t (Appendix C) were constructed from sorption data. The linear portion of the sorption curves and linear regression analysis were used to calculate the values of n and K as given in Table 4.6. All results are processed in duplicates with a good repeatability, SD = 0 - 0.07.

Table 4.6 Values of n and K analyzed from sorption data of membrane using lubricating oil as solvent

Membrane type	N				$Kx10^3$			
	1	2	Avg	SD	1	2	Avg	SD
Prevulcanized	0.54	0.52	0.53	0.014	3.0	3.0	3.0	0
31.3%PMMA	0.70	0.70	0.70	0	5.0	5.2	5.1	0.014
Sulfur vulcanized 31.3% PMMA grafted NR	0.82	0.84	0.83	0.014	5.2	5.1	5.2	0.07

The transport phenomenon could be classified by slope of the sorption curves (n values) into 3 categories.[29]

(a) n= 0.5, Fickian (or Case I) diffusion which refers to approaches when the rate of diffusion is much smaller than that of relaxation of polymer segments due to mechanical, structural or the other modes of penetrant-polymer system. Solution equilibrium is rapidly established, leading to time-independent boundary conditions that do not depend on swelling kinetics. This category comprises penetrants in rubber polymer ($T>T_g$).

(b) n=1, non- Fickian (Case II) diffusion, refers to a rapid process compared to simultaneous relaxation processes. Here the sorption processes are complicated by strong dependence on swelling kinetics. The transport of penetrants in glassy polymer has come to this case.

(c) $0.5<n<1$, anomalous which refers to a process when diffusion and relaxation rates are comparable. Sorption and transportation of penetrant molecules are affected in this case by the presence of pre-existing microvoids within the polymer matrix.

It was observed that the n values of all membranes varied from 0.54 to 0.83. This indicated an anomalous-type transport mechanism ($0.5<n<1$) with the diffusion slightly deviating from Fickian trend. This implied that solvent mobility and polymer segment relaxation rates were comparable indicating the presence of the microvoids in the matrix. It was interesting to note that the n values in the membrane casted from prevulcanized NR was close to Fickian mode than those in the other cases indicating that the relaxation of polymer segments was more than in other cases. However, it was observed that there was no significant variation in value of K. The n value of NR related with Monnasit's report that the n value of prevulcanized NR showed anomalous type in cyclohexane (n = 0.57-0.77). The higher D and lower S values of this film were found in NR/PS core-shell particle using *t*-butylhydroperoxide initiator.

4.3 Dialysis

From investigation in section 4.2, the suitable membrane for re-refined process was sulfur vulcanized of 31.3% PMMA grafted NR. The dialysis procedure was followed as in section 3.4.10. To characterize the dialysis process, the diesel engine oil was dialyzed under different condition such as dialysate (grams) *vs*. time, osmotic volume *vs*. time and % dialysate *vs*. time. The results from this study are presented in Tables 4.7-4.10 and grafted in Figures 4.6-4.9. The repeatability value (SD) was 0.05-1.2%.

Figure 4.6 showed the amount of dialysate oil from 15%, 25%, 50%, 100% concentration of lubricating oil between 10-100 hours of dialysis. The amount of dialysate oil was increased over time for all samples which is shown in Figure 4.6. The osmosis volume also increases with increased sample concentration which is shown in Figure 4.7. The effects of concentration on amount of percent dialysate oil are also illustrated in Figure 4.8. The lower concentration gave higher percent of dialysate than high concentration because of the effect of osmotic volume.

Table 4.7 Dialysis of used lubricating oil

Time(hr)	Dialysate (g)	Dialysate (%)	Osmotic (g)
10	1.85	1.83	12.34
20	3.90	3.87	19.94
30	5.95	5.90	27.54
50	10.05	9.97	42.74
70	14.15	14.04	57.94
90	14.35	14.23	73.14
110	14.49	14.37	74.24

Table 4.8 Dialysis of 50% used lubricating oil in hexane

Time(hr)	Dialysate (g)	Dialysate (%)	Osmotic (g)
10	2.55	5.34	7.96
20	4.54	9.51	16.38
30	6.53	13.68	24.8
50	10.51	22.03	33.22
60	12.50	26.20	41.64
70	14.49	30.37	46.49

Table 4.9 Dialysis of 25% used lubricating oil in hexane

Time(hr)	Dialysate (g)	Dialysate (%)	Osmotic (g)
10	4.11	14.25	9.67
20	4.83	16.75	11.12
30	5.55	19.24	12.57
40	6.27	21.74	14.02
50	6.99	24.24	15.47
60	7.71	26.73	16.92
70	8.43	29.23	18.37
80	9.15	31.73	19.82
90	9.87	34.22	21.27

Table 4.10 Dialysis of 15% used lubricating oil in hexane

Time(hr)	Dialysate (g)	Dialysate (%)	Osmotic (g)
10	1.81	10.37	4.66
20	2.96	16.94	7.05
30	4.11	23.51	9.44
40	5.264	30.08	11.83
50	5.37	30.69	14.22

