แอสฟัลต์ที่ดัดแปรด้วยน้ำยางธรรมชาติ สำหรับการลาดถนน

นายวชิระ เสาวภาคย์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรดุษฎีบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2559

NATURAL RUBBER LATEX – MODIFIED ASPHALTS FOR PAVEMENT APPLICATION

Mr. Wachira Saowapark

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2016

Thesis Title	NATURAL RUBBER LATEX – MODIFIED ASPHALTS FOR PAVEMENT APPLICATION
By	Mr. Wachira Saowapark
Field of Study	Chemical Engineering
Thesis Advisor	Associate Professor Sarawut Rimdusit, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Doctoral Degree

....Dean of the Faculty of Engineering

(Associate Professor Supot Teachavorasinskun, D.Eng.)

THESIS COMMITTEE

....Chairman

(Associate Professor Siriporn Damrongsakkul, Ph.D.)

....Thesis Advisor

(Associate Professor Sarawut Rimdusit, Ph.D.)

....Examiner

(Chutimon Satirapipathkul, D.Eng.)

....Examiner

(Pimporn Ponpesh, Ph.D.)

....External Examiner

(Associate Professor Chirakarn Muangnapoh, Dr.Ing.)

วชิระ เสาวภาคย์ : แอสฟัลต์ที่ดัดแปรด้วยน้ำยางธรรมชาติ สำหรับการลาดถนน (NATURAL RUBBER LATEX – MODIFIED ASPHALTS FOR PAVEMENT APPLICATION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.ศราวุธ ริมดุสิต, 90 หน้า.

อิลาสโตเมอร์เป็นพอร์ลิเมอร์ที่ถูกนำไปใช้เป็นวัสดุสำหรับการดัดแปรผลิตภัณฑ์แอสฟัลต์มากที่สุด ในปัจจุบันประเทศไทยมีการใช้ยางธรรมชาติเป็นวัสดุในการดัดแปรผลิตภัณฑ์แอสฟัลต์ที่ใช้สำหรับการลาดถนน ซึ่งเป็นการสนับสนุนการใช้ผลิตภัณฑ์ทางการเกษตรที่เป็นผลิตภัณฑ์หลักของประเทศ อย่างไรก็ตามเนื่องจากยางธรรมชาติมีขีดจำกัดด้านอายุการใช้งาน จึงต้องมีการศึกษาการยืดอายุความเสถียรของการใช้งานของแอสฟัลต์ที่ดัดแปรด้วยน้ำยางธรรมชาติต่อไป งานวิจัยนี้ศึกษาคุณสมบัติของผลิตภัณฑ์แอสฟัลต์ที่ถูกดัดแปรด้วยยางธรรมชาติ กรดพอร์ลิฟอสฟอริก และกำมะถัน ดังนี้ คุณสมบัติทางกายภาพ คุณสมบัติความเสถียรของการเก็บรักษา คุณสมบัติด้านสัณฐานวิทยา และคุณสมบัติเชิงรีโอโลยี ยางธรรมชาติเป็นอิลาสโตเมอร์ที่เป็นมิตรกับสิ่งแวดล้อม ซึ่งสามารถใช้ในรูปน้ำยางเพื่อหลีกเลี่ยงสภาวะการผสมที่รุนแรง ในงานวิจัยนี้มีการพิสูจน์ว่าการใช้ปริมาณเพียงเล็กน้อยของกรดพอร์ลิฟอสฟอริก และกำมะถันสามารถทำงานร่วมกันกับอิลาสโทเมอร์เพื่อเพิ่มความเสถียรของแอสฟัลต์ได้ การทดลองนี้แสดงผลการดัดแปรแอสฟัลต์เกรด AC 60/70 ด้วยยางธรรมชาติ 0.6 ถึง 4.5 เปอร์เซ็นต์โดยน้ำหนักแอสฟัลต์ กรดพอร์ลิฟอสฟอริก 1 ถึง 2 เปอร์เซ็นต์โดยน้ำหนักแอสฟัลต์ และกำมะถัน 0.3 ถึง 1.0 เปอร์เซ็นต์โดยน้ำหนักยางธรรมชาติ ผสมโดยใช้เครื่องผสม ค่าความต้านทานการเจาะทะลุ (Penetration) ของแอสฟัลต์ดัดแปรลดลง ในขณะที่จุดอ่อนตัว (Softening point) เพิ่มขึ้น และความหนืดบรุคฟิลด์ (Brookfield viscosity) เพิ่มขึ้น แปรผันตามปริมาณการใส่มากขึ้นของยางธรรมชาติและกรดพอร์ลิฟอสฟอริก การเติมกำมะถันทำให้เพิ่มค่าความเหนียว (Toughness) และค่าเทเนซิตี (Tenacity) การเติมกำมะถันทำให้ยางธรรมชาติผสมเข้ากับแอสฟัลต์ได้ดีขึ้น ทำให้เพิ่มความเสถียรของการเก็บรักษา จากงานวิจัยนี้สูตรแอสฟัลต์ดัดแปรที่มีความเสถียรสูงเหมาะสมสำหรับการลาดถนนคือ สูตรที่เติมยางธรรมชาติ 3.2 เปอร์เซ็นต์โดยน้ำหนักแอสฟัลต์ กรดพอร์ลิฟอสฟอริก 2 เปอร์เซ็นต์โดยน้ำหนักแอสฟัลต์ และกำมะถัน 0. 3 เปอร์เซ็นต์โดยน้ำหนักยางธรรมชาติ

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

ปีการศึกษา 2559

5371839621 : MAJOR CHEMICAL ENGINEERING

KEYWORDS:

WACHIRA SAOWAPARK: NATURAL RUBBER LATEX – MODIFIED ASPHALTS FOR PAVEMENT APPLICATION. ADVISOR: ASSOC. PROF. SARAWUT RIMDUSIT, Ph.D., 90 pp.

Elastomers are the most utilized modifiers for asphalt products worldwide. In Thailand, natural rubber is currently being used to modify asphalt for pavement throughout the country in order to promote the utilization of this major agricultural product. However, due to limited service life from poor stability of the obtained asphalt mixture, investigation to prolong the stability of the natural rubber-modified asphalt is necessary. This research aims to investigate physical, storage stability, morphology and rheological properties of asphalt using natural rubber (NR), polyphosphoric acid and sulfur as its modifiers. NR is a renewable and ecology friendly elastomer which can use in latex form to avoid severe mixing condition. In this work, small quantity of both PPA and sulfur are proved to be highly effective modifiers working in complementary with the elastomeric system to further enhance stability of the resulting asphalt. The experimental results reveal that when AC 60/70 penetration grade asphalt is modified with 0.6 to 4.5wt% of NR, 1 to 2wt% of PPA and sulfur (based on 100 parts NR) 0.3 to 1.0 wt% using a shear mixer, the penetration of the modified asphalt systematically decreases while its softening points and Brookfield viscosity increase with increasing NR and PPA contents. An addition of sulfur in the asphalt system shows improvement in toughness and tenacity property, as well as storage stability and also promotes compatibility between asphalt and natural rubber. Our results suggest the modified asphalt with 3.2 wt% of NR, 2 wt% of PPA and 0.3 wt% of sulfur (based on 100 parts NR) is a suitable formula to produce asphalt mixture with high stability for pavement application.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
Academic Year:	2016		

ACKNOWLEDGEMENTS

The author would like to express my sincerest gratitude and deep appreciation to my advisor, Assoc. Prof. Dr. Sarawut Rimdusit, for his kindness, invaluable supervision, guidance, advice, and encouragement throughout the course of this study.

I also gratefully thanks Assoc. Prof. Dr. Siriporn Damrongsakkul, Assoc. Prof. Dr. Chirakarn Muangnapoh, Dr. Chutimon Satirapipathkul and Dr. Pimporn Ponpesh for their invaluable comments as thesis committee.

This research is supported by the Ratchadapisek Sompoch Endowment Fund (2016), Chulalongkorn University (CU-59-041-EN).

Additionally, I would like to extend my grateful thanks to all members of Polymer Engineering Laboratory of the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, for their assistance, discussion, and friendly encouragement in solving problems. Finally, my deepest regard to my family and parents, who have always been the source of my unconditional love, understanding, and generous encouragement during my studies. Also, every person who deserves thanks for encouragement and support that cannot be listed.

CONTENTS

Page

LIST OF FIGURES

FIGURE Page

LIST OF FIGURES (Cont.)

FIGURE Page

LIST OF FIGURES (Cont.)

FIGURE **Page**

LIST OF TABLES

TABLE Page

CHAPTER I

INTRODUCTION

1.1 Overview

Asphalt is commonly used as a binder mixed with aggregate particles to create asphalt surface roads due to judging cost-effectiveness, reduction in noise pollution, and comfort. However, the asphalt surface road is not efficient for some specific applications such as airport runway, truck heavily used road or any highly used road because of deformation of the asphalt surface road categorized into five types: permanent deformation, thermal cracking, fatigue cracking, moisture damage, and ageing. In addition, asphalt will soften during a period of time in summer, while in winter it will be harder or stiffer. Therefore, designed asphalt surface roads in those practices require less repairing cycle and more durable to prevent the rutting under high traffic load in summer and cracking in winter. A strategy to enhance durable properties of asphalt is to modify it by mixing with polymeric materials to create polymer modified asphalt (PMA). In general, the addition of polymer to asphalt increases the softening point and decreases the brittle point resulting to reduce the temperature susceptibility. As a consequence, the rutting and cracking tendency of the asphalt can be suppressed [1].

Recently, asphalt was mostly modified by addition of solid thermoplastic elastomers to make PMAs. It was found that the solid thermoplastic elastomers-modified asphalt can reduce temperature susceptibility of asphalt by elevating the softening point and reducing the brittle point. It was also more viscous at high temperature and less brittle at low temperature than the unmodified asphalt. In addition, the fatigue resistance, hence the durability can be improved by adding of the solid thermoplastic elastomers as observed in styrene butadiene styrene (SBS)-modified asphalt [1, 2] and styrene butadiene rubber (SBR) [3-5]. However, the poor dispersion and compatibility in asphalt are the constraints for using the solid thermoplastic elastomers as its modifier. Furthermore, granulated recycled tire rubber, synthetic rubber, and carbon black, was also used as an asphalt modifier due to cost efficiency, while rendering poor dispersion, high quantity of the granulated recycled tire rubber is needed to improve asphalt quality [6-8]. Furthermore, blending solid thermoplastic elastomer and granulated recycled tire rubber with liquid asphalt are not easy. It requires specially designed blending equipment or blending at high temperature or blending at high shear rate that can result in degradation of the solid thermoplastic modifier [9-13].

On one hand, natural rubber (NR) is a renewable and ecology friendly elastomer. It also has good elasticity and properties under cyclical loads. It is more cost-effective compared with synthetic polymer modifiers for asphalts particularly in Thailand, one the leading producers of natural rubber in the world. For less severe mixing condition, NR in latex form will be used because the latex is ready to disperse in liquid asphalt at temperature of 150°C or lower, utilizing low shear rate of 500 rpm, and mixing time 30 min. On the contrary, SBS-modified rubber requires high mixing temperature of about 180°C, mixing time of 40 min at high shearing rate of 4,000 rpm followed by 2 h mixing using a mechanical stirrer [13]. In 2013, the Department of Highways, Ministry of Transport of Thailand has issued a specification of natural rubber-modified asphalt cement for road surfaces as well as maintenance of existing road surfaces in order to promote the utilization of this major agricultural product of Thailand [14]. That announcement provided a general guide line to the researchers to develop various NR-modified asphalt formulations to suit various types of road pavement conditions in Thailand. However, the use of natural rubber alone as an asphalt modifier has found to provide pavement with rather short service life.

To further improve the asphalt properties, polyphosphoric acid (PPA) has been used as a co-modifier in some polymer modified asphalts [3]. It has been reported with PPA can chemically react with the resin and asphaltene fractions in asphalt. Crosslinking of reactive segments may exist to form a covalently linked matter between the resins and asphaltenes resulting in the improvement of softening point and viscosity of the asphalt [3].

The objective of this research is to formulate NR-modified asphalt with PPA as a co-modifier. Small amount of sulfur, the rubber crosslinker, is also added to further evaluate its effect on the resulting NR-modified asphalt. The physical properties, storage stability and morphology of modified asphalt will then be evaluated.

1.2 Objectives

1. To develop NR-modified asphalt with PPA and sulfur as a co-modifier for pavement application.
2. To study the effect of addition of co-modifier into NR-modified asphalt on mechanical, storage stability, physical and rheological properties.
3. To evaluate the optimal NR-modified asphalt formulation for pavement application.

1.3 Scopes of Research

1. Preparation of polymer modified asphalts between asphalt and natural rubber at various weight ratios at 0, 0.6, 1.9, 3.2, 4.5 wt% of natural rubber
2. Preparation NR-modified asphalt with co-modifier such as PPA at 0, 1, 2 wt% and sulfur at 0, 0.3, 0.5, 0.7, 1.0 wt% (based on 100 parts NR)
3. Determine the effects of the NR-modified asphalt with PPA and sulfur on mechanical, storage stability, physical and rheological properties.
4. Analysis of properties of the obtained NR-modified asphalts

- Conventional test for asphalts
    - Brookfield viscosity
    - Penetration resistance
    - Softening point
    - Toughness and Tenacity
- Storage stability
- Physical properties
    - Morphology
- Rheological properties:
    - Dynamic shear rheometer (DSR)
- Chemical structure:
    - Fourier Transform Infrared Spectroscope (FTIR)

CHAPTER II
THEORY

Asphalt concrete street is the most popular type of street. However, it does not support high severe condition. Modifiers are added into asphalt to improve neat asphalt properties.

Polymer modified asphalts (PMA) are based mainly on thermoplastic polymers [15-21]. Other asphalt modifiers, such as crumb rubber [6-8] and PPA [22] , have been used. Certain chemical modifiers, e.g., sulfur and organometallic compounds, have been used and required to have a stiffening effect on asphalt. In the future the molecular simulation and model study can further give an understanding of asphalt mechanical, rheological, physical properties and storage stability [23-25].

2.1 Asphalt

Asphalt is residue from crude oil distillation unit. Generally this is a two-step process which atmospheric and vacuum distillations are combined to produce straight-run asphalt. When the straight-run asphalt is oxidized in an effort to change its consistency, blown asphalt is produced.

The structure of a asphalt is defined by the chemical composition of the molecular types. Asphalt is a chemical mixture of hydrocarbons with a small of structurally similar heterocyclic types and functional groups which compose of oxygen, nitrogen and sulfur. Asphalt composes trace amounts of metals for example vanadium, magnesium, iron, nickel and calcium, which appear in the form of salts and oxides. Elementary analysis of asphalt produced from many of crude oils shows that most asphalts compose: [26]

Component	Ratio (%)
Carbon	82-88%
Hydrogen	8-11%
Sulphur	0-6%
Oxygen	0-1.5%
Nitrogen	0-1%

The composition and properties of asphalt is very complicated and depends on the crude oil source and on the method of crude oil distillation. The chemical complexity of asphalt prevents any accurate molecular identification. It is frequently favorably characterized by its chromatographic fractions. The asphaltenes (As) and the maltenes, which are insoluble and soluble in n-heptane respectively. The maltenes can be separated into resins (R), aromatics (A), and saturates (S) [27-32].

The molecular weight of the SARAs increase as S < A < R < As between 300 and 1,000 Da [33, 34]. Figure 2.1 shows the schematic of the analysis for chemical structure of asphalt [26].

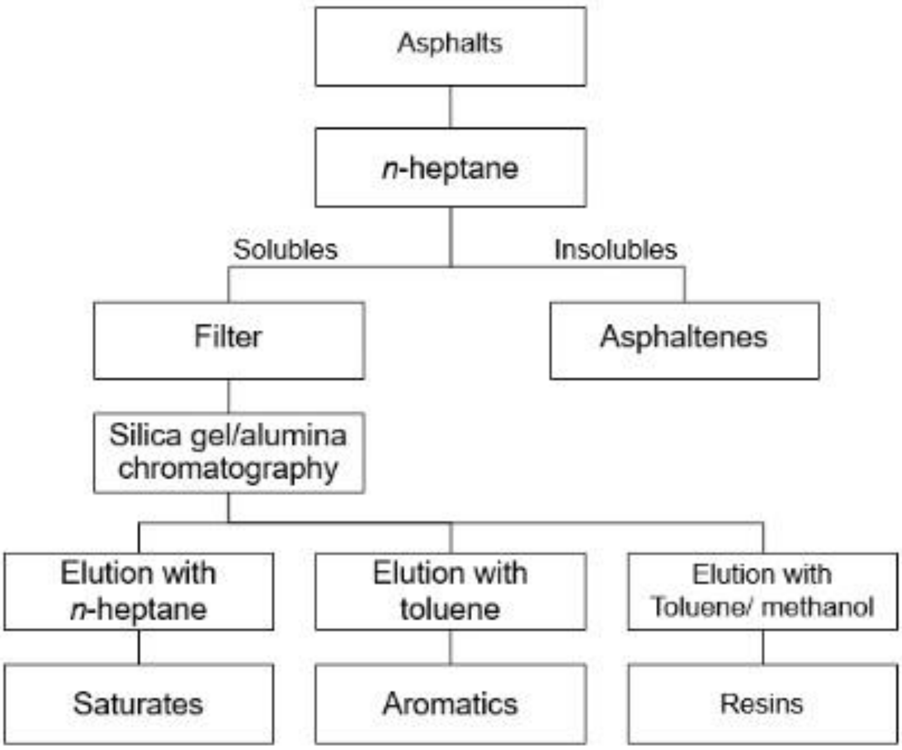


Figure 2.1 Schematic representation of the analysis for chemical structure of asphalt [26]

Table 2.1 The elemental analysis of the SARAs groups of asphalt [26]

Composition	Yield on asphalt	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	Aromatic ratio	Molecular weight
	wt %	wt %	wt %	wt %	wt %	wt %	H/C	
Saturates	9.6	85.6	13.2	0.05	0.3	-	1.8	835
Aromatics	62.4	83.3	10.4	0.1	5.6	-	1.5	870
Resins	19.8	81.6	9.1	1	5.2	-	1.4	1,270
Asphaltenes	5.7	82	7.3	1	7.8	0.8	1.1	11,300

2.1.1 Saturates [26, 35]

Saturates usually number for 9.6 wt.% of a asphalt [35-37]. They appear as a colourless or lightly coloured liquid at ambient temperature. Saturates have very low glass transition temperature around -70°C, that is typically 40°C below the glass transition of their parent asphalt.

The H/C ratio of Saturates is close to 2, with traces of hetero atoms. They compose a crystalline linear n-alkanes, typically number for 0-15 wt.% of the overall fraction. Their average molecular weight is 835 g/mol as shown in Table 2.1 and they are mainly aliphatic: Very few polar atoms or aromatic rings are presented. Saturates solubility parameter is between 15 and 17 $MPa^{0.5}$ and density at 20°C, is around 0.9 g/cm^3 [35].

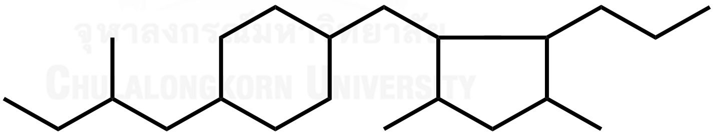


Figure 2.2 Chemical structure of saturates [26]

2.1.2 Aromatics [26, 35]

Aromatics are the most component of a asphalt together with the resins. Since aromatics number for 62.4 wt.% of the total asphalt, they appear as a yellow to red liquid at ambient temperature [37]. A viscosity of aromatics are higher than saturates at the same temperature. Because the glass transition temperature of aromatics are around -20°C, which is similar to parent asphalt.

Their carbon structure is slightly aliphatic with aromatic rings and a average molecular weight of order at 870 g/mol as shown in Table 2.1. Aromatics solubility parameter is between 17 and 18.5 MPa$^{0.5}$ and their density at 20°C is close to 1 g/cm^3 [37].

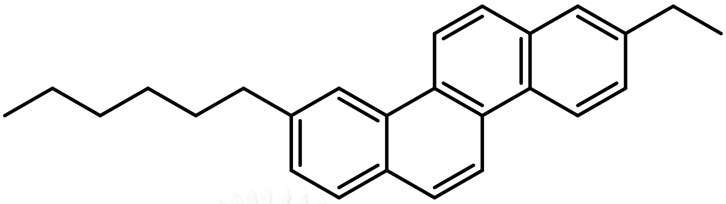


Figure 2.3 Chemical structure of aromatics [26]

2.1.3 Resins [26, 35]

Resins usually number for 9.6 wt.% of a asphalt. Depending on the solvent which is used to elute, the resins incorporate the portion which is eluted by the blending of methanol/benzene. ASTM D 4124 considers the methanol/toluene eluted portion as part of the aromatics.

The saturates and aromatics are liquids at ambient temperature but resins appear as a dark solid at ambient temperature. Resins solubility parameter is between 18.5 and 20 MPa$^{0.5}$ and their density at 20°C, is close to 1.07 g/cm^3 [37].

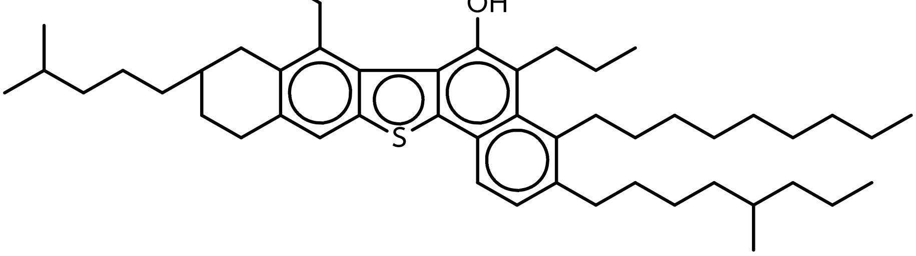


Figure 2.4 Chemical structure of resins [36]

2.1.4 Asphaltenes [35, 38-40]

Asphaltenes represent around 5.7 wt.% of a asphalt. There are many studies for asphalt portions because of each component generate different viscosity. Asphaltenes are explained as the insoluble part of a asphalt in n-heptane but soluble in toluene. Note that when contact with waxy components, the procedure might generate a joint-precipitation of polycristalline waxy components as observed with crude oils [41]. Asphaltene molecular diameters were in the range of 10-20 Å. A molecular weight of asphaltenes are evaluated in the range of 500-1,000 amu [33].

Asphaltenes appear as a black powder at ambient temperature and are responsible for the dark color of asphalt. Asphaltenes solubility parameter is between 17.6 and 21.7 $MPa^{0.5}$ and their density at $20^{o}C$ is close to 1.15 g/cm^3 [42, 43]. The solubility parameter can vary with the aggregation state and therefore these values must be utilized with care [44].

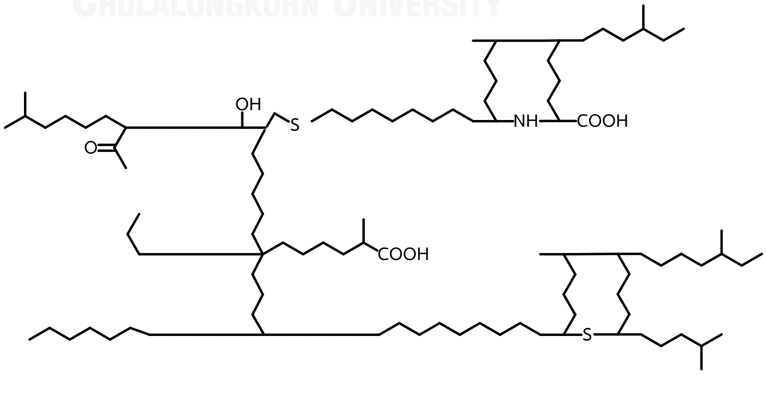


Figure 2.5 Chemical structure of asphaltenes [26]

2.2 Polymer for polymer-modified asphalt

Asphalt was modified by addition of many types of midifier such as thermoplastic elastomers, thermoplastic polymers, thermosetting polymers, chemical modifiers and fibres which contribute different benefits as shown in Table 2.2 [26].

Recently, thermoplastic elastomers are the most popular modifier for polymer modified asphalt production [15-21].

Table 2.2 Benefits of Different Types of Modifiers [26]

Modifier	Permanent deformation	Thermal cracking	Fatigue cracking	Moisture damage	Ageing
Elastomers	√	√	√		√
Plastomers	√				
Tyre rubber		√	√		
Carbon black	√				√
Lime				√	√
Sulfur	√				
Chemical modifiers	√				
Antioxidants					√
Adhesion improvers				√	√
Hydrated lime				√	√

2.2.1 Thermoplastic elastomers [45]

Thermoplastic elastomers are the most commonly used polymers in asphalt pavement products. The most frequently used thermoplastic elastomers contain synthetic rubber polymers, such as SBS [1, 2, 9-13], SBR [3, 4] and styrene ethylene butadiene styrene (SEBS) [17]. Typical thermoplastic elastomers properties are exhibited in Table 2.3. However, SBS offering the optimum combination such as performance, reliability and economy. Styrenic block copolymers are based on styrene, butadiene and isoprene feedstocks. The styrene is polymerised in a accurately controlled reaction with either butadiene or isoprene. Both linear and branched copolymers can be produced.

Table 2.3 Typical elastomeric polymer physical properties [45]

Property	Radial SBS 30% bound styrene	SEBS	SBR	SIS
Tensile strength, MPa	18	35	0.5	15
Elongation at break, % at 25°C	800	500	900	1,200
Specific gravity, g/cm^3	0.94	-	-	0.93
Hardness Shore A	81	-	-	45

A great distribute of information has been published on the use of polymer-modified asphalts more than 30 years and a good source of reference is the Shell Bitumen Handbook [26]. Dupont company and Kraton Corporation also provides good reference sources, although there are a number of polymer suppliers able to provide information [46, 47].

2.2.2 Thermoplastic plastomers

The second most popular polymer kind used for modified asphalt production is thermoplastic plastomers. Poly ethylene-vinyl acetate (EVA) is the most used to produce modified asphalt. [48, 49]. Various grades of the product are available by varying in terms of vinyl acetate content and molecular weight, which is usually explained in terms of a melt flow index. Table 2.4 shows thermoplastic plastomeric polymer physical properties. The kind of EVA used influences the degree of asphalt modification obtained. The modified binder's penetration value, softening point to a lesser extent, dynamic viscosity and asphalt stiffness always affected by the type of EVA.

Table 2.4 Typical plastomeric polymer physical properties [45]

Properties	EVA 18/150 grade	EVA 30/45 grade	LDPE	HDPE
Melt flow index, g/10 min	135-175	38-48	155	16-20
Density	-	-	0.91	0.94
Softening point, $^{\circ}$C	95	107	-	-
Tensile strength, MPa	5	10.5	-	-
Elongation at break, % at 25°C	500	800	-	-

Other kinds of thermoplastic plastomers such as ethylene methyl acrylate, PP [50-53], PS [9] and polyethylene (PE) [54, 55], have proven for less successful in asphalt but still investigated further for using in asphalt. They show that it make the asphalt too stiff and brittle, increasing the risk of premature asphalt failure. Some of thermoplastic plastomers are derived from waste plastic sources, though improved to supply a consistent product.

2.2.3 Natural Rubber

Natural rubber (NR) [56] is the rubber from Hevea brasiliensis tree. NR has been found as only naturally occurring rubber source, over 2,000 species of plants and fungi have been study to compose rubber hydrocarbon. The infrared, nuclear magnetic resonance (NMR) and X-ray studies is shown that the major component of NR is polyisoprene comprising of the isoprene unit C_5H_8 in the cis-1,4 chemical structure as shown in Figure 2.6 [57].

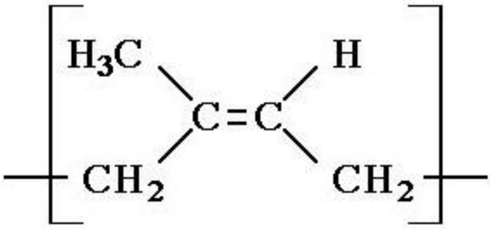


Figure 2.6 Chemical structure of cis-1,4 isoprene [57]

Other naturally cis-polyisoprenes are called wild rubbers such as guayule rubber and ficus rubber. Synthetic polyisoprene which is produced by Ti/Al catalyst contains isoprene units in the cis-1,4 configuration higher than 98%. In fact, the polyisoprene content in NR is about 94%, therefore the synthetic polyisoprene is predicted to show properties similar to NR.

Natural rubber [56, 58-60] has been used in PMA for in years and is expected to improve asphalt performance. For easy mixing and homogenization, latex form is a good optional.

2.2.4 Sulfur

Sulfur [61] is a odorless, brittle material with pale yellow. It appears in three allotropic forms: orthorhombic, monoclinic and amorphous. The most stable form of sulfur is orthorhombic form. Monoclinic sulfur form appears in range of the temperatures 96°C and 119°C and returns back to the orthorhombic form when it is cooled. Amorphous sulfur is formed by cooling down molten sulfur quickly. Amorphous sulfur is a soft and elastic and it eventually returns back to the orthorhombic form. Sulfur is produced from petroleum refining operations and being a byproduct of extracting from sulfur containing ores.

Sulfur normally use in natural rubber vulcanization process [62, 63] because the uncured natural rubber is sticky, deforms easily at high temperature condition, and is brittle at cold condition. Meaning that it cannot be used to make articles with a satisfied level of elasticity.

2.2.5 Polyphosphoric Acid [22, 64, 65]

Polyphosphoric Acid (PPA) is normally adopted to improve asphalt properties. Figure 2.7 shows phosphorus pentoxide (P_2O_5) and phosphoric acid (H_3PO_4) which are the basic compounds for the production of PPA. Phosphorus is firstly oxidized to phosphorus pentoxide, which crystallizes as P_4O_{10}. When it reacts with water, phosphoric acid is produced. This path to H_3PO_4 is dry process, which is used to provide high-purity material. Wet process is cheaper to produce H_3PO_4 from the reaction of sulfuric acid on ground apatite phosphate rock, $Ca_3(PO_4)_2CaF_2$.

$$P_4 + 5\,O_2 \rightarrow 2\,P_2O_5 \text{ (i.e., } P_4O_{10}\text{)}$$

$$2\,P_2O_5 + 6\,H_2O \rightarrow 4\,H_3PO_4 \text{ (or } 2\,P_2O_5 \cdot 3H_2O\text{)}$$

Figure 2.7 Production and reaction of phosphorus pentoxide [22]

PPA is an oligomer of H_3PO_4. High-purity material is generated either by heating P_2O_5 dispersed in H_3PO_4 or from the dehydration of H_3PO_4 at high temperatures. Figure 2.8 demonstrates the equilibrium for these reactions, which produce various of chain lengths and distributions. The dehydration method has tendency to produce short chains, whereas the dispersion method normally produces chains with more than 10 repeat units.

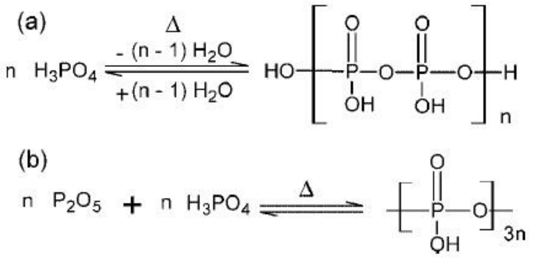


Figure 2.8 Production of PPA from the (a) dehydration
and (b) dispersion method. n is an integer [22]

Table 2.5 shows PPA which is available in various grades, the naming of which can be confusing because the percentage can exceed 100%. The 100% phosphoric acid contains 72.4% P_2O_5 which is calculated from the formula weight ratio of P_2O_5/H_3PO_4. Similarly, pyrophosphoric acid ($H_4P_2O_7$) comprises of 79.8% P_2O_5 which calculated from the ratio $P_2O_5/H_4P_2O_7$. The ratio of these P_2O_5 contents provides a relative phosphoric acid content. The relative content can be calculated by putting

79.8% divided by 72.4%, which results in 110%. Other examples are shown in Table 2.5.

Table 2.5 Grade and Designation of Phosphoric Acids (PA) [22]

PA	formula 1	formula 2	formula 3	designation	P_2O_5 (%)	PA(%)	Molar ratio of P_2O_5/H_2O
ortho	H_3PO_4	$P_2O_5.3H_2O$	$HO(HPO_3)H$	solid anhydrous	72.4	100	0.33
		$P_2O_5.2.35H_2O$		super-PA	75.9	105	0.40
Pyro	$H_4P_2O_7$	$P_2O_5.2H_2O$	$HO(HPO_3)_2H$		79.8	110	0.50
Tri	$H_5P_3O_{10}$	$3P_2O_5.5H_2O$	$HO(HPO_3)_3H$		82.6	114	0.60
meta	$H_2P_2O_6$	$P_2O_5.H_2O$	$(HPO_3)_n$	meta-PA	88.8	123	1.00

Figure 2.8 shows that the production of PPA obtains a various distribution of chain lengths, where the number of repeat units in the PPA chain, n. Jameson characterized this distribution and has found that 100% phosphoric acid was a mixture of H_3PO_4 with about 10% dimer by weight. Figure 2.9 shows the distribution of chain lengths for three commercial grades that have used to modify asphalt. The 105% PA grade contains mostly short mono- and dimeric segments, and ortho- and pyrophosphoric acids. Contrary, the 110% grade has the same dimeric content but little monomer. The 110% grade can be converted to segments with n > 3. In the higher 114% grade, little monomer is left. They have all been converted to chains with 2-14 units. This incremental in chain length resulting in chain entanglements and contributes to the increasing viscosity of the higher grades.