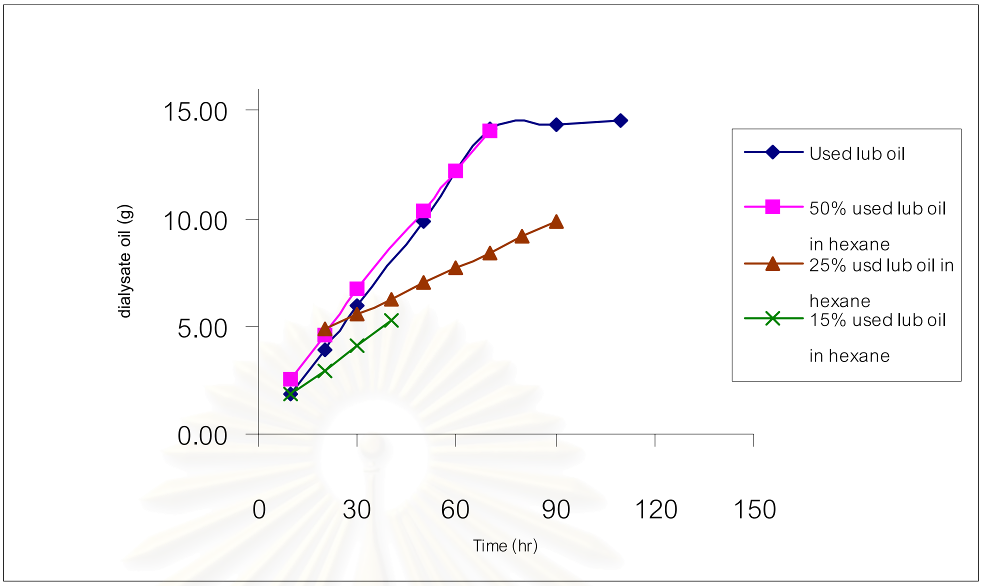


Figure 4.6 The relationship of dialysate oil *vs.* time

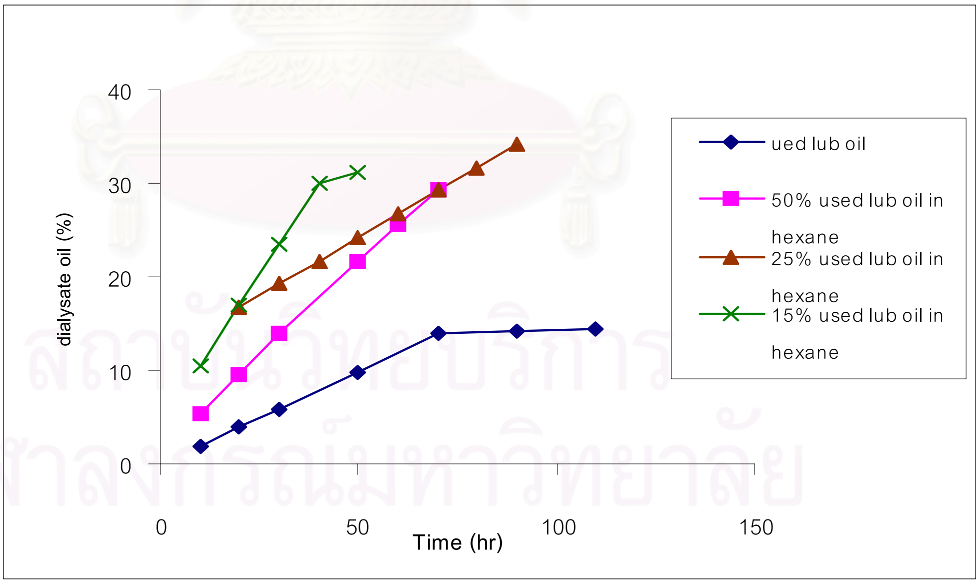


Figure 4.7 The relationship of percent dialysate oil *vs.* time

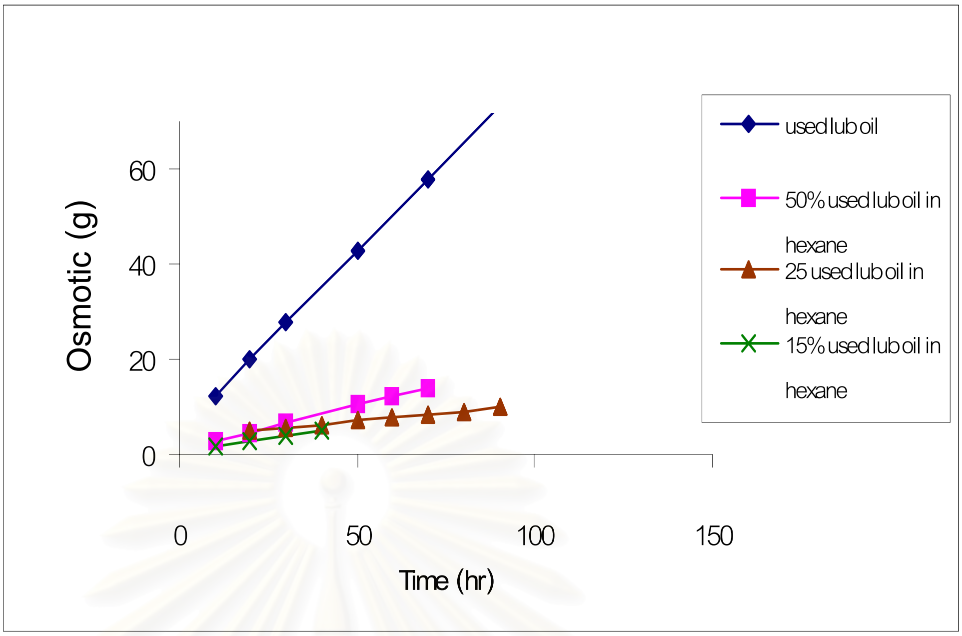


Figure 4.8 The relationship of osmotic *vs.* time

4.4 Re-refined used oil

The definition of oil re-refining is the process of cleaning and upgrading waste lubricating oil to produce a high quality base oil; the base oil is then blended with additives. The product of this process is called re-refined lubricating oil. Thailand had standard for re-refined base oil by TISI. The specification of this standard is shown in Table 4.11. Re-refined base oils in this standard are divided into two grades: the base oil for automotive lubricating oil and the base oil for general purpose.

This research of re-refining used oil provided a process which could save energy and had little impact on environment by using dialysis processes. The method was explained in 3.4.9. The high molecular weight hydrocarbon was termed “the dialysis residue” in one side of membrane and the low molecular weight base oil, low molecular weight materials that pass through the membrane was the dialysate. Arrangements were made to collect used oil from Nguan Chang Food Industry Co., Ltd., since only one brand of diesel engine lubricating oil grade 40w was used. This gave a more consistent sample of used lubricating oil to work than that obtained from a service station. Additionally, a sample of new oil was available for comparison. Many of the tests used for evaluating the quality of new, used, and re-refined lubricating oils were standard ASTM inspection tests, shown in appendix A. The composition of virgin lubricating oil and used oil are shown in Table 4.13. It showed that the compositions of used oil varies considerably from the virgin oil and significant difference were observed with respect to color, carbon residue, corrosion, acid number, water content. They occur during oil usage, form the chemical breakdown of additives and subsequent interaction among the compounds to produce corrosive acid and undesired substances.

4.4.1 Property of re-refined lubricating oil

After removal of solvent from dialysate by evaporation to yield the re-refined lubricating oil, the properties of oils at 30, 50, 60, 75% recovers were investigated and are shown in Table 4.12. This process produced good quality oil at 75% yield. The appearance of re-refined lubricating oil was clear and bright without any suspension particles as shown in Figure 4.9.

Figure 4.9 The appearance of oil, a) used lubricating oil, b) re-refined oil form dialysis process, and c) re-refined oil percolation through activated clay

The re-refined oils had some different value in viscosity and acid number. This could be described by the difference in rate of diffusion. The rate of diffusion depended on multi-factors such as temperature, concentration, diffusate molecular size and shape *etc*. Lubricating oil had different molecular weight (MW). The low MW could diffuse faster than high MW.

Table 4.11 Properties of re-refined base oil TISI standard

Property	Units	TISI STD[30]	
		Type 1	Type 2
1.Kinematic viscosity@$100^{O}C$	mm^2/sec	>5	>5
2.Kinematic viscosity@$40^{O}C$	mm^2/sec	-	-
3.Viscosity index	-	>92	0
4.Flash point(Cleveland Open Cup)	^{O}C	>180	>170
5.Acid number	mg KOH/g	<0.05	<1
6.Water	%	<0.05	<0.05
7.Ash	%	<0.01	<.2
8.Color	ASTM	<6	-
9.Conradson carbon residue	%	<0.9	-
10.Pour point	^{O}C	<-6	-
11.Sulfur	%	<1	-
12.Sulfate ash	%	<0.05	-
13.Copper Strip Corrosion@100 ^{o}C,3hrs	-	<1b	-

Table 4.12 Properties of dialysate oil

Property	Units	Recovered oil (%)			
		30	50	60	75
1.Kinematic viscosity @ 40^{O}C	mm^2/sec	78.03	87.48	87.88	90.32
2.Kinematic viscosity @ 100^{O}C	mm^2/sec	10.03	10.47	10.50	10.72
3.Viscosity index	-	109	102	102	102
4.Flash point(Cleveland Open Cup)	^{O}C	222	228	228	228
5.Acid number	mgKOH/g	0.17	0.20	0.26	0.27
6.Water	%	traces	traces	traces	traces
7.Ash	%	0.04	0.04	0.04	0.05
8.Color	ASTM	L6.0	L6.0	L6.0	L6.5
9.Conradson carbon residue	%	0.28	0.28	0.28	0.33
10.Pour point	^{O}C	-9	-9	-9	-9
11.Sulfur	%	0.40	0.40	0.47	0.52
12.Sulfate ash	%	0.04	0.04	0.04	0.05
13.Copper Strip Corrosion@100 ^{o}C,3hrs	-	1a	1a	1a	1a
14.Base number	mgKOH/g	0.20	0.20	0.19	0.20

The properties of standard re-refined base oil, re-refined oil, used oil and virgin oil are shown in Tables 4.11-4.13. The data showed that the characteristics of re-refined oils indicated the removal of contaminants from used oil. The physical and chemical properties of re-refined oil were within the specification of standard. The other characteristics were:

- The color of re-refined oil was lighter than that of used oil and within the specification of TISI standard but darker than virgin oil. It indicating the possible contaminants with another product such as higher-viscosity grade material and/or the presence of higher amount of sulfur or oxygenated compound in re-refined oil.

-The water content of re-refined oil was lower than that of used oil, indicating that the NR-g- PMMA membrane had semipermeable property to prevent high polarity compound from passing through the other side of membrane.

- The acid number of re-refined oil was low, indicating that the oxidation reaction by products had been removed in the re-refined process.

- The base number of re-refined oil was reduced by 80%, indicating that the oxidation products and residue of high molecular weight additives such as, dispersants, detergens had been removed in the re-refined process.

Comparing with used oil, re-refined oil had lower ash, carbon residue, sulfur and sulfate ash. The lower values of all those indicated the efficiency of membrane to remove oxygenate by product, corrosion compounds and metal. Copper corrosion of re-refined oil was better than that of used oil. This was a direct indication of the reduction of corrosion compounds formed from some sulfur compounds. The data showed that the process contaminant could be reduced by 70-80%. Thus the properties of re-refined base oil were met with specification in type 2 of TISI standard and met the type 1 specification except the acid number, ash and sulfated ash.

4.4.2 Quality of re-refined oil percolation through caustic-treated clay

The result in Table 4.13 showed that percolation through caustic-treated clay was effective in removing acid number and metallic components. The received oil had good quality and met specification of TISI standard.