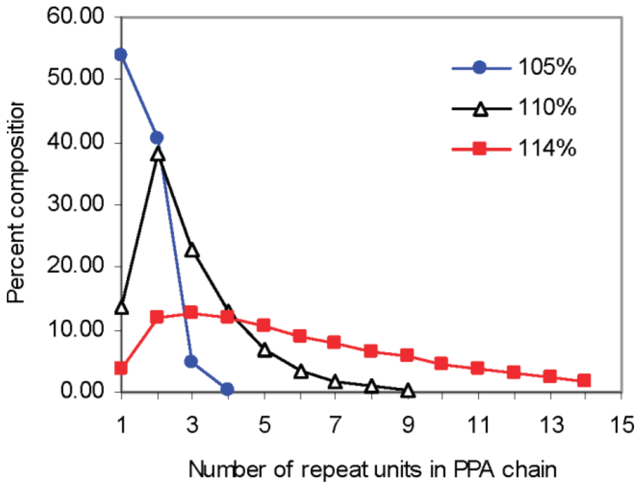


Figure 2.9 Distribution of chain lengths in three PPA grades [22]

2.3 Polymer-modified asphalt storage stability [21]

The lack of storage stability at high temperatures is the major problem of modified asphalt. A satisfied compatibility of the asphalt and the modifier is a important contributor to avoid separation in storage tank, processing and application the asphalt and to meet the expected properties in the pavement. Storage stability tests can be used to define the interactions between the asphalts and modifiers during mixing are severe enough to avoid a separation of the modifier in the conditions of storage tank.

Storage stability of modified asphalt was evaluated by the difference in softening point between the top and bottom samples. Aluminum tube of modified asphalt was cut into three sections. The samples taken from the top and bottom sections were used to measure their softening points [10].

Figure 2.10 Aluminum tube of storage stability test

2.4 Problem of road surface

2.4.1 Rutting deformation [18, 66]

The rutting deformation is defined as collapsion of the surface layer or structure permanently. In general, the rutting deformation take places in the groove of the wheel loads passing or in a pause of heavy trucks. This may be contributed to instability of the materials used in the construction of pavement. Rutting deformation because of deposition or flow of the layer permanently can occur after bleeding at surface.

Most streets in areas outside the city can found the rutting deformation because traffic will move at a speed is higher. Rutting deformation has been found in city areas, especially around intersections with traffic lights, bus stop or a traffic jammed area. The quality of the asphalt material is plays as important properties, which affects the rutting deformation of asphalt pavement.

Figure 2.11 Rutting deformation [67]

2.4.2 Thermal cracking [68]

Cracking take places because of temperature changes in the surface of the asphalt pavement. In contrast, the stresses occur due to the fast decreasing of temperatures. In case of the stress is worth much more than the tensile strength of the asphalt concrete mixture that can be obtained, it would cause a cracking. The cracking are cracks in direction of the perpendicular to the flow of traffic. For cracking resulting from changeing in surface temperature of asphalt pavement, that is a direct result of the quality of asphalt materials at low temperatures. The crack occurs because asphalt materials are brittle. Asphalt materials are varied by depending on a grade, source of crude oil and ageing. Asphalt that is sensitive to changes of temperature are likely to cracking.

Figure 2.12 Thermal cracking [67]

2.4.3 Fatigue cracking [69]

Cracking occurs due to fatigue of the payload on the surface of the asphalt pavement-because the surface supports the load of traffic over for a long period. These are the important factors that resulting in fatigue cracking.

When a vehicle axle passes over a pavement surface, the applied load induces a bending action with two shear stresses. Temperature variations resulting in reproduced compression and expansion, which contribute to tensile stresses in the pavement. The repeated loading of traffic, along with the leverage effect created by stresses because of temperature variation, triggers a fatigue process that resulting in the appearance and reproduction of fatigue cracking [70].

Figure 2.13 Fatigue cracking [67]

2.4.4 Moisture damage [71]

Moisture damage in asphalt reduces the stiffness and strength of the mixture which leads to failure of asphalt pavements. Moisture damage affects the performance of asphalt mixtures because of a loss of cohesion in the binder or failure of adhesion between aggregate and asphalt binder. Ultimately this affects the structural performance of the mixture.

Therefore, both mechanisms cause destroy to asphalt mixtures. The damage reduces the stiffness modulus and causes a reduction in the strength of an asphalt pavement. The damage also causes peeling of the aggregate of asphalt concrete pavement named as raveling. The fine material at the surface of asphalt materials is sheared by the shear strength of the wheel until scraped off. The surface appears rough then a stone expose. Such damage of the structure of the pavement layer resulting in reduction of strength of the pavement and lead to rutting or cracking.

Figure 2.14 Moisture damage [67]

2.4.5 Aging [11, 13]

Aging is a changing in the quality of asphalt pavement materials. Even through a variable does not cause direct damage to asphalt pavement but it will the causes the damage in the future. The asphalt will cause changes in the quality of asphalt pavement materials because of the lifetime that create a brittle solid. Although the strength of asphalt will be satisfied for the permanent deformation resistance, solid asphalt may cause cracking and lead to stripping. Aging may take places both in the mixing process with aggregates and during use in the street.

Aging is understand as a very complex process in asphalts [72, 73]. The degree of complexity increases after modification. The aging properties of asphalts are usually identified by rheological and physical properties measuring before and after aging in the laboratory [74, 75]. Many of analysis techniques have been adopted to analyst the characterization such as gel permeation chromatography, NMR and FTIR. Most of published shows are limited in the aging process without aging resistance improvement except that phosphorus compounds which can achieve in the aging resistance improvement [76].

Figure 2.15 Aging [67]

CHAPTER III

LITERATURE REVIEWS

The literature reviews suggests that the study of PMA can be divided into two groups: the study of modifier compositions and the study of such specific properties as rheology and structure of PMA or such application properties as aging and storage stability.

Bonemazzi, F. and Giavarini, C., 1999 [77] studied the shifting of bitumen structure from sol to gel. Their findings can be summarized as below.

The structures of both air-blown and acid treated asphalts were reported to shift from sol to gel. The Cole–Cole curves and Tgδ vs. temperature plots, performed with rheometers, were used to study the macroscopic structure and performances of such materials. Gel structure has less permanent deformation and better storage stability at high temperatures (lower Tg).

Both air-blowing and chemical addition highly improved the storage stability of blends with olefinic copolymers. Furthermore, the addition of 2 wt% polymer to PPA treated asphalts and the addition of 5 wt% to neat asphalts produced the same effect.

In spite of their usual impact on asphalt colloidal structure, blowing and PPA addition affected differently on the low-temperature performance: blowing increased brittleness, while chemical treatment did not change the Fraass brittle point.

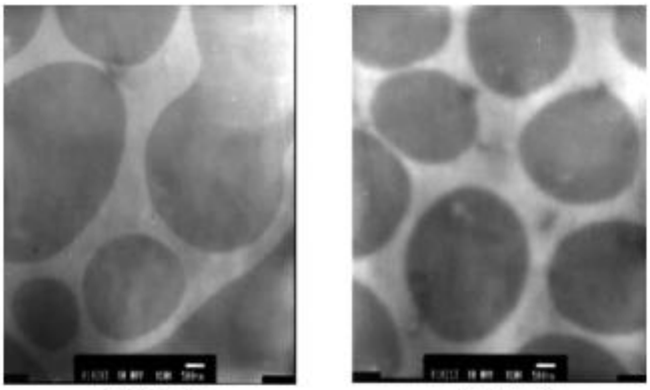
Chen, J.S. and Huang, C.C., 2007 [78] study the characteristic of the mechanical behavior of modified asphalt by styrene-butadiene-styrene and sulfur.

Table 3.1 Engineering and Chemical Properties of Base Asphalts [78]

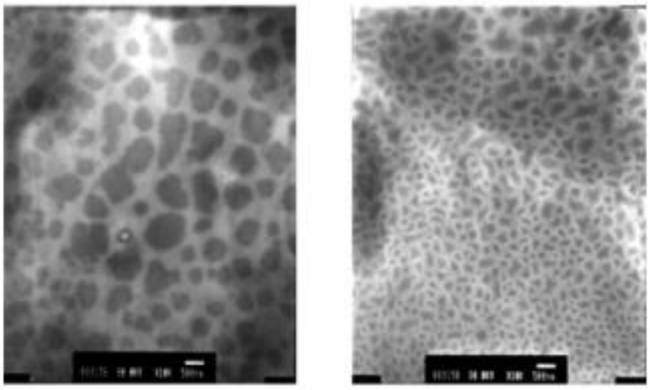
Grade	Penetration 25°C (dmm)	Softening point (°C)	Viscosity 60°C (poise)	Asphaltenes (%)	Resins (%)	Aromatics (%)	Saturates (%)
AC-10	96	38	987	11.7	17.3	58.8	11.4
AC-20	68	50	2098	12.2	17.7	57.1	12.1

Table 3.2 Properties of SBS Copolymer [78]

	Structure	Styrene–butadiene ratio	Specific gravity	Volatile matter (%)	Number average, M_n	Molecular weight, M_n
SBS-l	linear	31 : 69	0.94	0.6	170,000	200,000
SBS-r	radial	30 : 70	0.95	0.6	320,000	460,000



(a) 0% sulfur (b) 1% sulfur



(c) 3% sulfur (d) 5% sulfur

Figure 3.1 Micrographs of AC-10 asphalt mixed 7 wt % SBS-l blends with various sulfur contents [78]

Figure 3.1(a-d) shows the micrographs of the asphalt-SBS blend mixed with 0,1.3 and 5 wt % sulfur respectively. It is observed that the more addition of the vulcanizing agent, sulfur, the smaller asphalt particles, the better compatibility. Hence, asphalt–SBS-sulfur blends would be more stable and more compatible than pure SBS-modified asphalt.

The effects of sulfur content on the physical properties and storage stability of SBS modified asphalt are shown in Figures 3.2–3.5. As illustrated in Figure 3.2, the R&B softening point of SBS-modified asphalt increased with increasing sulfur. As shown in Figure 3.3, the penetration of the SBS-modified asphalt decreased with increasing sulfur. Figure 3.4 shows that the elastic recovery of the asphalt-SBS blends increased with increasing sulfur. The test results shown in Figures 3.2-3.4 illustrate that the addition of sulfur clearly enhanced the engineering properties. Figure 3.5 shows a marked difference between the top and bottom sections of pure SBS-modified asphalt, indicated by 0% sulfur content. The difference in the softening point between the top and bottom of PMAs after the stability test should not have been greater than 5°C in order to show there was no substantial phase separation. The storage stability of the asphalt-SBS blends was effectively improved with the addition of sulfur.

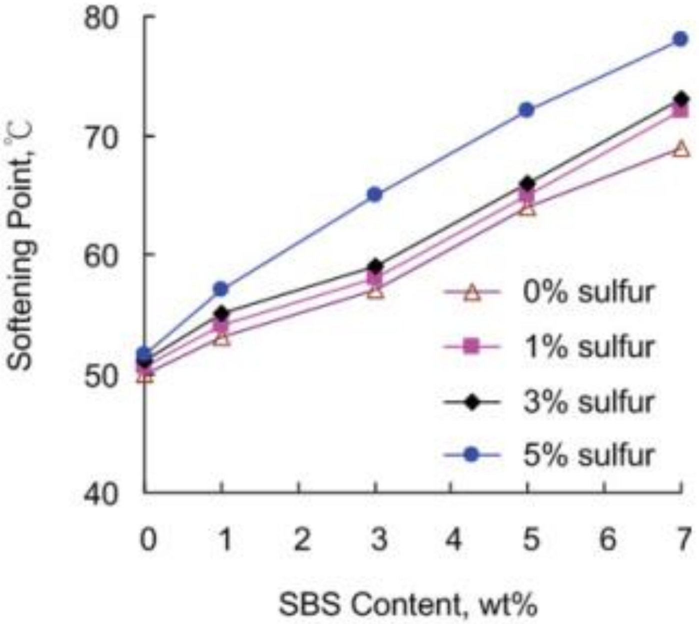


Figure 3.2 Changes in R&B softening point of AC-20 asphalt mixed with SBS-r with various sulfur contents [78]

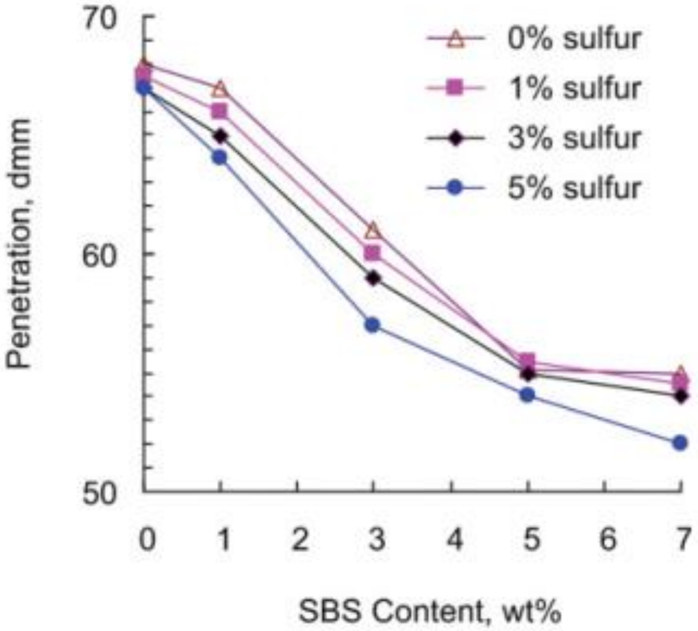


Figure 3.3 Change in 25°C penetration of AC-20 asphalt mixed with SBS-r with various sulfur contents [78]

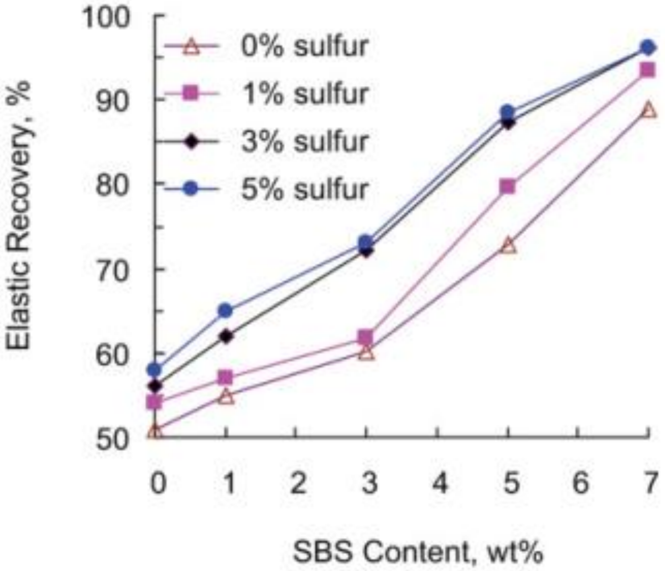


Figure 3.4 Changes in 25^{o}C elastic recovery of AC-20 asphalt mixed with SBS-r with various sulfur contents [78]

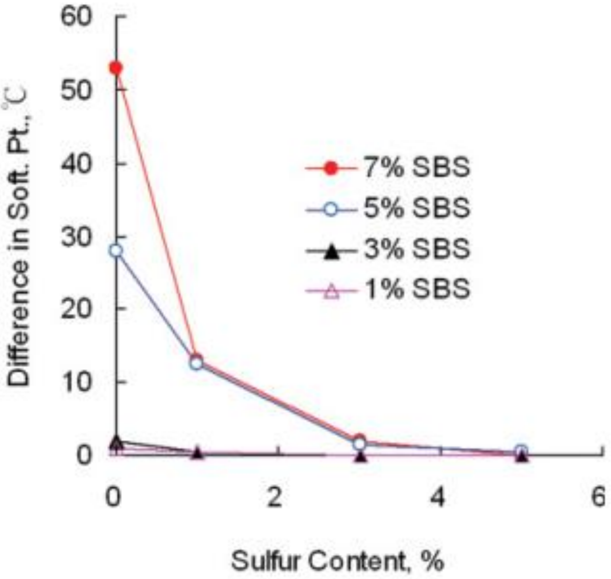


Figure 3.5 Effect of sulfur content on storage stability of AC-10 asphalt mixed with SBS-r [78]

The master complex moduli (G*) curves at different loading times and test temperatures can characterize the rheological properties of sulfur-added asphalt-SBS blends. Figure 3.6 shows a typical set of master curves for sulfur-added AC20-SBS system. The pure asphalt has lower G* than that of SBS-modified asphalt. Both asphalt and PMA have similar shapes. It may be because the asphalt binder is responsible for the PMA viscoelastic. However, the addition of sulfur helps SBS shift vertically up the PMA master curve. Similar results were observed from the sets of master curves generated for other systems including AC-10 asphalt and SBS-l.

The addition of sulfur enhanced PMA behave as an elastic network resulting in decreasing the hot-weather-rutting tendency. In addition, the smaller phase angles due the sulfur addition could reduce the fatigue cracking tendency on pavement.