Table 4.13 Properties of used lubricating oil, new lubricating oil, re-refined oil and TISI standard

Property	Units	New lub oil	Used lub oil	75% Recovered oil after clay treatment		TISI std type 1
				Averange value	SD	
1.Kinematic viscosity @ 40^{O}C	mm^{2}/sec	135.2	124.7	90.02	0.59	>5
2.Kinematic viscosity @ 100^{O}C	mm^{2}/sec	14.10	13.79	10.72	0.25	>95
3.Viscosity index	-	101	108	102	-	>92
4.Flash point(Cleveland Open Cup)	^{O}C	-	226	228	3	>180
5.Acid number	mg KOH/g	-	2.42	0.04	0.01	<0.05
6.Water	%	Traces	2.2	Traces	0	<0.05
7.Ash	%	1.1	1.15	0.003	0.001	<0.01
8.Color	ASTM	4.5	>8	3	0	<6
9.Conradson carbon residue	%	1.45	2.42	0.21	0.03	<0.9
10.Pour point	^{O}C	-18	-18	-9	0	<-6
11.Sulfur	%	-	0.64	-	-	<1
12.Sulfate ash	%	1.3	0.96	0.003	0.001	<0.05
13.Copper Strip Corrosion@100 ^{o}C,3hrs	-	1a	1b	1a	0	<1b

CHAPTER V

CONCLUSION

5.1 Preparation of NR-g-PMMA

The graft copolymer of polymethylmethacrylate on natural rubber latices was prepared by emulsion polymerization at room temperature. Initiator was *tert*-butyl hydroperoxide/tetraethylenepentamine. The room temperature was sufficient to complete polymerization. The reaction was strong exothermic reaction and had long term stability. The formation of grafted natural rubber was confirmed by FT-IR spectrum. The FT-IR spectrum showed new peaks at 1733 cm^{-1} and 1148 cm^{-1}, corresponding to C=O and C-O-C groups in methyl methacrylate chain. The study was carried out for the effect of MMA monomer concentration on conversion, grafting efficiency and percentage grafted natural rubber. It was found that the %conversion, grafting efficiency and percentage grafted natural rubber decrease but % homopolymer increased with increase of the MMA ratio.

5.2 Properties of latex films

The increasing of MMA ratio had affected on the properties of films and these effects were even more when vulcanized with sulfur. Because of the hardness of PMMA, core shell of PMMA around the particle was formed resulting in high cross-link of films. These could reduce interface adhesion of film. The cast film of grafted NR was transparent but more rigid than that of NR film. It was found that when MMA content exceeded ca 22.5% the film would exhibit film cracking and decrease film forming ability. The SEM micrograph showed the roughness of film increased with increasing of MMA content. The durability of films in hexane and lubricating oil were in the order of 36.0% PMMA >31.3% PMMA> prevulcanize> 24.8%PMMA >22.5%PMMA>NR(HA). The study of transportation behavior of prevulcanized film, 31.3% PMMA grafted NR film and sulfur vulcanized 31.3%PMMA grafted NR film were explained in terms of diffusion coefficient (D) and permeability coefficient (P).

The D, P values varied in the order of sulfur vulcanized 31.3%PMMA grafted NR film>31.3% PMMA grafted NR film> prevulcanized film. Due to the high roughness of film so the solvent could easily penetrate into it. The transport mechanism of all films was anomalous-type diffusion.

The study on the properties of film could be concluded that the suitable film for separation of used oil was sulfur vulcanized of 31.3%PMMA grafted NR.

5.3 Re-refined used oil

The qualities of re-refined oils from dialysis technique showed that this technique could remove about 70-80% of oxidation material, water, carbon particle and some additive. Production yield was 75%. When percolation through caustic clay and sorption clay, the acid value, ash and sulfated ash were reduced. The product met specification of re-refined base oil standard of Thailand Industry Standard Institute.

5.4 Suggestion

The properties of the other polymer graft with NR should be investigated for used as membrane for used lubricating oil separation. The other polymer such as, polyacryllonitrile,poy vinyl alcohol,polymethacrylic acid.

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APPENDICES

APPENDIX A

A1. Standard Test Method for
Sulfated Ash from Lubricating Oils and Additives
ASTM D874-96

This test method covers the determination of the sulfated ash from unused lubricating oils containing additive and from additive concentrates used in compounding. Sulfated ash is the residue remaining after the sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to constant weight.

Summary of Test Method

The sample is ignited and burned until only ash and carbon remains. After cooling, the residue is treated with sulfuric acid and heated at 775^0C until oxidation of carbon is complete. The ash is then cooled, re-treated with sulfuric acid, and heated at 775^0C to constant weight.

Calculate the sulfated ash as a percentage of the original sample as follows:

$$\text{Sulfated ash, mass \%} = (w/W)*100$$

w = grams of sulfated ash, and
W = grams of sample used.

A2. Standard Test Method for
Conradson Carbon Residue of Petroleum Products
ASTM D 189-88

This test method covers the determination of the amount of carbon residue left after evaporation and pyrolysis of oil. Carbon residue is the residue formed by evaporation and thermal degradation of a carbon containing material

Summary of The test method

A weight quantity of sample is placed in a crucible and subjected to destructive distillation. The residue undergoes cracking and coking reactions during a fixed period of severe heating. At the end of the specified heating period, the test crucible contain the carbonaceous residue is cooled in a desiccator and weighed. The residue remaining is calculated as a percentage of the original sample, and reported as Conradson carbon residue.

Significant and used

The carbon residue value of motor oil, while at one time regarded, as indicative of the amount of carbonaceous deposits motor oil would form in the combustion chamber of an engine, is now considered to be of doubtful significance due to the presence of additive in many oils. For example, an ash forming detergent additive may increase the carbon residue value of oil yet will generally reduce its tendency to form deposits.

Calculation

Calculation the carbon residue of the sample as follows

Carbon residue = (A*100)/W

Where

A= mass of carbon residue, g, and

W = mass of sample, g.

A3. Standard Test Method for

Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test

ASTM D130

This test method covers the detection of the corrosiveness to copper of aviation turbine fuel, automotive gasoline

Summary of test method

A polished copper strip is immersed in a given quantity of sample and heated at a temperature and for a time characteristic of the material being tested. At the end of this period the copper strip is removed, washed, and compared with the ASTM Copper Strip Corrosion Standards.

Significance and use

Crude petroleum contains sulfur compounds, most of which are removed during refining. However, of the sulfur remaining in the petroleum product, some can have a corroding action on various metals and this corrosivity is not necessarily related directly to the total sulfur content. The effect can vary according the chemical types of sulfur compounds present. The copper strip corrosion test is designed to assess the degree of corrosion test is designed to assess the relative degree of corrosivity of a petroleum product.

A4. Standard Test Method for
Flash and Fire Point by Cleveland Open Cup
ASTM D92

<u>Summary of test method</u>

Approximate 70 ml of test specimen is filled into a test cup. The top of the meniscus of the test specimen is exactly at the filling mark and place the test cup on the center of the heater. The temperature of the test cup and the sample shall not excess 56^{O}C below the expected flash point. The temperature of the test specimen is increased rapidly at rate 14 to 17 ^{O}C /min. When the test specimen temperature is approximately 56 ^{O}C below the expected flash point, decrease the heat so that the rate of temperature rise during the last 28 ^{O}C before the flash point, is5 to 6 ^{O}C /min.

Apply the test flame when the temperature of the test specimen is approximately 28 ^{O}C below the expected flash point and each time thereafter at a temperature reading that is a multiple of 2^{O}C. Pass the test flame across the center of the test cup, at right angles to the diameter, which passes through. The temperature measuring device. Record, as the observed flash point, the reading on the temperature-measuring device at the time the test flame causes a distinct flash in the interior of the test cup.

A5. Standard Test Method for
Water in petroleum Products and Bituminous Materials by Distillation
ASTM D95-83

<u>Summary of test method</u>

Measure liquid sample 100 ml in a graduated cylinder. Rinse the material adhering to the cylinder with one 50-ml and 25-ml portions of the solvent carrier liquid (petroleum distillate). Drain the cylinder thoroughly after the simple transfer and each rinsing. Assemble the component of the apparatus as illustrated in figure1. Sample is heated with condensed rate from the condenser at 2 to 5 drops per second. Continue distillate until volume of water in the trap remains constant for 5 min. Allow the trap and contents to cool to room temperature. Dislodge any drops of water adhering to the side of the trap with a glass rod. Read the volume of the water in the trap to the nearest scale division. Calculation the water in the sample, as follows:

$$\text{Water, \%} = v/w*100$$

Where:
V= volume of water in trap and
W= weight (or volume of sample)

A6. Standard Test Method for
ASTM Color of Petroleum Products (ASTM Color Scale)
ASTM D 1500-91

Fill the sample container to a depth of 50mm or more and observe the color. When the sample is Dark than 8 color at the temperature.

A7. Standard Test Method for
Acid Number of Petroleum Products by Potentiometric Titration
ASTM D664-95

Summary of test method

Prepare 5.0g±25 of sample dissolved in 125ml of mixture of toluene and propan-2-olcontaining small amount of water and titrated potentiometrically with 0.1N alcoholic potassium hydroxide using a glass indicating electrode and a calomel reference electrode. The meter readings are plotted between volumes of solution and voltage. The end points are taken at meter readings corresponding to those found for freshly prepared non aqueous acidic buffer solutions. Calculation the acid number as follows:

$$\text{Acid number, mg KOH/g} = (A-B)*M*56.1/W$$

A= alcoholic KOH solution used to titrate sample to end point, ml.
B= volume corresponding to A for blank titration, ml
M= concentration of alcoholic KOH solution, mol/L

APPENDIX B.