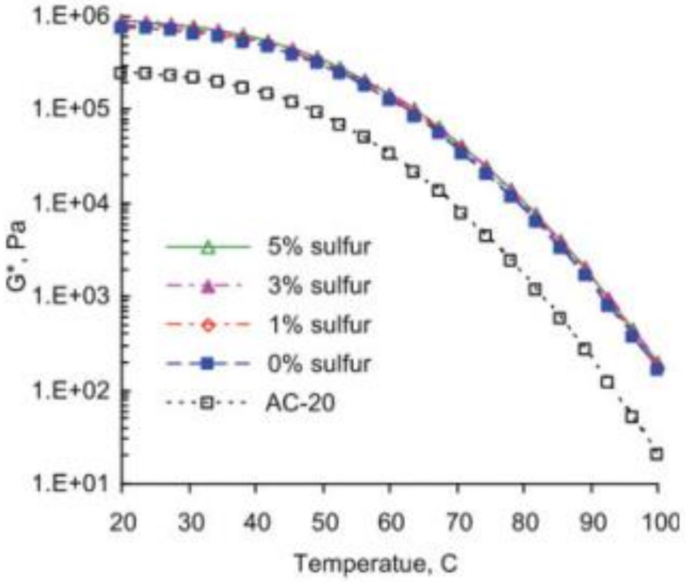


Figure 3.6 Complex modulus (G*) of AC-20 asphalt mixed with 5 wt % SBS-r with various sulfur contents [78]

Summary, the polymer and asphalt are compatible making PMA elastic. The addition of sulfur made more elastic substantially improving the PMA rheological properties. Without sulfur addition, PMA was micro heterogeneous containing two separate finely interlocked phases, especially at high SBS concentrations. The physical-chemical interaction between SBS and asphalt significantly improved viscosity, microscopy, and rheological properties. The difference in the softening point between the top and bottom layers decreased significantly, and elastic recovery increased in the presence of sulfur.

Cortizo, M.S., Larsen, D.O., Bianchetto, H., and Alessandrini, J.L., 2004 [11] studied the impact of the thermal degradation of SBS copolymers during the ageing of modified asphalts. The samples of SBS1, SBS2 and SBS3 contained base asphalt and the same content of each of the polymers. The corresponding modified asphalts were named as AM1, AM2 and AM3, respectively.

The polymer modified asphalts were aged by two methods. The first method rolling thin film oven test (RTFOT, ASTM D 2872) simulates aging during the hot mixing unit and the paved process. The second method, pressure ageing vessel (PAV) tests on the residue from RTFOT test for the in situ field ageing.

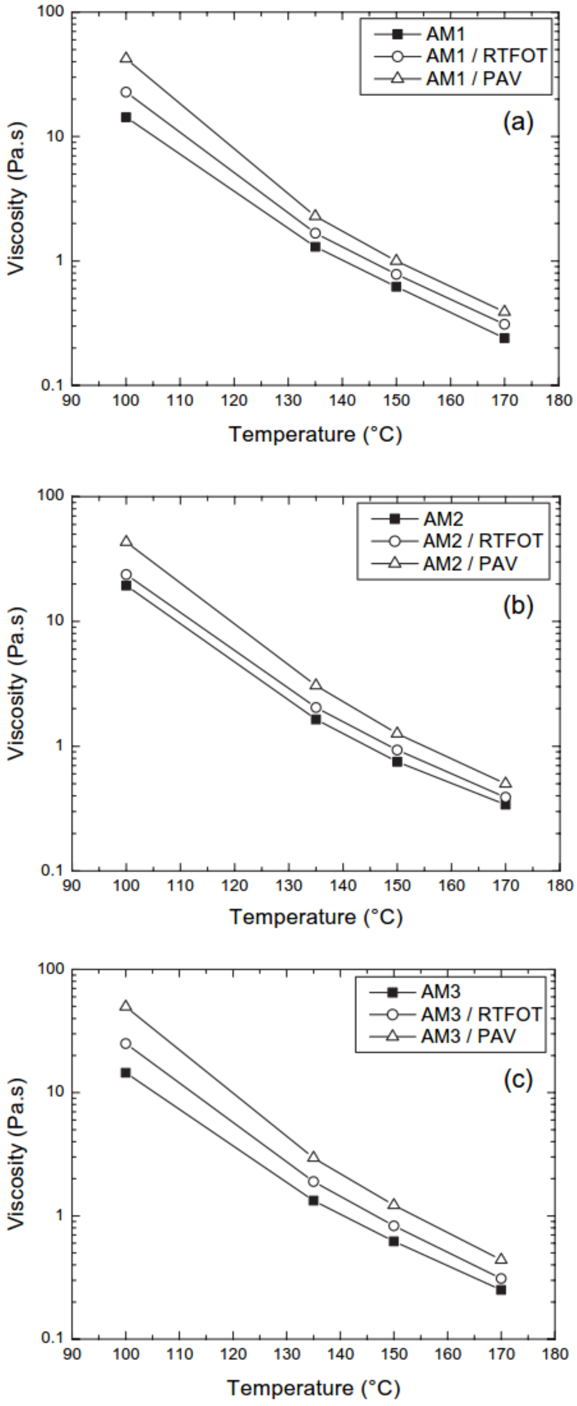


Figure 3.7 Rotational viscosities of SBS modified asphalts versus temperature before and after ageing: (a) AM1, (b) AM2, (c) AM3 [11]

Figure 3.7 shows the impact of the ageing of the three modified asphalts on the rotational viscosity between 100 and 170°C. In all cases, the viscosity decreased with the increasing temperature. The AM1 asphalt (Figure 3.7a) using SBS1 of smaller molecular weight showed smaller viscosity than the AM2 asphalt (Figure 3.7b) using higher SBS2 of higher molecular weight, AM3 asphalt using lineal SBS3 of similar molecular weight to that of SBS1, had slightly higher viscosity due to the higher hydrodynamic volume of the SBS3 lineal copolymer.

The RTFOT and PAV aging test showed the viscosity increase in all the samples, indicating again a hardening of the asphalts during RTFOT and PAV ageing processes. Therefore, the modifications of the rheological properties of asphalts during RTFOT and PAV ageing processes depend commonly on the structural characterizations of the modifier.

In summary, the addition of SBS improved the rheological and physical properties of asphalt as evidenced by rotational viscosimetric and conventional properties. The structural characterizations of the modifier and the ageing conditions affected on them. Moreover, the thermal degradation of the neat polymers by heating method at 180^{o}C during 30 min. has been studied to understand more clearly about PMA aging.

Thermal oxidative degradation of polymer was observed different from the neat polymer degradation. In this case, Thermal oxidative degradation of neat polymer formed mainly cross-linked products whereas the degradation of PMA produced chain scission and radical addition to some asphalt components via the free radical reactions. The most polar compounds which increased the portion of higher molecular size as verified by SEC and infrared analysis, were formed. The higher molecular sizes were gained starting from the SBS star copolymer. This structural modification described the behavior of PMA in ageing period.

Dehouche, N., Kaci, M., and Mokhtar, K.A., 2012 [79] studied thermo-oxidative aging on chemical composition and physical properties of PMA. It may be determined that addition of both SBS and EVA improves such properties of unmodified asphalt as penetration, softening point, penetration index, stiffness and temperature susceptibility.

However, SBS modified asphalt was found to be better than EVA one. After thermo-oxidative aging, unmodified asphalt and EVA modified asphalt were found harder than SBS modified one. In addition, PI decrease and thus the increased PI noticed for the modified samples show a crucial decrease in temperature susceptibility with polymer modification, especially at higher polymer contents (7 wt.%). The SBS modified asphalts had more decrease of PI.

Fang, C., Yu, R., Liu, S., and Li, Y., 2013 [80] studied the modified asphalt with different nanomaterials to improve the properties of asphalt. Mechanisms of using nanomaterials with the base asphalt and polymer modified asphalt and the nano/polymer/asphalt system from different aspects have been concluded and examined. As more examiners pay attention to asphalt modification with nanomaterials, nanotechnology and nanoscience will enhance make major progress in modified asphalt work.

The conventional polymer modified asphalt preparation methods have been used to prepare the modified asphalt without investigating the impact of such preparation parameters as temperature, shearing speed and time. It is believed that there are chemical reactions between nanomaterials with base asphalt or modified asphalt. Methods for introducing a optimal amount of nanomaterials into the base asphalt to accomplish nanoscale dispersion and enhance the compatibility between each phase and the understanding properties of the modified asphalt will be the focal point of the nanomaterials modified asphalt research. Concurrently, additional research on the microstructure of nanomaterials modified asphalt and its mechanism will be crucial in guiding engineering practices.

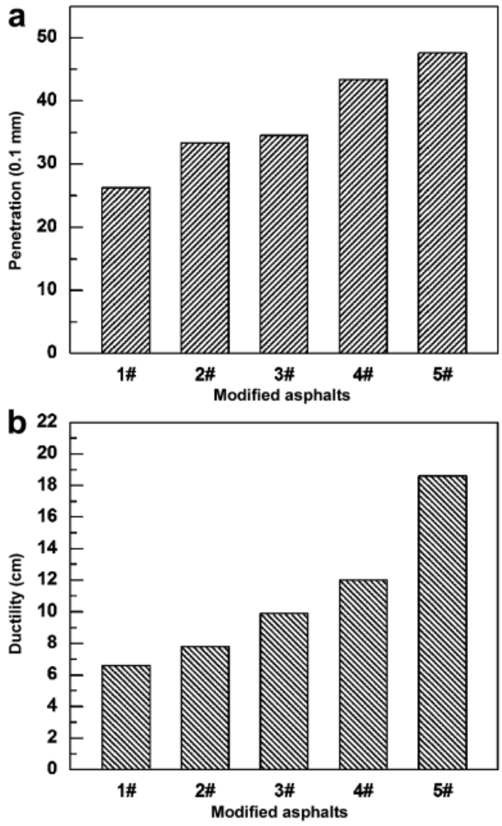


Figure 3.8 Physical properties indexes of modified asphalt [80]

Figure 3.8 shows penetration and ductility properties of modified asphalts. It can be seen, penetration and ductility are improved with the increase of organic montmorillonite content, the resistance deformation of the modified asphalt is increased and the stiffness modulus is decreased. Consequently, mixing waste polyethylene and organic montmorillonite in the asphalt can enhance the cracking resistance of asphalt pavement.

Ghaly, N.F., 2008 [81] study effect of sulfur on the storage stability of tire rubber modified asphalt. Tire rubber (TR) can be used as modifier to enhance performance of asphalt. The main problem of TR modified asphalt is poor compatibility between asphalt and TR. The objective of this work is to improve the storage stability properties of TR modified asphalt by SBS and sulfur addition. The 60/70 penetration grade asphalt was modified with 2-5 wt% TR and equal parts of SBS and sulfur. Physical properties such as ductility, softening point, penetration, penetration index and penetration temperature susceptibility were study. Modified and unmodified base asphalt were trial at 140, 160 and 200°C for storage stability test to study the optimum and vulcanization temperature.-Flow test and Marshall stability were study by the addition of either SBS or SBS/sulfur into TR modified asphalt. The impact of the vulcanized blend to improve deformation of modified asphalt was study by wheel tracking test

Penetration temperature susceptibility of modified asphalt was decreased both before and after vulcanization. The storage stability has been completed at 160°C for

TR/SBS modified asphalt after vulcanization process while the critical degradation temperature is 200°C. The addition of sulfur can improve plastic deformation resistance and Marshall stability of TR/SBS modified asphalt. Optimal modified asphalt formulation should contain 4 wt% TR and 4 wt% SBS and 1 wt% sulfur.

Liu, J., Yan, K., You, L., Ge, D., and Wang, Z., 2016 [82] studied a laboratory investigation of rheological and morphological properties of warm mix asphalt containing polyphosphoric acid. The impact of polyphosphoric acid on warm mix asphalt were determined by carrying out such laboratory tests as viscosity measurement, dynamic shear rheometer, bending beam rheometer, fluorescence microscopy, Fourier transform infrared spectroscopy, thermogravimetric and differential scanning calorimetry.

Figure 3.9 shows the infrared spectra of neat asphalt, WMA asphalt and WMA-PPA (1.5 wt% PPA) asphalt. Compared with neat asphalt, the spectra band of warm mix asphalt has clear upward trend as a whole. The characteristic absorption peaks at 2800-3000 cm^{-1} and 1350-1650 cm^{-1} of neat asphalt and warm mix asphalt can be noticed in almost the same peaks, and some absorbance of the spectral bands (2920 cm^{-1}, 2855 cm^{-1}, 1458 cm^{-1}, 1375 cm^{-1}) look precisely alike. Figure 3.9 also shows that polyphosphoric acid-warm mix asphalts and warm mix asphalts have some drops in the areas of 3200-3500 cm^{-1} and 2100-2800 cm^{-1} and some rises in the areas of 1800-2300 cm^{-1}. Some remarkable wave motions are observed in the area of 800-1300 cm^{-}

^{1}, which is frequently stretching vibration area of phosphorus atoms. It may attribute to (ArO_3) P=O symmetric stretching vibrations of P-O-C.

The alcohol functional group components in asphalt can react with polyphosphoric acid, so the hydroxyl (-OH) is easy to phosphorylated. Moreover, new functional groups are found in the area of 950-1000 cm-^{1}. Above observations imply that the modification impact of PPA on warm mix asphalt is a chemistry process.

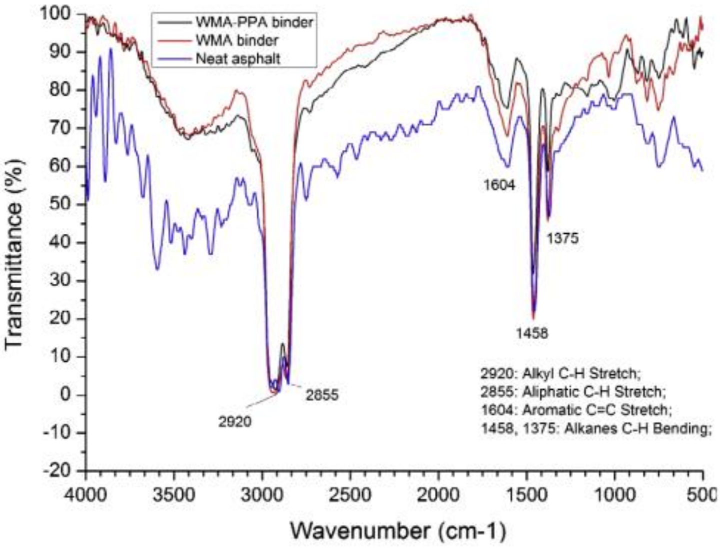


Figure 3.9 FT-IR spectra of neat asphalt, WMA asphalt and WMA-PPA (1.5% PPA) asphalt [82]

Rotational viscosity revealed that the neat asphalt had a insignificantly higher viscosity than warm mix asphalt binder and the addition of polyphosphoric acid into warm mix asphalt increased the viscosity at various test temperatures, indicating that the addition of polyphosphoric acid improved the high-temperature performances of warm mix asphalt.

The polyphosphoric acid-warm mix asphalt had G*/sinδ value higher than warm mix asphalt. Polyphosphoric acid-warm mix asphalt (with 2 wt% PPA) had the highest G*/sinδ value, the second highest was polyphosphoric acid-warm mix asphalt that contained 1.5 wt% PPA. In conclusion, polyphosphoric acid addition improved rutting resistance of warm mix asphalt binders at high performance temperature.

By fluorescence microscopy, it was observed that polyphosphoric acid addition significantly affected on the microstructures and storage stability of polyphosphoric acid-warm mix asphalts, and the modification impact of polyphosphoric acid on warm mix asphalt is a chemistry process. The optimal content of polyphosphoric acid was 1.5 wt% within the investigated weight percentages (0.5 wt%, 1.0 wt%, 1.5 wt% and 2.0 wt%) because the polyphosphoric acid-warm mix asphalt (with 1.5 wt% PPA) achieved relatively satisfied intermediate and high temperature rheological properties while considered economical.

Parvez, M.A., Al-Mehthel, M., Wahhab, H.I.A.-A., and Hussein, I.A., 2014 [83] studied a crumb rubber and sulfur modified asphalt to explore rheological properties of application at medium and high temperatures.

Figure 3.10 shows the FTIR spectra of base asphalt. The analysis method will not be described in detail. The bonding of sulfur-modified asphalts binders were also similar to that of base asphalt showed in Figure 3.10 but with different intensities. The FTIR spectra for base and 30 wt% sulfur-modified asphalts were shown in Figure 3.11.

The main differences between them were in the area 600-1250 cm^{-1}. The FTIR spectra of several sulfur-modified asphalts were also similar to that showed in Figure 3.11. It was observed that the intensities of the bonds had changed in modified asphalts.

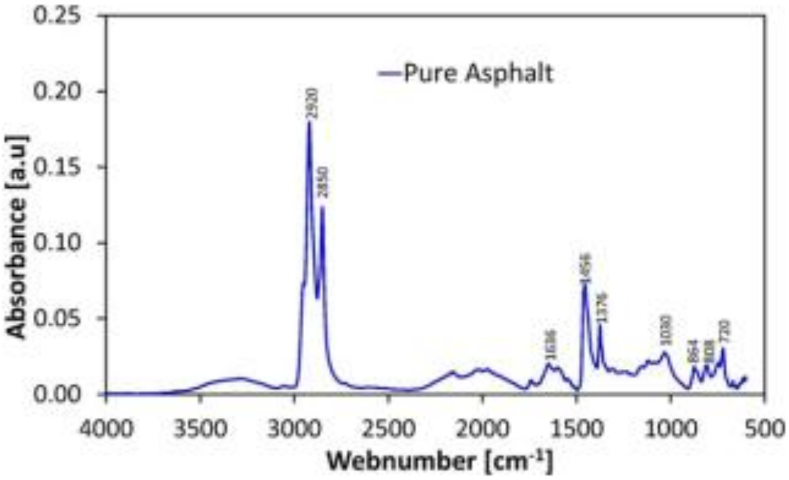


Figure 3.10 FTIR spectra of base asphalt binder [83]

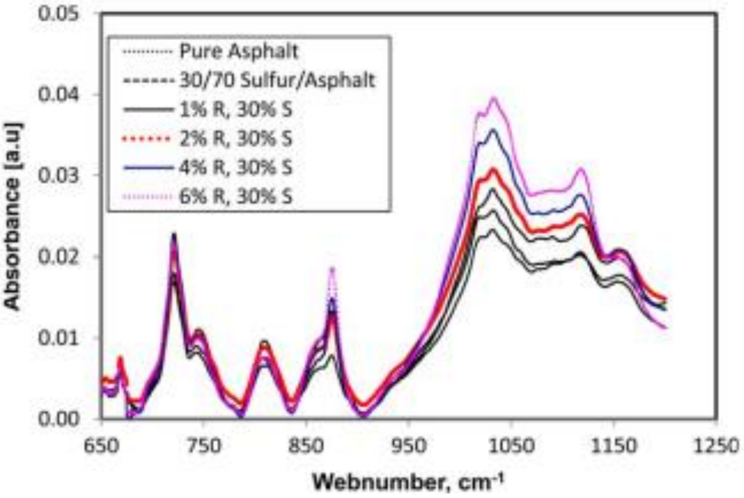


Figure 3.11 FTIR spectra of base and modified asphalt binders [83]

About 20-50% of sulfur and 1-6% crumb rubber were used. Both steady and dynamic shear rheology revealed that crumb rubber enhanced the viscoelastic properties of sulfur modified asphalt. Crumb rubber modification decreased temperature susceptibility of sulfur modified asphalt, and increased the higher temperature performance of sulfur modified asphalt. The sulfur and crumb rubber together decreased the activation energy compared with base asphalt. The crumb rubber dosing into the sulfur modified asphalt improved the rutting parameter (G*/sinδ). Short-term aging enhanced G*/sinδ with small increase in activation energy. The viscoelastic properties (G' and G'') were improved by addition of sulfur.

Figure 3.12 shows the effect of crumb rubber content on storage modulus, G'. The storage modulus, G' of sulfur modified asphalts were increased linearly by crumb rubber content. The straight line slope increased by sulfur content increment showing that the number of sulfur enhances to the increase in storage modulus. It was also found that the increase in G' at high ω is lower than that at low ω. The crumb rubber and sulfur modified asphalt revealed properties better than the base asphalt.

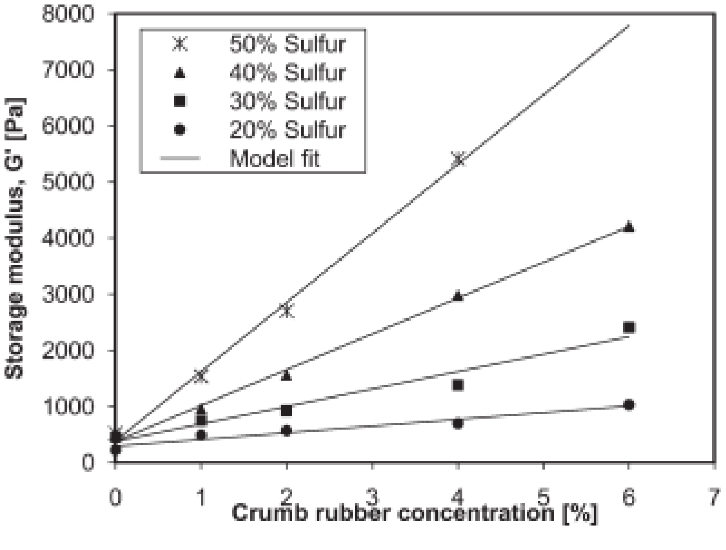


Figure 3.12 Storage modulus as function of sulfur and crumb rubber concentration (ω=1 rad s^{-1} at 50°C) [83]

Vichitcholchai, N., Panmai, J., and Na-Ranong, N., 2012 [58] From the experimental results by using Ribbed Smoked Sheet (RSS) NR it has been found that the asphalt product quality can be improved such as low penetration, high softening point, high penetration index, high torsional recovery, and high toughness-tenacity. At 6 wt% of natural rubber in asphalt is the most effective ratio of RSS in asphalt. With improved quality as mentioned above, NR-modified asphalt can be used as roads paving with more strength and durability than using non-modified asphalt. Viscosity of asphalt is increased by adding polymer. However, mixing process is not affected but required high efficiency mixer in pilot scale.

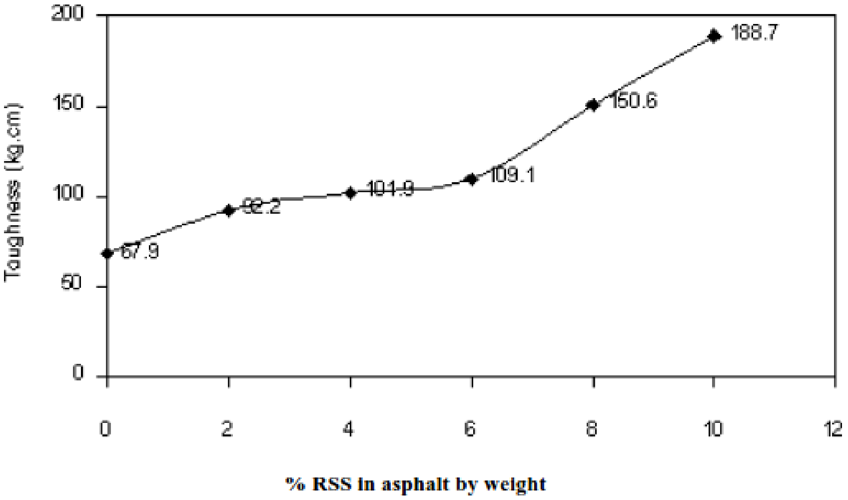


Figure 3.13 Toughness of asphalt improved with Ribbed Smoked Sheet [58]

From figure 3.13 and 3.14, it show that with ratio of 2, 4 and 6 wt% of asphalt better toughness and tenacity of mixed asphalt but the ratio of 8 and 10 wt% values are increased very rapidly. It can be interpreted that increasing RSS to 8 and 10 wt% resulting in high viscosity mixture, therefore the strength of modified asphalt provides higher values of toughness and tenacity.

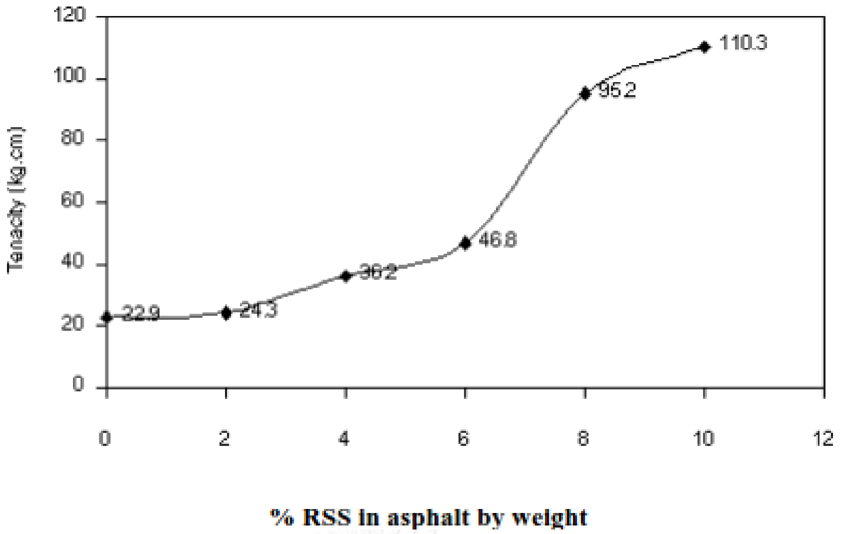


Figure 3.14 Tenacity of asphalt improved with Ribbed Smoked Sheet [58]

Zhang, F. and Yu, J., 2010 [3] initiated a study of high-performance SBR compound modified asphalt by mixing of PPA, SBR, sulfur to the base asphalt with objective to improve the performance for pavement applications in terms of physical and rheological properties.

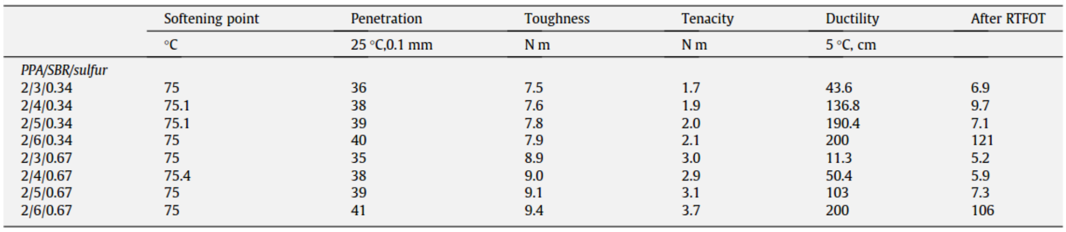
Table 3.3 Effect of PPA, SBR, on the physical properties of the original asphalt [3].

	Softening point	Penetration	Toughness	Tenacity	Ductility	After RTFOT
	°C	25 °C, 0.1 mm	N m	N m	5 °C, cm	
Asphalt/SBR						
100/0	48	80	–	–	6.4	3.7
100/3	56	46	1.2	0.5	200	56
100/4	58	44	1.4	0.8	200	120
100/5	60	42	2.0	1.0	200	200
100/6	60.2	41	2.2	1.1	200	200
Asphalt/PPA						
100/1	62	43	–	–	4.3	2.5
100/2	75	36	–	–	3.7	2.3
100/3	92	29	–	–	1.4	0.8

Table 3.4 The physical properties of the PPA/SBR-modified asphalt [3].

	Softening point	Penetration	Toughness	Tenacity	Ductility	After RTFOT
	°C	25 °C, 0.1 mm	N m	N m	5 °C, cm	
PPA/SBR						
2/3	75.4	38	6.0	1.0	137.6	12.1
2/4	75	40	6.5	1.2	200	190.2
2/5	75	43	6.7	1.5	200	200
2/6	75.1	46	6.6	1.4	200	200

Table 3.5 The physical properties of the PPA/SBR/sulfur modified asphalt [3].



	Softening point	Penetration	Toughness	Tenacity	Ductility	After RTFOT
	°C	25 °C,0.1 mm	N m	N m	5 °C, cm	
PPA/SBR/sulfur						
2/3/0.34	75	36	7.5	1.7	43.6	6.9
2/4/0.34	75.1	38	7.6	1.9	136.8	9.7
2/5/0.34	75.1	39	7.8	2.0	190.4	7.1
2/6/0.34	75	40	7.9	2.1	200	121
2/3/0.67	75	35	8.9	3.0	11.3	5.2
2/4/0.67	75.4	38	9.0	2.9	50.4	5.9
2/5/0.67	75	39	9.1	3.1	103	7.3
2/6/0.67	75	41	9.4	3.7	200	106

The pure PPA modified asphalts and the pure SBR-modified asphalts physical properties are shown in Table 3.3. By increasing PPA content in pure PPA modified asphalt, the softening point increased evidently and the penetration decreased correspondingly. It can be implied that PPA is contributed to improving of the high temperature properties of asphalt PPA/SBR-modified asphalts with various SBR contents has been prepared with expectation to improve the low-temperature resisting-cracking property of the pure PPA modified asphalt. The physical properties are shown in Table 3.4. It shown that the low-temperature ductility of asphalt before and after RTFOT ageing increased dramatically by increasing SBR content. On the other hands, the low-temperature resisting-crack property of asphalt was improved.

In the application of SBR-modified asphalt, the toughness and tenacity are two important properties to be investigated, It relate to the adhesion ability of modified binder to stone matrix. In order to improve the toughness and the tenacity of the PPA/SBR-modified asphalt, the physical properties of the PPA/SBR/sulfur modified asphalts were analyzed and shown in Table 3.5. It has been found that the toughness and the tenacity of the PPA/SBR/sulfur modified asphalt were improved to some extent through dynamic vulcanization. With increasing sulfur content, the toughness and the tenacity increased correspondingly additional of sulfur also improve the toughness and the tenacity, the low-temperature ductility of asphalt after ageing declined rapidly because of the increasing crosslinking density and the degradation of SBR molecules. The modified binder with 6 parts SBR still provides a good low-temperature ductility after ageing. By focusing on the main properties of SBR compound modified asphalt including the softening point, the low-temperature ductility, the toughness and the tenacity, it has been found that the PPA/SBR/sulfur (2/6/0.67) modified asphalt was the optimal one.

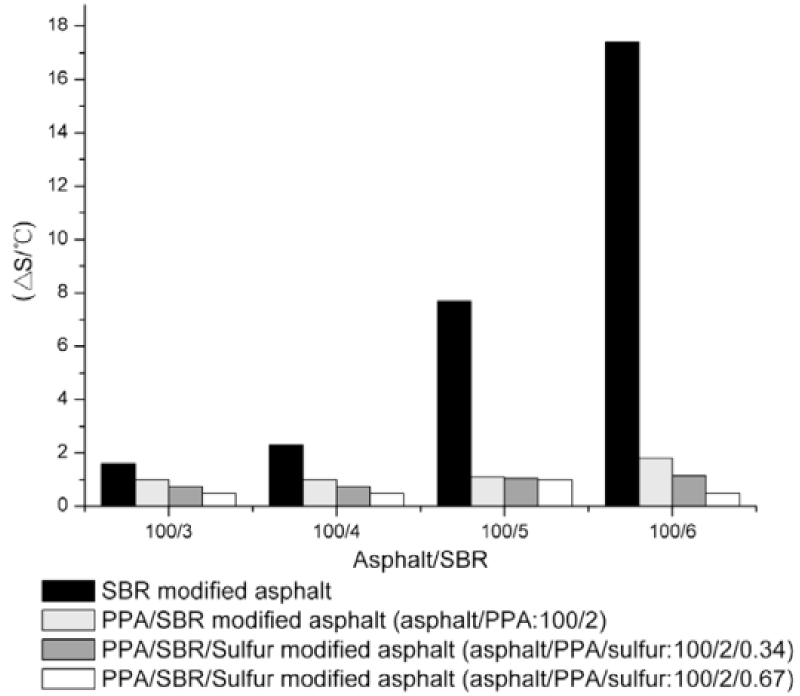


Figure 3.15 Storage stabilities of SBR compound modified asphalts [3]

The PPA/SBR-modified asphalts and the PPA/SBR/sulfur modified asphalts have been tested and the results is shown in Figure 3.15. It is clearly that for the pure SBR-modified asphalt, the differences of the softening points between the top and bottom sections of the samples are significant, it can be implied that the phase separation is the key parameter. By increasing SBR content, the phase separation turn to be a key parameter. Polyphosphoric acid provides the shift from sol to gel structure. The shift form sol to gel structure in asphalt make asphalt becomes a solid material and therefore affected the stability of PMA. The storage stability of the PPA/SBR-modified asphalt can be improved further by reaction with sulfur. By adding sulfur, the difference in the softening points of the PPA/SBR/sulfur modified asphalt declined further shows the presence of sulfur improved the compatibility between asphalt and SBR through a dynamic vulcanization process.

Figure 3.16 provides the comparison of rheological properties of the original asphalt, the pure PPA modified asphalt, the PPA/SBR-modified asphalt, the PPA/SBR/sulfur modified asphalt. By increasing the temperature, tanδ increased and G* decreased for the original asphalt. The varying trend of tanδ and G* is slowed down significantly when 2 parts PPA was added to the asphalt. The addition of SBR to the hard PPA modified asphalt increases the flexibility of asphalt and resulting in the modified binder soft. Therefore, the resistance of modified binders to rutting declined. The G* of the PPA/SBR/sulfur modified asphalt with 0.67 part sulfur is higher than that of the modified binder with 0.34 part sulfur at high-temperature and the change in tanδ was also reduced to some extent. It can be interpreted that the increasing sulfur level enhanced the degree of chemical vulcanization of SBR, by which the dynamic mechanical properties of the PPA/SBR/sulfur modified asphalt were influenced.