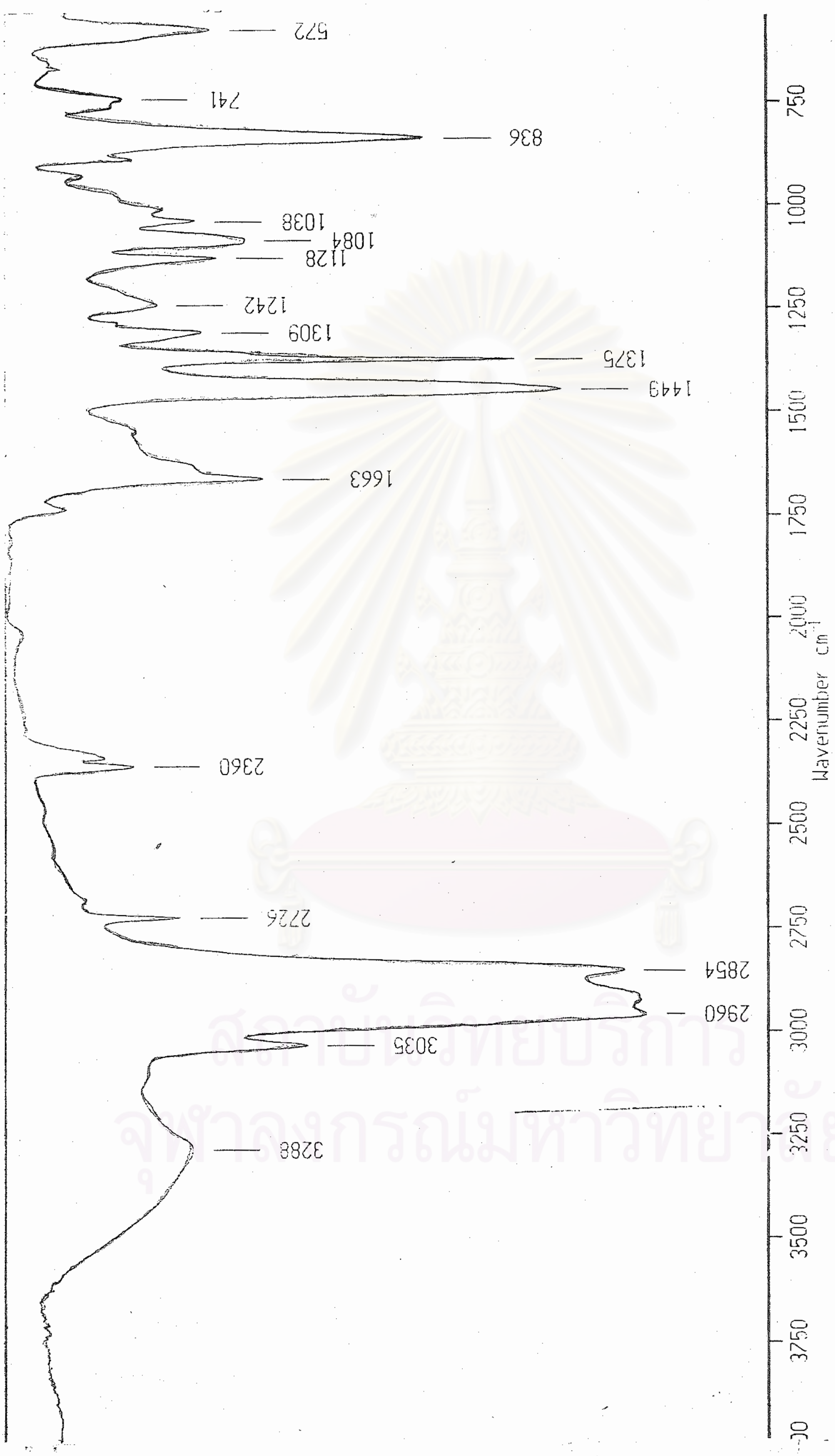

Figure B1 The infrared spectrum of natural membrane NR (HA)