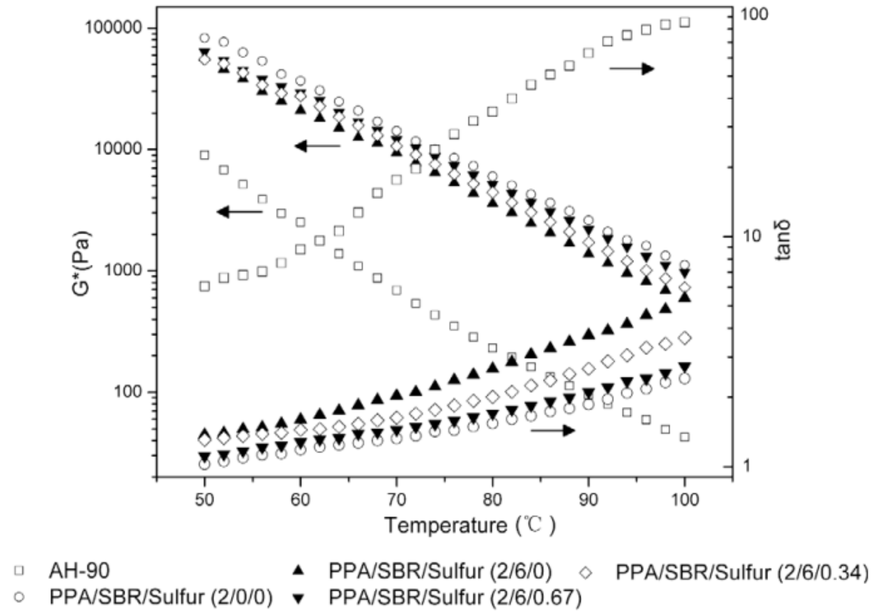


Figure 3.16 The viscoelasticity of SBR compound modified asphalt [3]

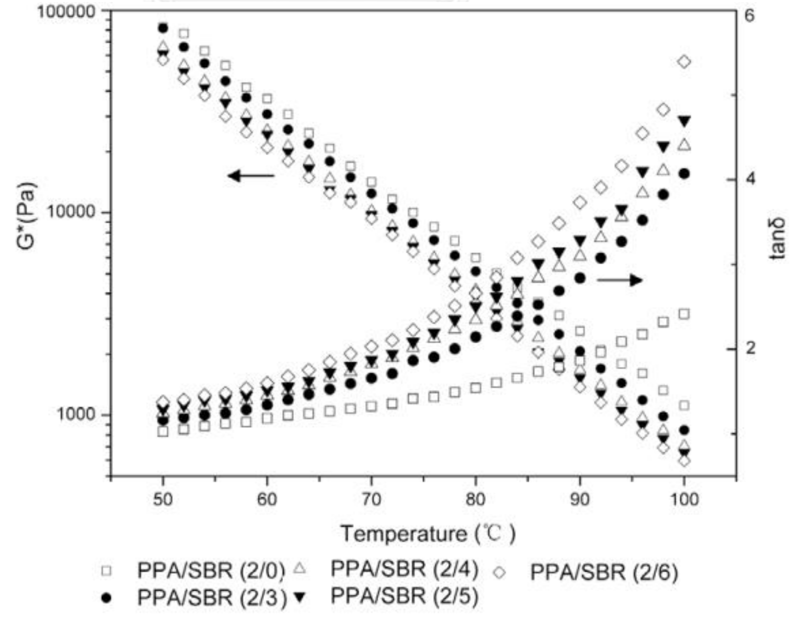


Figure 3.17 The rheological properties of the PPA/SBR-modified asphalt [3]

Figure 3.17 shows the dynamic rheological properties of the PPA/SBR-modified asphalts with various SBR contents. It shows that when 3 parts SBR is added to the pure PPA modified asphalt, the G* of the modified binder declined, the tanδ increased obviously at high-temperature. As SBR content is increased, the G* of the modified binders declined continuously in the whole temperature range, the tanδ increased correspondingly. It can be concluded that to the soft characteristic of SBR powder and the increasing SBR content, with increasing SBR content, the modified binder become more flexible.

The morphologies of the base asphalt and the pure PPA modified asphalt comprises of 2 parts PPA are shown in Figure 3.18. It can be explained by Figure 3.18A and B that some white materials appeared in some areas of asphalt matrix compared with the base asphalt, which indicated PPA reacted with some constituents of asphalt and new complexes is main contributor. This can be concluded to the presence of charge-transfer complexes between phosphorous and aromatic structures of asphaltenes after adding PPA. The condensation of the complexes resulting in forming of microscopy and can be confirmed by presenting the white materials.

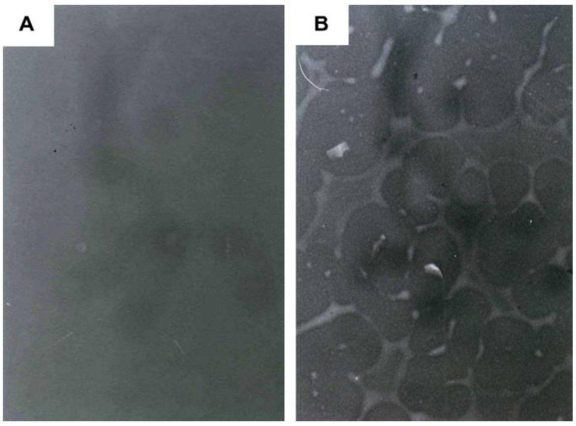


Figure 3.18 Micrographs of the original asphalt and the pure PPA modified asphalt (optical microscopy) at a magnification of 400
(A) original asphalt (B) the pure PPA modified asphalt (asphalt/PPA:100/2) [3]

Figure 3.19 shows the comparisons among the morphologies of the pure SBR-modified asphalt containing 6 parts SBR, the PPA/SBR (2/6) modified asphalt and the PPA/SBR/sulfur (2/6/0.67) modified asphalt. In Figure 3.19C, shows the pure SBR-modified asphalt with the presence of a lot of coarse particles in asphalt matrix which can be interpreted that SBR was difficult to disperse into asphalt. This incompatibility provides information that pure SBR-modified asphalt has the poor stability. The morphology of the PPA/SBR-modified asphalt is shown in Figure 3.19D. It can be explained that the SBR particles became dim in asphalt matrix and seemed smaller than that in the base asphalt, which indicated the good dispersion of SBR in acid-treated asphalt. In the Figure 3.19E, it is shown the vulcanization of SBR improved the dispersion of it in asphalt matrix evidently.

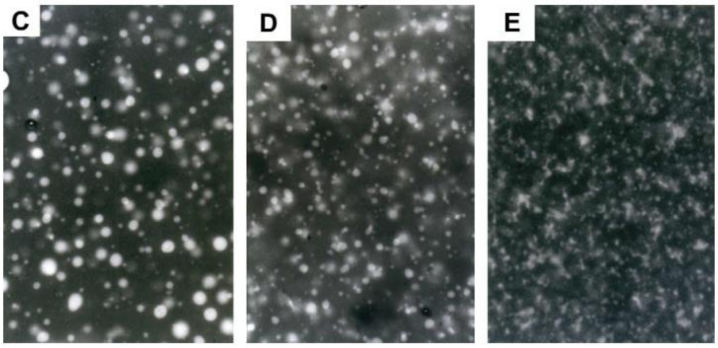


Figure 3.19 Micrographs of the pure SBR-modified asphalt, the PPA/SBR-modified asphalt, the PPA/SBR/sulfur at a magnification of 400
(C) the pure SBR-modified asphalt (asphalt/SBR:100/6)

(D) the PPA/SBR (2/6) modified asphalt

(E) the PPA/SBR/sulfur (2/6/0.67) modified asphalt [3]

The FTIR spectra of the base AH-90 asphalt and PPA are shown in Figure 3.20. In the FTIR spectrum of the base asphalt, the strong peaks within 2850-2960 cm^{-1} area are typical C–H stretching vibrations in aliphatic chains. The peak at 1605.11 cm^{-1} is attributed to C=C stretching vibrations in aromatics. The C–H asymmetric deforming in CH_2 and CH_3, and C–H symmetric deforming in CH_3 vibrations is found at 1458.86 cm^{-1} and 1375.01 cm^{-1}, respectively. The peak at 1215.15 cm^{-1} corresponded to the frame vibration of $(CH_3)_3$–C–R. The small peaks within 650–910 cm^{-1} region are typical C–H vibrations of benzene ring. In the FTIR spectrum of PPA, the broad and low peak at 2843 cm^{-1} is attributed to the P–OH stretching vibrations, the peaks were observed at 2350 cm^{-1} corresponding to P–H stretching vibrations; 1645 cm^{-1} corresponding to the O–H deforming vibrations; 1007.82 cm^{-1} corresponding to the P–O–P stretching vibrations; 925 cm^{-1} and 699.2 cm^{-1} corresponding to the asymmetric vibrations of P–O–P; 494.3 cm^{-1} corresponding to the bending vibrations of P–O–P.

The FTIR spectrum of the pure PPA modified asphalt containing 2 parts PPA is shown in Figure 3.21, it can be observed that new absorption peaks appeared at 1007.82 cm^{-1}, 699.2 cm^{-1}, 494.3 cm^{-1} respectively compare with the original asphalt, however these peaks also can be found in the FTIR spectra of PPA. Though PPA reacted with some constituents of asphalt, the absorption peaks of new complexes caused cannot be found in the FITR spectra of the pure PPA modified asphalt due to the overlap of other peaks.

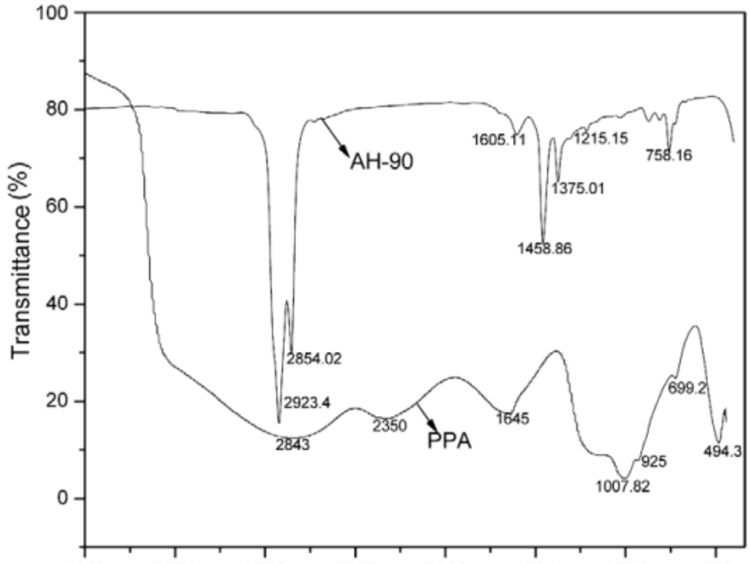


Figure 3.20 FTIR spectra of the original asphalt and PPA [3]

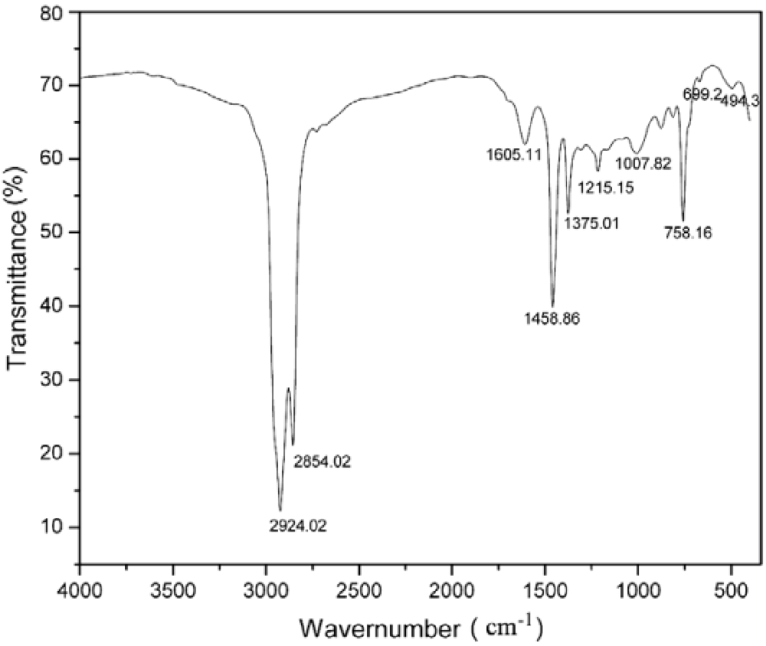


Figure 3.21 FTIR spectra of the pure PPA modified asphalt (asphalt/PPA:100/2) [3]

In conclusion, because of the structure shift of asphalt from sol to gel, PPA can improve the high-temperature physical and rheological properties of asphalt with an unfavorable effect on the low-temperature ductility. The low-temperature ductility can be improved dramatically by additional of SBR to the pure PPA modified asphalt, however it influenced the dynamic rheological properties to some extent, this affect to the soft characteristics of SBR rubber mainly. The high-temperature rheological properties can be improved by additional of sulfur to the PPA/SBR-modified asphalt, the adhesion to stone matrix and the compatibility between asphalt and polymer through dynamical vulcanization with a small effect on the thermal stability. The PPA/SBR/sulfur modified asphalts with the same sulfur content shows the similar rheological behavior. The suitable proportion of PPA, SBR, sulfur in asphalt can improve the properties of SBR compound modified asphalt roundly.

CHAPTER IV

EXPERIMENTAL

4.1 Materials

Asphalt penetration grade, AC60/70, was supplied by IRPC Public Company Limited. The properties are as follows: softening point, 46°C (ASTM D36); penetration resistance, 67 dmm at 25°C (ASTM D 5); Brookfield viscosity, 306 cP at 135°C (ASTM D4402). Natural rubber in latex form, which contains of 64% dry rubber content, was purchased from Yang Thong Latex Ltd. (Thailand). Polyphosphoric acid contains 84% P_2O_5 was purchased from Sigma-Aldrich Co. LLC. Sulfur, the NR crosslinker, is obtained from Suksapanpanit Ltd. (Thailand).

4.2 Sample Preparation

NR-modified asphalts were prepared using a shear mixer model RW20DZM from IKA Labortechnik Staufen Co., Ltd. Asphalt (150 g) was heated until it became fluid in a metal container. Then upon reaching about 150°C, calculated amount of PPA was added, shearing time was fixed at 30 min and then sulfur (based on 100 parts NR) was added and mechanically stirred for 10 min. Finally, NR in latex form was added and sheared for 30 min at a shearing speed of 500 rpm. The latex was intentionally incorporated in the final stage of the modified asphalt preparation to avoid premature crosslinking with the sulfur.

4.3 Sample Characterizations

4.3.1 Physical Properties Tests

Brookfield viscosity (135°C) was used to evaluate the difference in viscous behavior of sample according to ASTM D 4402. The penetration test was performed according to ASTM D5 under the condition of applying a 100 g weight on the penetration probe at 25°C and reported the value in tenths of millimeters. The softening point was determined according to ASTM D36.

4.3.2 Morphological Properties

The sample morphology was obtained using a fluorescence microscope model BX53 from Olympus Co., Japan. Thin layer of the modified asphalt was casted on a glass slide and viewed under the microscope with a magnification of 400.

4.3.3 Storage Stability Test

The storage stability of modified asphalt samples was tested in accordance with IS 15462. The sample was poured into an aluminum tube with 25.4 mm in diameter and 136.7 mm in height. The tube was closed and stored vertically in a convection oven at 163°C for 24 h. The tube was then cooled to 6.7°C for 4 h. and cut horizontally into three equal sections. Softening point at the top and the bottom sections was measured. Modified asphalt stability was evaluated by the difference in softening point between the top and bottom samples. If the difference temperature was less than 4°C, the sample was considered to have good storage stability.

4.3.4 Toughness and Tenacity

Toughness and tenacity were tested in accordance with ASTM D5801-95. Toughness and tenacity are also two important parameters for characterizing elastomer modified asphalts. This test method is useful in confirming the ability of the rubber modified asphalt to be stretched to a large elongation while at the same time resisting further stretching.

4.3.5 Dynamic Shear Rheometry

Rheological properties of each sample were investigated using a rheometer model Physica MCR301 from Anton Paar Company under parallel plate geometry with 1 mm gap and 25 mm diameter. Dynamic shear properties under a frequency sweep mode were obtained over a frequency range of 0.1-100 rad/s at a fixed temperature 60^{o}C.