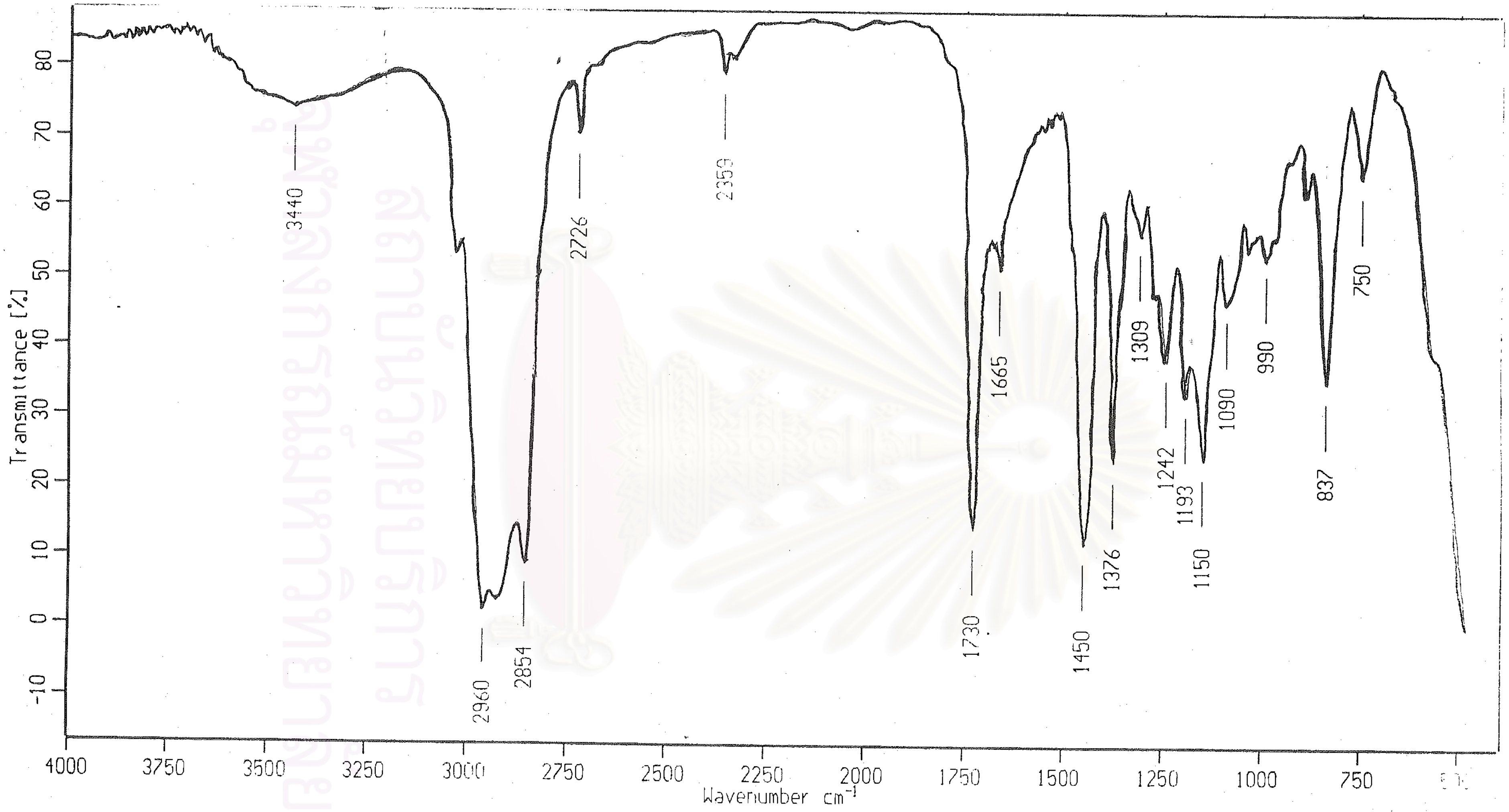

Figure B2 The infrared spectrum of 20%PMMA grafted NR

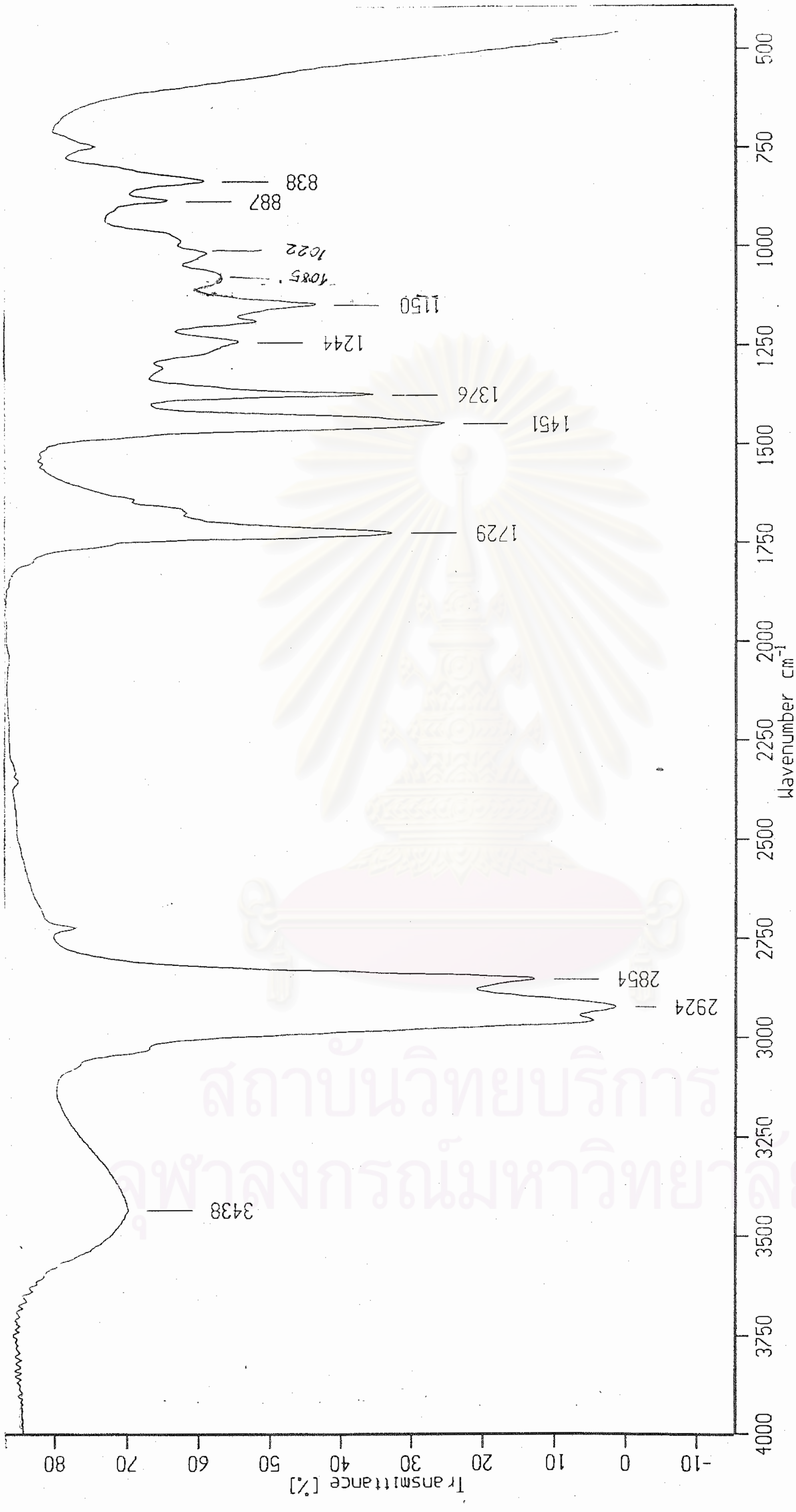

Figure B3 The infrared spectrum of 30%PMMA grafted NR

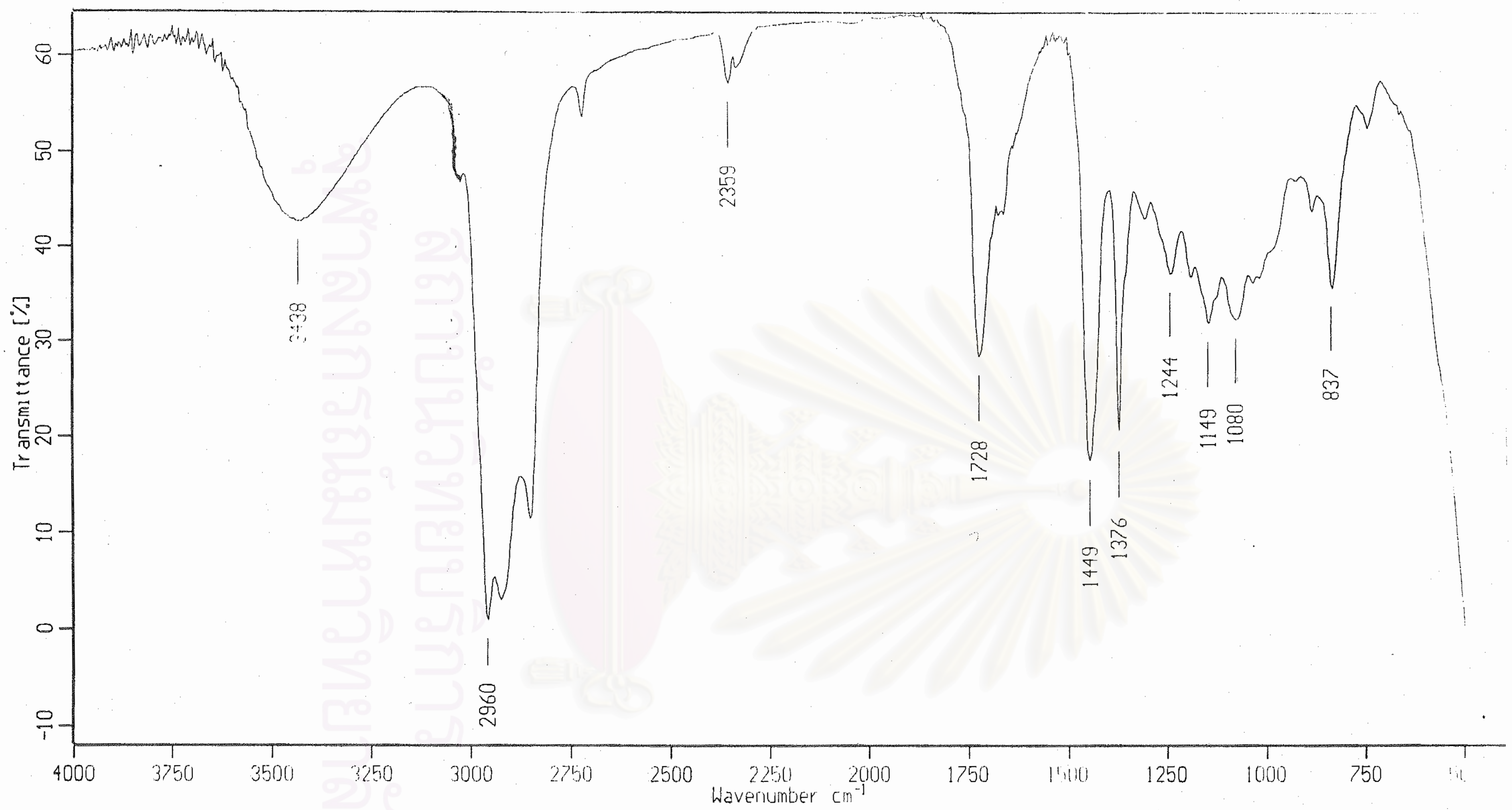

Figure B4 The infrared spectrum of 40%PMMA grafted NR

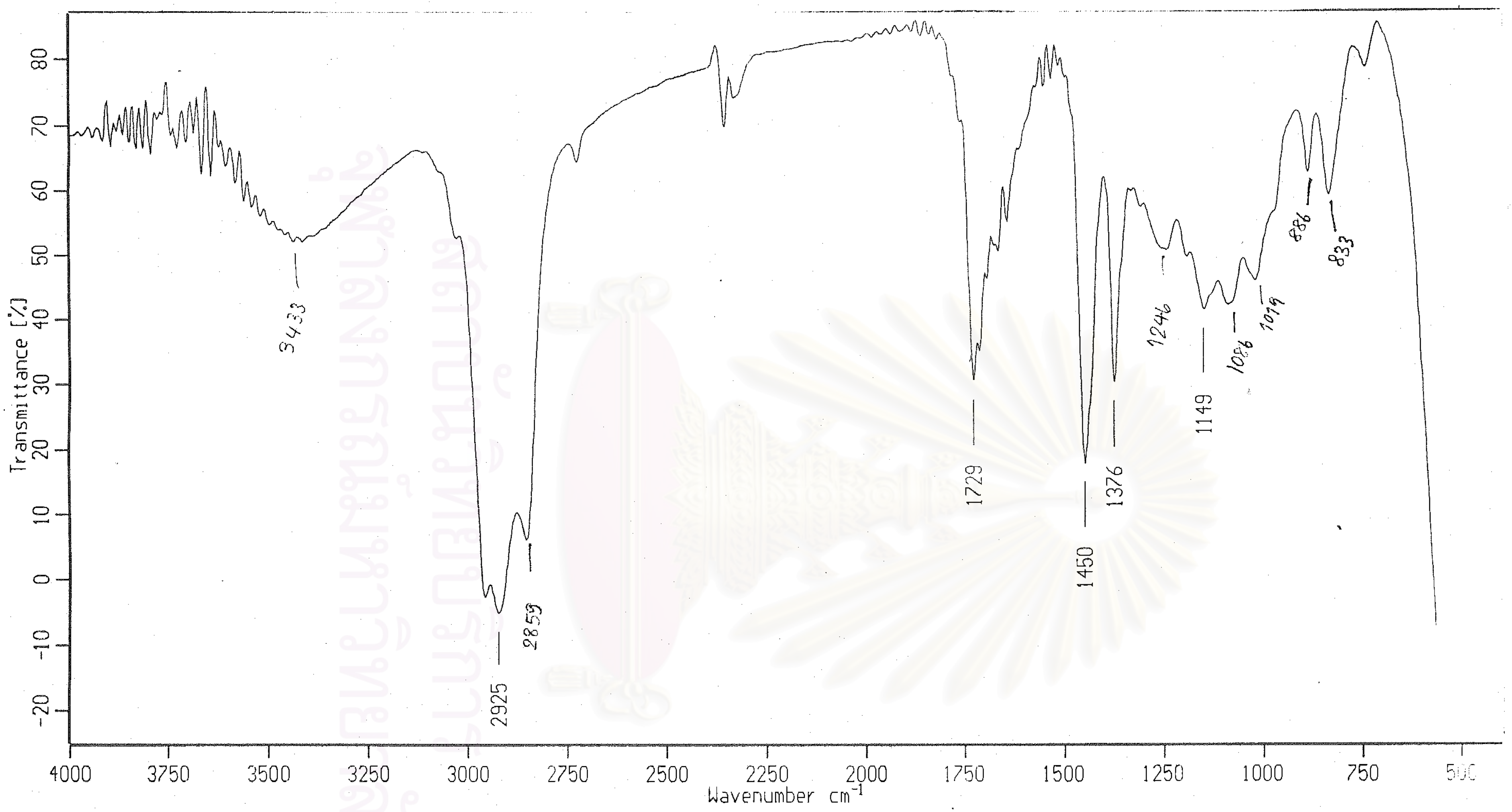

Figure B5 The infrared spectrum of 50%PMMA grafted NR

APPENDIX C

Table C1 Sorption data of prevulcanized film (A)

Time(sec)	Weight(g)	Q (g)	$t^{1/2}$ (sec)	%Q (g)	Q/Q_{eq}	log t	log Q/Q_{eq}	
30	0.1093	0.0052	5.48	5.00	0.02	1.48	-1.67	
120	0.1123	0.0082	10.95	7.88	0.03	2.08	-1.47	initial weight 0.1041g
240	0.1164	0.0123	15.49	11.82	0.05	2.38	-1.30	thickness0.038cm.
360	0.1204	0.0163	18.97	15.66	0.07	2.56	-1.17	Slope=1.03
480	0.1236	0.0195	21.91	18.73	0.08	2.68	-1.10	Q_{eq}=233.72
600	0.1265	0.0224	24.49	21.52	0.09	2.78	-1.04	$D=5.51*10^{-9}$
2430	0.1542	0.0501	49.30	48.13	0.21	3.39	-0.69	LogK=-2.54
4230	0.1681	0.064	65.04	61.48	0.26	3.63	-0.58	K=0.003
6030	0.187	0.0829	77.65	79.63	0.34	3.78	-0.47	n=0.54
9630	0.2068	0.1027	98.13	98.66	0.42	3.98	-0.37	
16830	0.275	0.1398	129.73	134.29	0.57	4.23	-0.24	
24030	0.2579	0.1682	155.02	161.58	0.69	4.38	-0.16	
27630	0.2816	0.1775	166.22	170.51	0.73	4.44	-0.14	
45630	0.3221	0.218	213.61	209.41	0.90	4.66	-0.05	
87030	0.3352	0.2311	295.01	222.00	0.95	4.94	-0.02	
128430	0.3463	0.2422	358.37	232.66	1.00	5.11	0.00	
135630	0.3453	0.2412	368.28	231.70	0.99	5.13	0.00	
160830	0.3474	0.2433	401.04	233.72	1.00	5.21	0.00	
164430	0.3474	0.2433	405.50	233.72	1.00	5.21	0.00	

Table C2 Sorption data of prevulcanized film (B)

Time(sec)	Weight(g)	Q (g)	$t^{1/2}$ (sec)	%Q (g)	Q/Q_{eq}	log t	log Q/Q_{eq}	
30	0.1078	0.004	5.48	3.85	0.02	1.48	-1.78	
120	0.1125	0.0087	10.95	8.38	0.04	2.08	-1.45	
240	0.1167	0.0129	15.49	12.43	0.05	2.38	-1.27	Initial weight .1038g
360	0.1202	0.0164	18.97	15.80	0.07	2.56	-1.17	Thickness0.048cm.
480	0.1226	0.0188	21.91	18.11	0.08	2.68	-1.11	Slope=0.82
600	0.1247	0.0209	24.49	20.13	0.09	2.78	-1.06	Q_{eq}=233.82
720	0.1269	0.0231	26.83	22.25	0.10	2.86	-1.02	$D=5.51*10^{-9}$
840	0.1273	0.0235	28.98	22.64	0.10	2.92	-1.01	logK=-2.51
4440	0.1601	0.0563	66.63	54.24	0.23	3.65	-0.63	K=0.003
8040	0.184	0.0802	89.67	77.26	0.33	3.91	-0.48	n=0.52
15240	0.215	0.1112	123.45	107.13	0.46	4.18	-0.34	
22440	0.239	0.1352	149.80	130.25	0.56	4.35	-0.25	
29640	0.2522	0.1484	172.16	142.97	0.61	4.47	-0.21	
43800	0.2745	0.1707	209.28	164.45	0.70	4.64	-0.15	
57960	0.2986	0.1948	240.75	187.67	0.80	4.76	-0.10	
92400	0.3203	0.2165	303.97	208.57	0.89	4.97	-0.05	
126840	0.3392	0.2354	356.15	226.78	0.97	5.10	-0.01	
159240	0.345	0.2412	399.05	232.37	0.99	5.20	0.00	
162840	0.344	0.2402	403.53	231.41	0.99	5.21	0.00	
166440	0.3465	0.2427	407.97	233.82	1.00	5.22	0.00	
173640	0.3465	0.2427	416.70	233.82	1.00	5.24	0.00	

Table C3 Sorption data of 31.3% PMMA grafted NR film (A)

Time(sec)	Weight(g)	Q(g)	t1/2(sec)	%Q(g)	Q/Qeq	log t	log Q/Qeq	
30	0.0251	0.0015	5.48	6.36	0.05	1.48	-1.31	
60	0.0267	0.0031	7.75	13.14	0.10	1.78	-1.00	
120	0.0283	0.0047	10.95	19.92	0.15	2.08	-0.82	
150	0.0292	0.0056	12.25	23.73	0.18	2.18	-0.74	Initial weight0.0236 g
180	0.0299	0.0063	13.42	26.69	0.20	2.26	-0.69	Thickness0.009cm.
210	0.0306	0.007	14.49	29.66	0.23	2.32	-0.64	Slope=3.13
300	0.0314	0.0078	17.32	33.05	0.25	2.48	-0.60	Qeq=130.51
360	0.0327	0.0091	18.97	38.56	0.30	2.56	-0.53	D=9.15*10-9
390	0.0332	0.0096	19.75	40.68	0.31	2.59	-0.51	log K=-2.30
420	0.0336	0.01	20.49	42.37	0.32	2.62	-0.49	K=0.0050
480	0.0344	0.0108	21.91	45.76	0.35	2.68	-0.46	n=0.70
570	0.0367	0.0131	23.87	55.51	0.43	2.76	-0.37	
600	0.037	0.0134	24.49	56.78	0.44	2.78	-0.36	
660	0.0386	0.015	25.69	63.56	0.49	2.82	-0.31	
780	0.0407	0.0171	27.93	72.46	0.56	2.89	-0.26	
810	0.0413	0.0177	28.46	75.00	0.57	2.91	-0.24	
840	0.042	0.0184	28.98	77.97	0.60	2.92	-0.22	
870	0.0425	0.0189	29.50	80.08	0.61	2.94	-0.21	
900	0.0429	0.0193	30.00	81.78	0.63	2.95	-0.20	
930	0.0434	0.0198	30.50	83.90	0.64	2.97	-0.19	
960	0.0438	0.0202	30.98	85.59	0.66	2.98	-0.18	
990	0.0441	0.0205	31.46	86.86	0.67	3.00	-0.18	
1890	0.0512	0.0276	43.47	116.95	0.90	3.28	-0.05	
5490	0.0544	0.0308	74.09	130.51	1.00	3.74	0.00	
9090	0.0544	0.0308	95.34	130.51	1.00	3.96	0.00	
9690	0.0544	0.0308	98.44	130.51	1.00	3.99	0.00	