4.3.6 Fourier Transform Infrared Spectroscopy

The chemical structure and network formation behavior of the modified asphalt sample was also studied by a Fourier transform infrared spectroscopy (FTIR). fourier transform infrared spectra of all samples were acquired using a Spectrum GX FTIR spectrometer from Perkin Elmer. All spectra were taken as a function of time with 64 scans at a resolution of 4 cm^{-1} and a spectral range of 4000-500 cm^{-1}, a small amount of a viscous liquid sample was casted as thin film on a potassium bromide window.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Physical property

5.1.1. Effects of NR and PPA on Brookfield Viscosity

Figure 5.1 exhibits effects of NR contents on Brookfield viscosity of asphalt at various PPA contents from 0 wt% to 2 wt%. It can be seen that the viscosity at 135°C of the neat asphalt was determined to be 306 cP. The incorporation of 0.6-4.5 wt% NR into asphalt without PPA was found to increase the viscosity in a range of 397-1,268 cP. Asphalt is a viscoelastic liquid. Its viscosity changes with temperature and shear. As increasing temperature, the rheology of asphalt changes and begins to flow, while NR acts like a polymer chain and resists the flow of the asphalt resulting in an increasing its resistance to shear meaning its viscosity [2]. In addition, it was found that the lower viscosity of our modified asphalt in comparison with commercial SBS-modified asphalt was obtained. Brookfield viscosity of commercial 3.5 wt% SBS 1301- and 3.5 wt% SBS 4303-modified asphalt was reported to be 1,270 cP and 1,655 cP, respectively [84], while the Brookfield viscosity for our modified asphalt of 3.2 wt% NR-modified asphalt without PPA was measured to be 890 cP. Since the lower viscosity of asphalt suggests better mixing or blending with other pavement ingredients, therefore, it can be concluded that NR-modified asphalt showed the good property than SBS-modified asphalt in term of its processing ability compared at the same amount of the modifier used.

Furthermore, the effects of PPA contents on Brookfield viscosity of NR-modified asphalt are also depicted in Figure 5.1. It can be seen that the addition of PPA was found to increase the Brookfield viscosity of the asphalt modified with all PPA contents. Moreover, at a fixed amount 3.2 wt% NR with an addition of 1 wt% and 2 wt% PPA, the viscosity of the modified asphalt were further increased to 1,513 cP and 2,131 cP, respectively. Comparing with the Brookfield viscosity, i.e. 1,560 cP of commercial 3.5 wt% SBS 1301-modified asphalt with 0.5%wt PPA [84], the 3.2 wt% NR-modified asphalt mixed with 1 wt% PPA showed the same viscosity values. This characteristic was suggested that PPA is a reactive additive used to increase the viscosity of asphalt [85-86].

5.1.2. Penetration Resistance

Figure 5.2 exhibits effects of NR contents on penetration resistance of asphalt at various PPA contents from 0 wt% to 2 wt%. The penetration resistance of the neat asphalt was determined to be 67. While, the incorporation of 0.6-4.5 wt% NR into asphalt without PPA was found to decrease the penetration resistance to 64-57 because NR chains was dispersed within asphalt holding the asphalt more tightly. The asphalt thus becomes harder resulting in lower penetration resistance. Moreover, the neat asphalt and the asphalt modified with NR was made stiffer by adding PPA modifier. This behavior was due to reaction between PPA and asphalt can generate higher molecular weight structure that results in significantly low penetration [85, 86]. With the addition 3.2 wt% NR and 2 wt% PPA, the penetration will be 51, the lowest acceptable standard values issued by the Department of Highways, Ministry of Transport, Thailand.

5.1.3. Effects of NR and PPA Addition on Softening Points

Figure 5.3 exhibits effect of NR contents on softening point of asphalt at various PPA contents from 0 wt% to 2 wt%. The softening point of the neat asphalt was determined to be 46°C. The incorporation of 0.6-4.5 wt% NR into the neat asphalt was found to increase the softening point in a range of 48-58°C. This result implies the strong effect of the NR on enhancing the softening point of the asphalt that was consistent with decreasing of the penetration values. In addition, at 0-4.5 wt% NR content-modified asphalt, the softening point of the asphalts increased with increasing PPA contents suggesting the positive effect of the PPA to further increase softening point of the asphalt. However, it seem like that the effect of PPA on the softening point tends to be less pronounced than that of the NR.

The lowest acceptable standard of softening point value issued by the Department of Highways, Ministry of Transport Thailand is 50°C. From Figure 5.3 adding PPA can increase softening point from 46°C of the original asphalt to 56°C at 2 wt% PPA content. In addition, PPA can combine homogeneously with NR and shows very good compatibility with the asphalt. On an average, adding 2 wt% PPA resulted in about 7°C enhancement in the softening point of the asphalt comparing at the same NR content.

The softening point is a critical property of PMA. The softening point of conventional asphalt is usually at 46°C. When the NR is added to 3.2 wt%, the softening point increases from 46 to 54°C, or 17%. Furthermore, the addition of 2 %wt PPA, the softening point will further increase from 54 to 60°C, or 11%. From Figure 5.3, the addition of 1 wt% PPA results in significantly higher softening point. Likewise, the addition of 2 wt% PPA also results in the higher softening point at the lower rate. Thus, 2 wt% PPA is a suitable quantity to improve the softening point.

5.2 Toughness and Tenacity

Two important properties considered the adhesive ability of modified asphalts to stone matrix are toughness and tenacity [3]. Figure 5.4 shows toughness of the neat asphalt and NR/PPA-modified asphalt mixed with sulfur at various sulfur contents, the toughness of the neat asphalts was improved by adding NR that provides a significant elastomeric component.

The addition of PPA in NR-modified asphalt results in the reaction between PPA and asphalt [85, 86]. PPA added in NR-modified asphalt can created longer chain structure then the toughness and tenacity property were improved but effect of PPA not much. Due to formation of the vulcanization reaction between NR and sulfur [63] can created longer chain structure in modified asphalt also. From Figure 5.4, the toughness of NR/PPA-modified asphalt is found to increase with sulfur addition. It can be seen that the toughness of NR/PPA-modified asphalt modified with 0.3 wt% and

0.5 wt% sulfur was further increased. Sulfur 0.5 wt% added in NR/PPA-modified asphalt can increase toughness 18% compare with original NR/PPA-modified asphalt.

Figure 5.5 shows tenacity of the neat asphalt and NR/PPA-modified asphalt mixed with sulfur at various sulfur contents. It seem like that the effect of NR, PPA and sulfur on the tenacity tends to be same as toughness. Sulfur 0.5 wt% added in NR/PPA-modified asphalt can increase tenacity 25% compare with original NR/PPA-modified asphalt. However suitable sulfur content has to consider with other study such as storage stability which treats modified asphalt at high temperature.

5.3 High Temperature Storage Stability

The high-temperature storage stability of the NR-modified asphalt series are shown in Table 5.1. In this table, it was observed that the difference of softening point between the top and the bottom sections of 3.2 wt% NR-modified asphalt was found to be 1.1°C. It was in agreement with the IS15462 standard the specification No. DH-SP 409/2013 announced by the Department of Highways, Ministry of Transport Thailand [14] that the top and the bottom discrepancy of softening point was not more than 4°C. In addition, the result points out that NR liquid form is a modifier capable of dispersing and not separating at the temperature of 163°C. This characteristic is different from the result of other modifiers such as SBS that the difference of softening point between the top and the bottom sections can be 60°C [84].

Obviously, the difference of softening point of NR-modified asphalt decreases when PPA component was mixed in system. This is due to the fact that an addition of PPA in NR-modified asphalt results in the reaction between PPA and asphalt [85, 86]. Moreover, the effect of sulfur on high-temperature storage stability of the NR-modified asphalt was also investigated. The difference of softening point tended to decrease with increasing sulfur content in the NR/PPA-modified asphalt as a result of sulfur improved the compatibility of NR/PPA-modified asphalt via a vulcanization process [3, 63]. In addition, it can be seen that it has no gap on the difference of softening point of NR/PPA-modified asphalt with 0.3 wt% of sulfur.

Figure 5.6 shows the comparison of softening point of NR-modified asphalt series after storage stability test. It can be seen that the softening point of the NR/PPA-modified asphalt slightly increased with increasing sulfur content of 0.3 wt% in NR/PPA-modified asphalt, while, the decrease of the softening point of the NR/PPA-modified asphalt with more than 0.3 wt% sulfur was observed. This characteristic may be due to the more severe breakdown of a vulcanized polymer substructure into smaller copolymer structures [8]. Consequently, from those results, it can be concluded that an ability of 3.2 wt% PPA and 0.3 wt% sulfur to enhance the storage stability and softening point by increasing crosslinked chain of NR-modified asphalts was observed.

5.4 Fluorescent Micrographs

Compatibility between the modifier and asphalt is important property of modified asphalt such as its storage stability. Therefore, in this work, the morphology of NR-modified asphalt was evaluated by fluorescence microscopy and the micrographs were depicted in Figure 5.7. Figure 5.7a shows a micrograph of the neat asphalt, Figure 5.7b is a micrograph of NR-modified asphalt containing 3.2 wt% of NR. The micrograph in Figure 5.7b displays relatively fine NR domains to uniformly disperse in asphalt. Such character can be interpreted that modified asphalt is in good homogeneity with the domain size of NR of approximately 10 micron. Figure 5.7c reveals the effect of PPA addition on the morphology of the modified asphalt which showing the NR domains to disperse in the asphalt is better i.e. with finer and more uniform domain size. As discussed in the previous section, the addition of PPA will enlarge the aggregation size of the asphalt thus the viscosity of the modified product [81, 82]. This PPA modification tends to enhance shear force during mixing with the natural rubber thus the observed finer domain size of the rubber.

Figure 5.7d is a micrograph of NR-modified asphalt containing 3.2 wt% of NR, 2 wt% of PPA and 0.3 wt% of sulfur, the optimal formula in our investigation. The relatively stable NR-modified asphalt can be obtained by the addition of 0.3 wt% of sulfur. Because of the crosslinking reaction among the unsaturated rubber molecules, the smaller rubber particles can be formed with less chance of domain size coarsening. During mixing, the crosslinked rubber particles coalescence was suppressed thus the preservation of the fine domain size as seen in the Figure 5.7d. Suitable amount of sulfur for crosslinking therefore promotes good dispersion of the polymer-rich phase in the modified asphalt [78, 87]. The micrograph revealed the domain size of the crosslinked NR to be less than 5 micron. On the other hand, the domain size of the commercial 3.5 wt% SBS 4303 in asphalt was reported to be significantly larger in a range of 20-30 micron. Furthermore, it was reported that the sulfur addition in SBS-modified asphalt can generate filamentous network which a dimension of longer than 300 micron suggesting better compatibility of NR compared to SBS system using the same modification strategy [84].

5.5 Rheological Property

In general, the addition of modifiers in the asphalt shows significant impact on the rheological characteristics of asphalt [74, 75], especially, rutting factor ($G^*/\sin\delta$) which is a factor used to estimate rutting resistance of asphalt binder [83]. Figure 5.8 reveals the effect of PPA and sulfur modifiers on the rutting factor of NR-modified asphalt. It is clearly observed that the rutting factor of the NR/PPA-modified asphalt and the NR/PPA/sulfur-modified asphalt is higher or better than the neat asphalts, especially at a low frequency range. In principle, NR acts like a polymer chain to reinforce asphalt aggregates thus rutting resistance was improved. In addition, due to a structure shift of asphalt from sol to gel, PPA can also help to further improve the rutting factor [77, 88].

According to Figure 5.8, the rutting factor was also found to slightly increase with increasing the amount of sulfur content in a range of 0.3-0.5 wt%. As the sulfur content at 0.5 wt% showed only slightly higher rutting factor than 0.3 wt% of sulfur, the sulfur content at 0.3 wt% was used as an optimal content in our formulation. However, these results suggested that the strength can be improved by adding small amount of the sulfur in asphalt due to its crosslinking ability as previous discussion.

5.6 Fourier Transform Infrared Spectroscopy

The chemical structures of neat asphalt, NR-modified asphalt and their network formation reactions between NR-modified asphalt and PPA were analyzed by Fourier transform infrared spectroscopy (FTIR). The FTIR spectrum of neat asphalt and NR-modified asphalt were shown in Figure 5.9. Characteristic absorption bands of neat asphalt has absorption peaks at 2950 cm^{-1} assigned to C-H asymmetric stretch in CH_3, 1456 cm^{-1} assigned to C-CH_3 and methylenic asymmetric, 1376 cm^{-1} assigned to C-CH_3 asymmetric [86].

The FTIR spectrum of the addition of NR into asphalt was examined in NR/PPA/sulfur (3.2/0/0) sample. The NR-modified asphalts do not contain any new functional groups compared to neat asphalts. This fact implied that natural rubber was dispersed into asphalt molecules without any chemical reaction with asphalt molecules.

The FTIR spectrum of the addition of PPA into NR-modified asphalt was examined in NR/PPA/sulfur (3.2/2/0) specimen. In the spectrum of this sample, it was observed that there was appearance of additional new absorption peaks in the ranges of 1740 cm^{-1} and a rather broad peak in a range of 1250-1150 cm^{-1} which were assigned to the vibrational band of phosphate ester in the modified asphalt. This observation suggested that the PPA had chemical reaction with the hydroxyl group in the asphalt to form phosphate ester. Furthermore, these phosphate ester absorption bands were also found in the FTIR spectra of NR/PPA/sulfur (3.2/2/0.3) and NR/PPA/sulfur (3.2/2/0.5) confirming the above reaction of PPA with the asphalt. The presence of phosphate ester in synthetic oil was also reported to be in the same range of FTIR absorption bands [89].

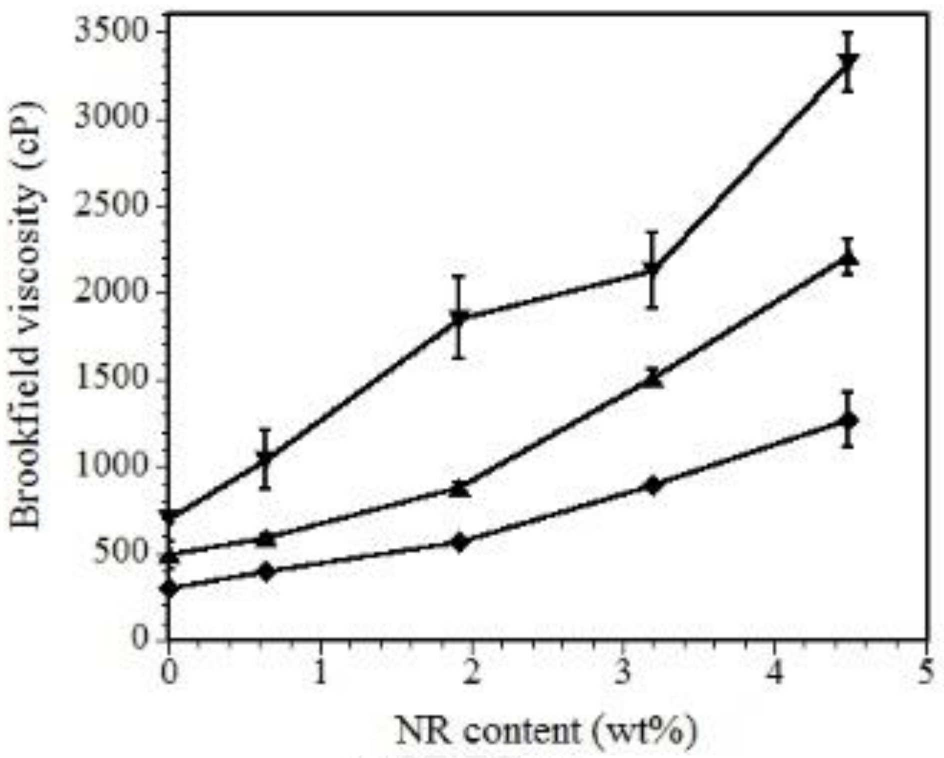


Figure 5.1 Effects of PPA modifiers on Brookfield viscosity at 135°C of NR-modified asphalt: (◆) Neat asphalt, (▲) 1 wt% PPA, (▼) 2 wt% PPA.

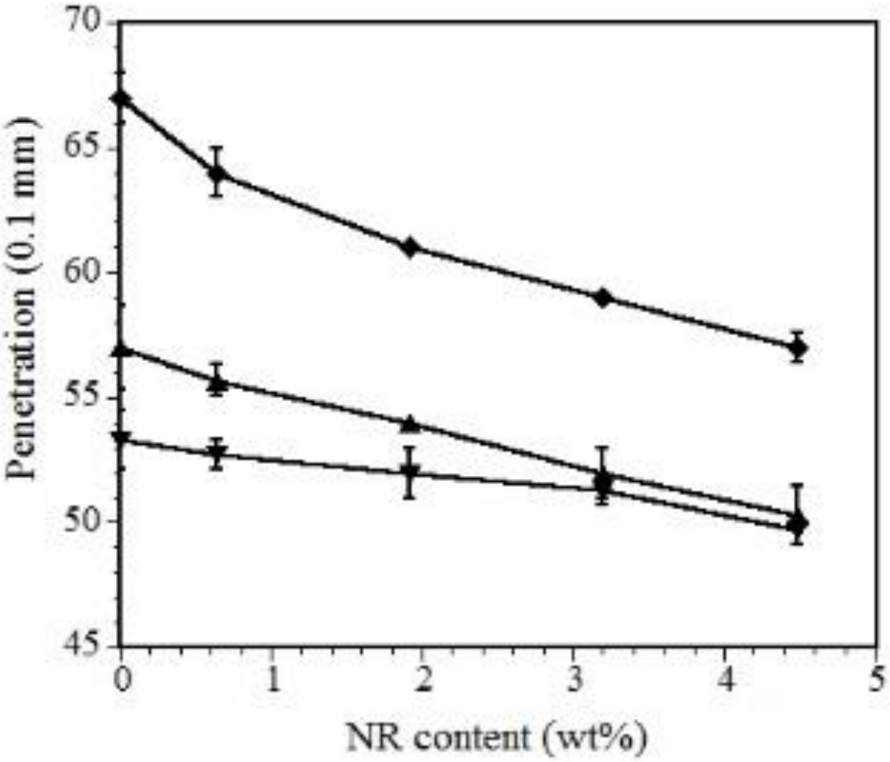


Figure 5.2 Penetration resistance of NR-modified asphalt at various NR contents: (◆) Neat asphalt, (▲) 1 wt% PPA, (▼) 2 wt% PPA.