Table C4 Sorption data of 31.3% PMMA grafted NR film (B)

Time(sec)	Weight(g)	Q (g)	$t^{1/2}$ (sec)	%Q (g)	Q/Q_{eq}	log t	log Q/Q_{eq}	
30	0.0396	0.003	5.48	8.2	0.06	1.48	-1.2	
60	0.0411	0.0045	7.75	12.3	0.09	1.78	-1.03	
120	0.0439	0.0073	10.95	19.95	0.15	2.08	-0.82	
180	0.0465	0.0099	13.42	27.05	0.21	2.26	-0.68	Initial weight 0.0366g
240	0.0485	0.0119	15.49	32.51	0.25	2.38	-0.6	thickness0.0085cm.
300	0.0521	0.0155	17.32	42.35	0.32	2.48	-0.49	Slope=3.32
360	0.0543	0.0177	18.97	48.36	0.37	2.56	-0.43	Qeq=130.33
420	0.056	0.0194	20.49	53.01	0.41	2.62	-0.39	$D=9.2*10^{-9}$
480	0.0575	0.0209	21.91	57.1	0.44	2.68	-0.36	log K-2.30
540	0.0589	0.0223	23.24	60.93	0.47	2.73	-0.33	K=0.0052
600	0.0604	0.0238	24.50	65.03	0.5	2.78	-0.3	n=0.70
660	0.062	0.0254	25.69	69.4	0.53	2.82	-0.27	
1560	0.08	0.0434	39.50	118.58	0.91	3.19	-0.04	
2460	0.0823	0.0457	49.60	124.86	0.96	3.39	-0.02	
3360	0.0838	0.0472	57.97	128.96	0.99	3.53	0	
4260	0.0843	0.0477	65.27	130.33	1	3.63	0	
5160	0.0843	0.0477	71.83	130.33	1	3.71	0	
8760	0.0843	0.0477	93.60	130.33	1	3.94	0	

Table C5 Sorption data of sulfur vulcanized 31.3% PMMA grafted NR film (A)

Time(sec)	Weight(g)	Q (g)	t1/2 (sec)	%Q (g)	Q/Qeq	log t	log Q/Qeq	
30	0.018	0.0018	5.48	11.11	0.08	1.48	-1.07	
60	0.0193	0.0031	7.75	19.14	0.15	1.78	-0.83	
90	0.0208	0.0046	9.49	28.40	0.22	1.95	-0.66	
120	0.0218	0.0056	10.95	34.57	0.26	2.08	-0.58	
150	0.0229	0.0067	12.25	41.36	0.32	2.18	-0.50	
180	0.0242	0.0080	13.42	49.38	0.38	2.26	-0.42	
210	0.0252	0.0090	14.49	55.56	0.42	2.32	-0.37	initial weight 0.0162g
240	0.026	0.0098	15.49	60.49	0.46	2.38	-0.34	Thickness0.007cm.
270	0.0271	0.0109	16.43	67.28	0.51	2.43	-0.29	Slope=5.84
300	0.0285	0.0123	17.32	75.93	0.58	2.48	-0.24	Qeq=130.86
330	0.0292	0.0130	18.17	80.25	0.61	2.52	-0.21	D=1.92*10-8
360	0.0299	0.0137	18.97	84.57	0.65	2.56	-0.19	log K=-2.285
390	0.0312	0.0150	19.75	92.59	0.71	2.59	-0.15	K=0.0052
420	0.0316	0.0154	20.49	95.06	0.73	2.62	-0.14	n=0.82
450	0.0328	0.0166	21.21	102.47	0.78	2.65	-0.11	
480	0.0337	0.0175	21.91	108.02	0.83	2.68	-0.08	
510	0.0346	0.0184	22.58	113.58	0.87	2.71	-0.06	
540	0.0353	0.0191	23.24	117.90	0.90	2.73	-0.05	
570	0.0356	0.0194	23.87	119.75	0.92	2.76	-0.04	
600	0.0359	0.0197	24.49	121.60	0.93	2.78	-0.03	
630	0.0363	0.0201	25.10	124.07	0.95	2.80	-0.02	
660	0.0366	0.0204	25.69	125.93	0.96	2.82	-0.02	
690	0.0369	0.0207	26.27	127.78	0.98	2.84	-0.01	
720	0.0371	0.0209	26.83	129.01	0.99	2.86	-0.01	
750	0.0373	0.0211	27.39	130.25	1.00	2.88	0.00	
780	0.0374	0.0212	27.93	130.86	1.0000	2.89	0.00	

Table C6 Sorption data of sulfur vulcanized 31.3% PMMA grafted NR film (B)

Time(sec)	Weight(g)	Q (g)	$t^{1/2}$ (sec)	%Q (g)	Q/Q_{eq}	log t	log Q/Q_{eq}	
30	0.015	0.00	5.48	11.11	0.09	1.48	-1.07	
60	0.0161	0.00	7.75	19.26	0.15	1.78	-0.83	
90	0.0174	0.00	9.49	28.89	0.22	1.95	-0.65	
120	0.0184	0.00	10.95	36.30	0.28	2.08	-0.56	
150	0.0193	0.01	12.25	42.96	0.33	2.18	-0.48	initial weight 0.0135g
180	0.0206	0.01	13.42	52.59	0.40	2.26	-0.39	thickness0.007cm.
210	0.0216	0.01	14.49	60.00	0.46	2.32	-0.34	Slope=5.79
240	0.0226	0.01	15.49	67.41	0.52	2.38	-0.29	Q_{eq}=130.37
300	0.0236	0.01	17.32	74.81	0.57	2.48	-0.24	$D=1.90*10^{-8}$
330	0.0244	0.01	18.17	80.74	0.62	2.52	-0.21	log K=-2.30
360	0.0252	0.01	18.97	86.67	0.66	2.56	-0.18	K=0.0051
390	0.0258	0.01	19.75	91.11	0.70	2.59	-0.16	n=0.84
420	0.0268	0.01	20.49	98.52	0.76	2.62	-0.12	
450	0.0279	0.01	21.21	106.67	0.82	2.65	-0.09	
480	0.0289	0.02	21.91	114.07	0.88	2.68	-0.06	
510	0.0293	0.02	22.58	117.04	0.90	2.71	-0.05	
540	0.0305	0.02	23.24	125.93	0.97	2.73	-0.02	
570	0.0311	0.02	23.87	130.37	1.00	2.76	0.00	

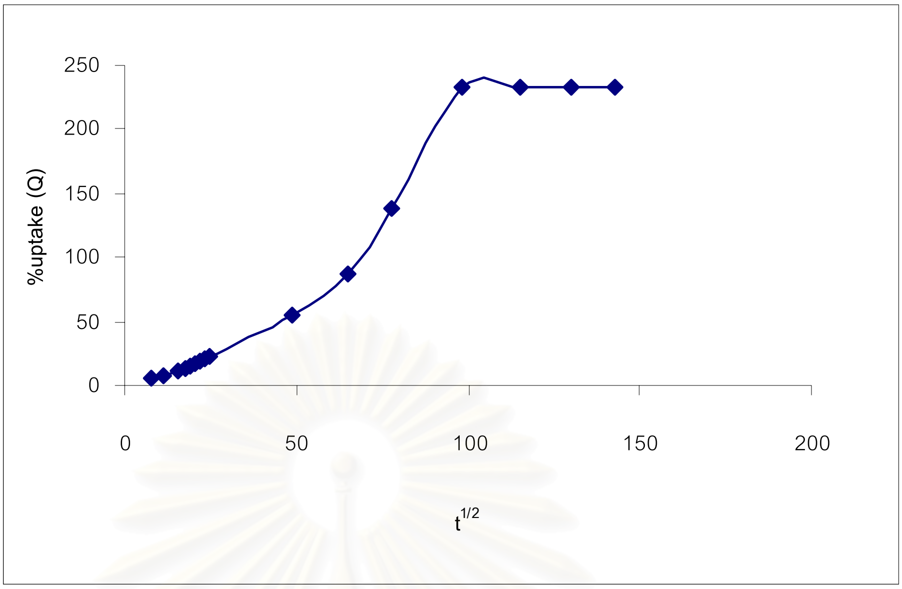

Figure C1 Sorption curve of prevulcanized latex film

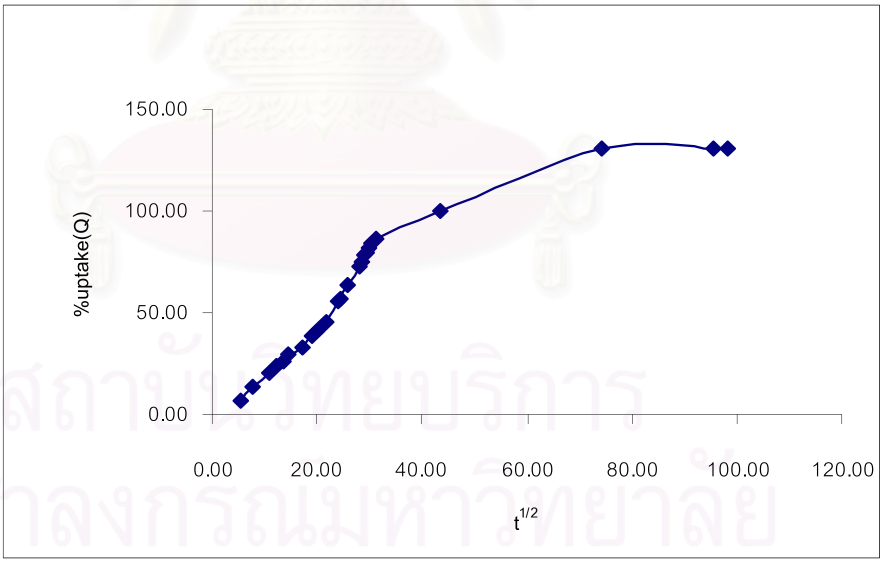

Figure C2 Sorption curve of 40%PMMA grafted NR latex film

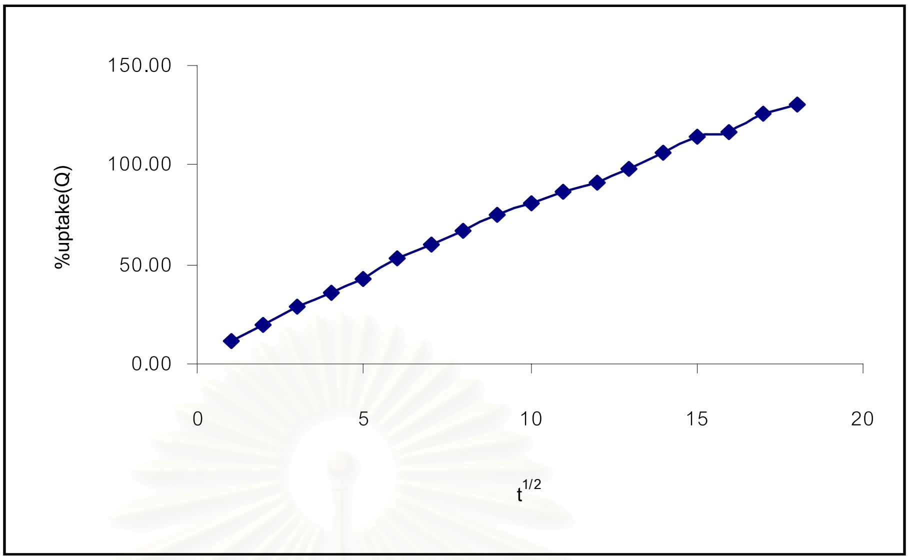

Figure C3 Sorption curve of Sulfur vulcanized 40%PMMA grafted NR film

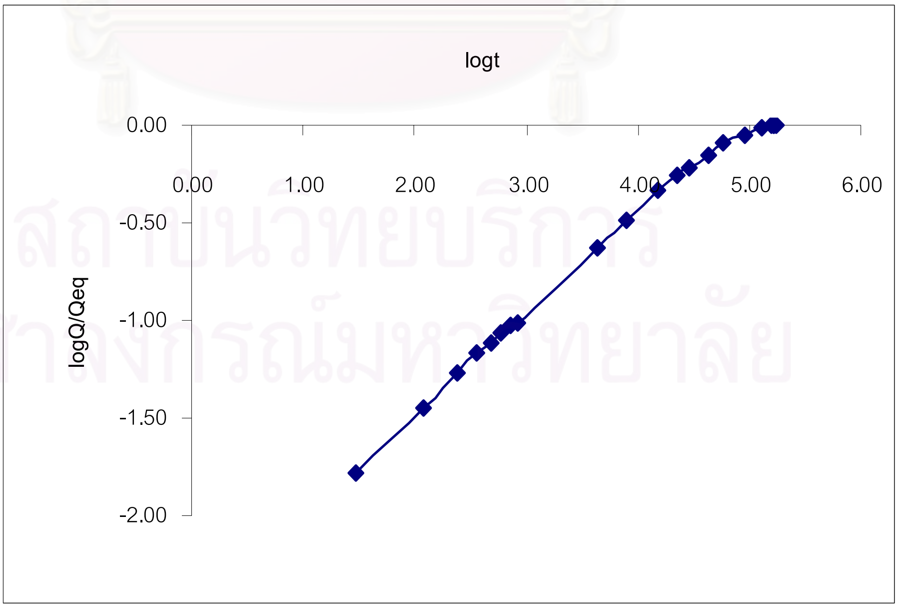

Figure C4 Fickian curve of prevulcanized latex film

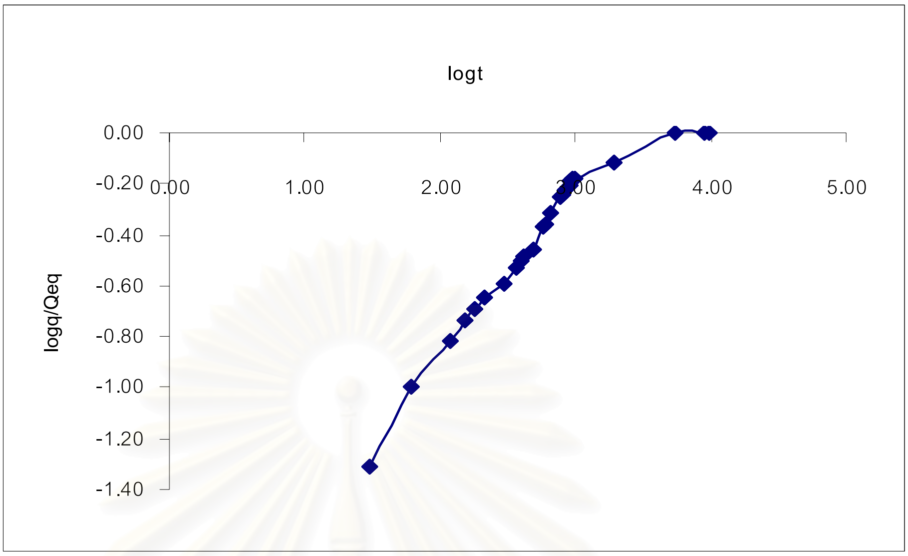

Figure C5 Fickian curve of 40%PMMA grafted NR latex film

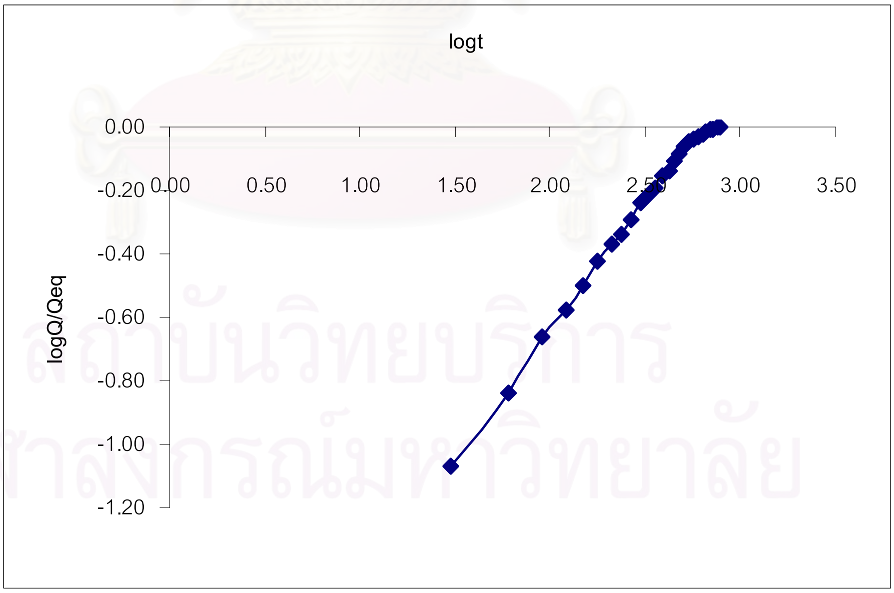

Figure C6 Fickian curve of Sulfur vulcanized 40%PMMA grafted NR film

VITAE

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