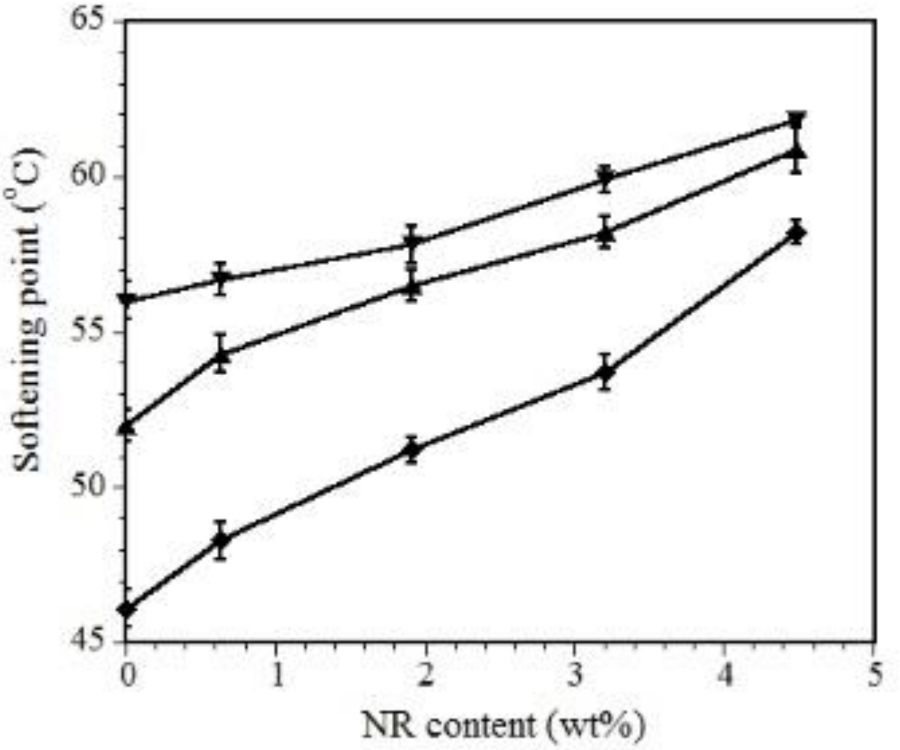


Figure 5.3 Softening point of NR-modified asphalt at various NR contents: (◆) Neat asphalt, (▲) 1 wt% PPA, (▼) 2 wt% PPA.

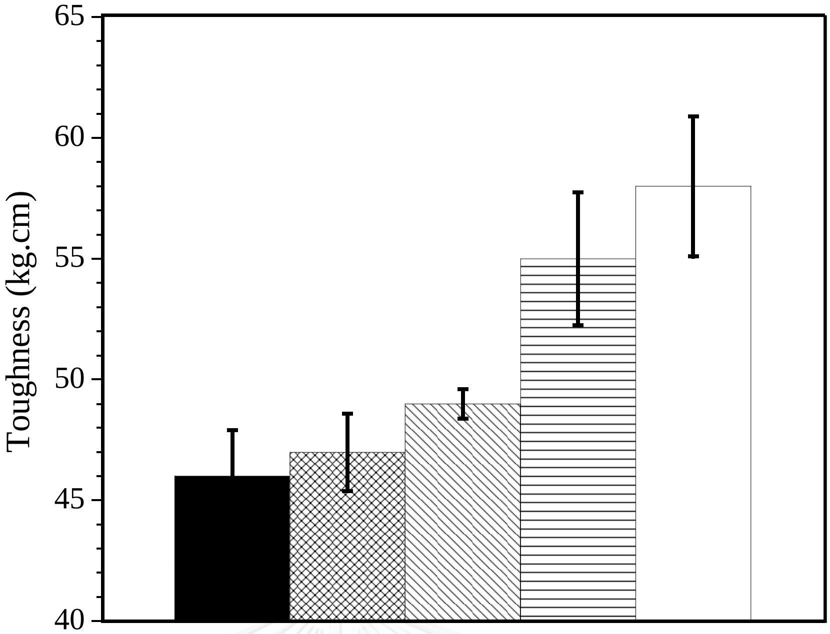


Figure 5.4 Effects of PPA and sulfur modifiers on toughness of the NR-modified asphalt:

(■) Neat asphalt, (▩) NR/PPA/sulfur (3.2/0/0), (▧) NR/PPA/sulfur (3.2/2/0),

(▤) NR/PPA/sulfur (3.2/2/0.3), (□) NR/PPA/sulfur (3.2/2/0.5).

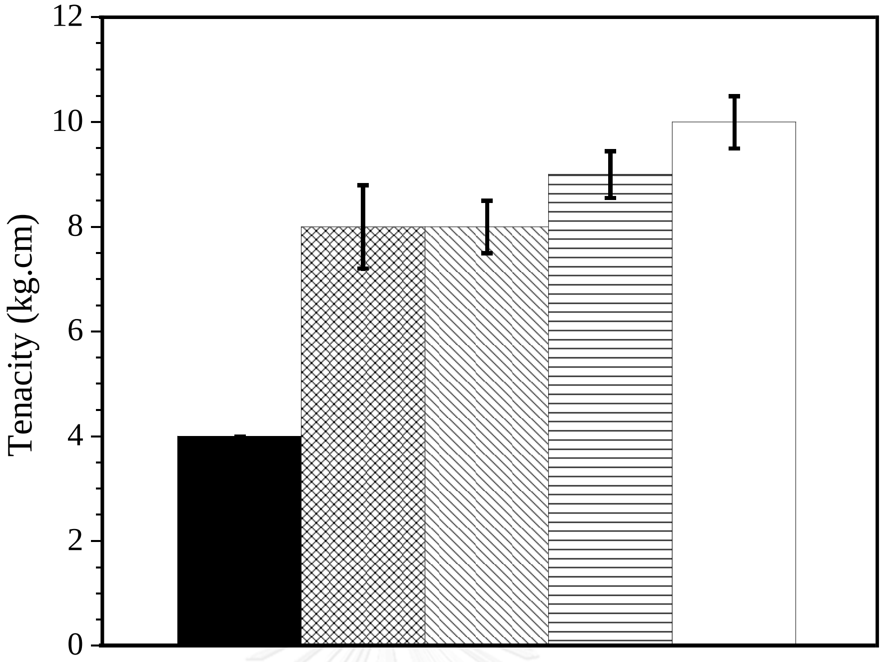


Figure 5.5 Effects of PPA and sulfur modifiers on tenacity of NR-modified asphalt: (■) Neat asphalt, (▩) NR/PPA/sulfur (3.2/0/0), (▧) NR/PPA/sulfur (3.2/2/0),

(▤) NR/PPA/sulfur (3.2/2/0.3), (□) NR/PPA/sulfur (3.2/2/0.5).

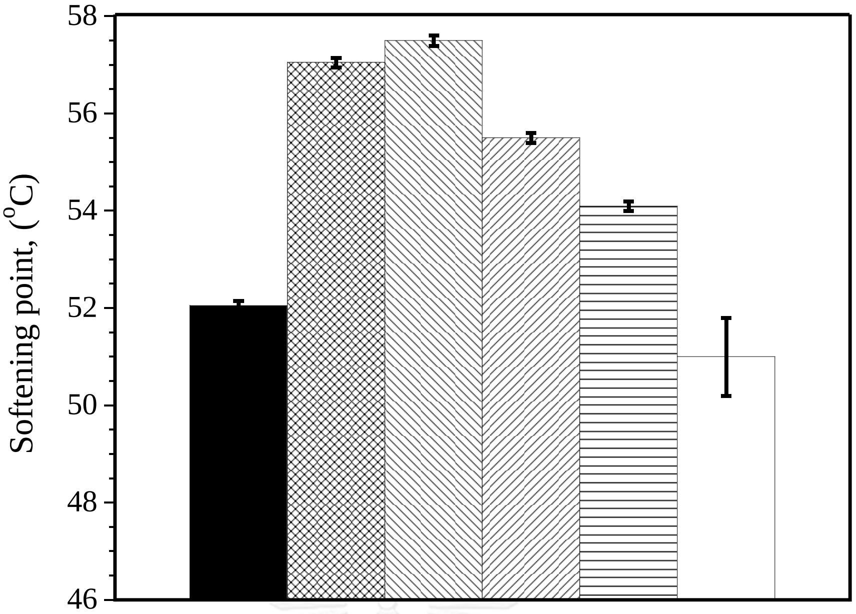


Figure 5.6 Softening points of NR-modified asphalt after storage stability test:
(■) NR/PPA/sulfur (3.2/0/0), (⊠) NR/PPA/sulfur (3.2/2/0),

(▧) NR/PPA/sulfur (3.2/2/0.3), (▨) NR/PPA/sulfur (3.2/2/0.5),

(▤) NR/PPA/sulfur (3.2/2/0.7), (□) NR/PPA/sulfur (3.2/2/1.0).

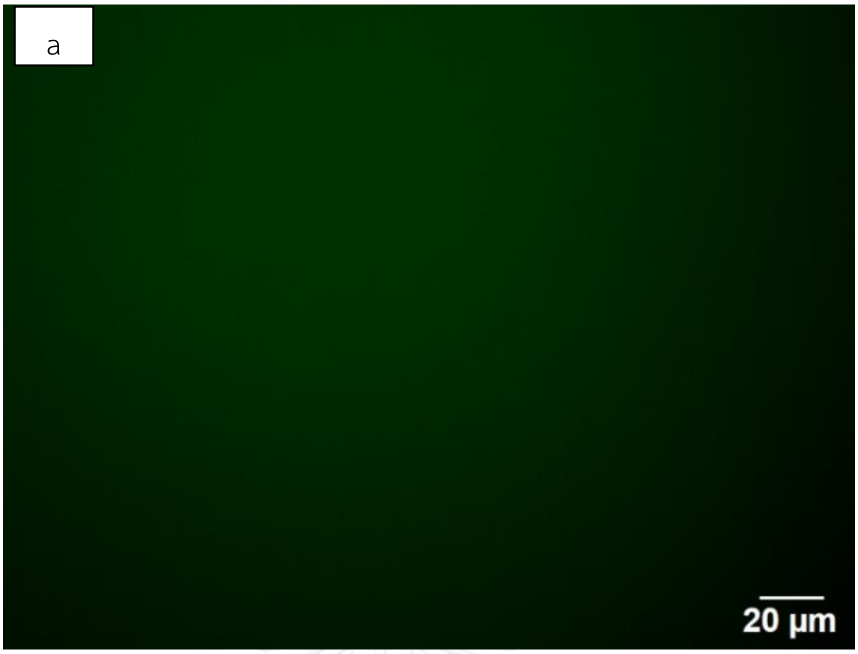


Figure 5.7a Fluorescent micrographs of neat asphalt

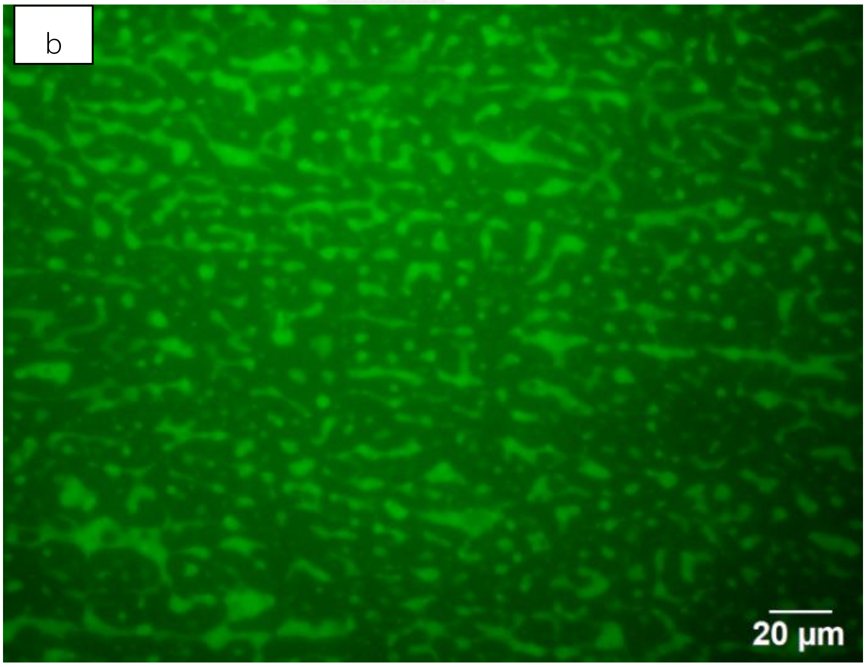


Figure 5.7b Fluorescent micrographs of modified asphalt: 3.2 wt% NR

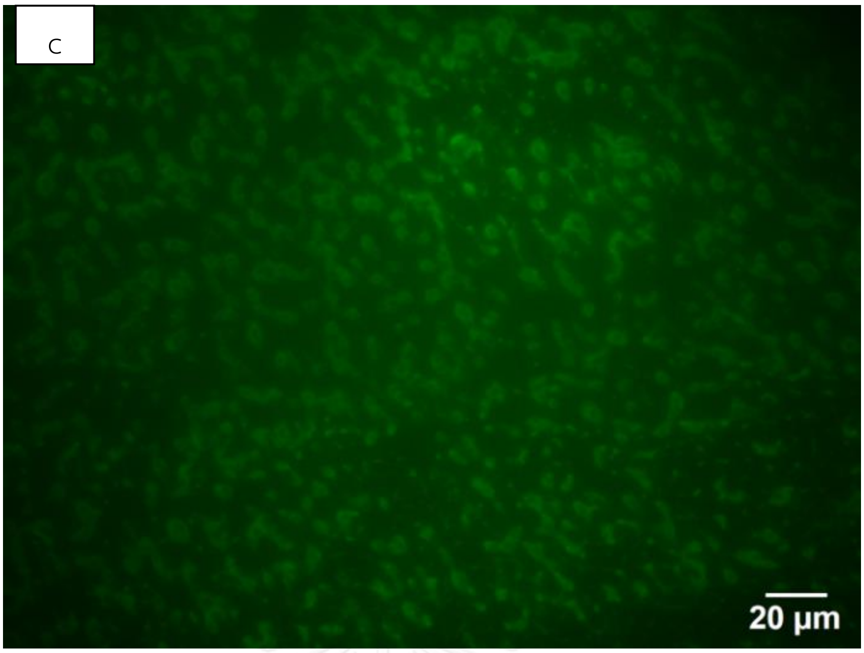


Figure 5.7c Fluorescent micrographs of modified asphalt: 3.2 wt% NR and 2 wt% PPA

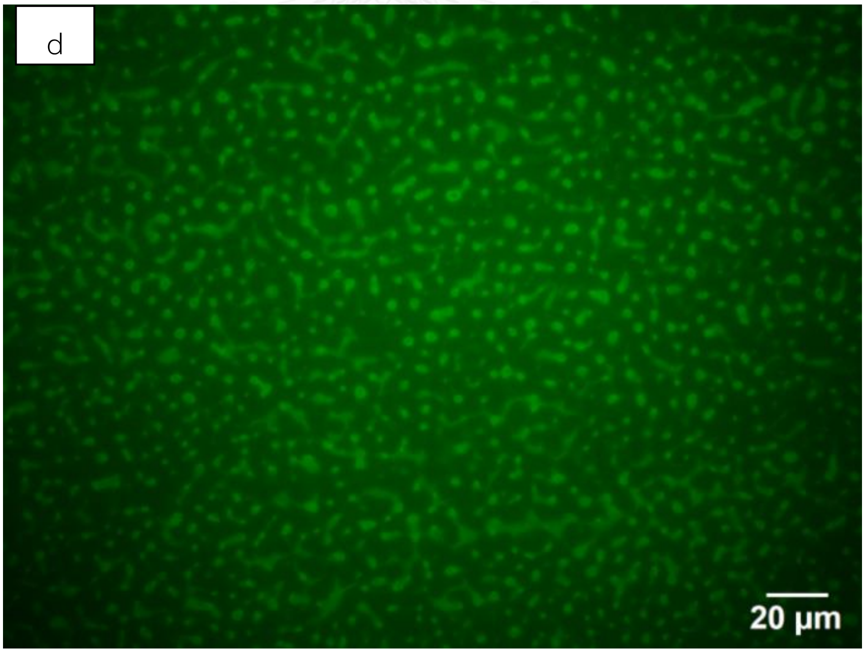


Figure 5.7d Fluorescent micrographs of modified asphalt: 3.2 wt% NR and 2 wt% PPA and 0.3 wt% sulfur

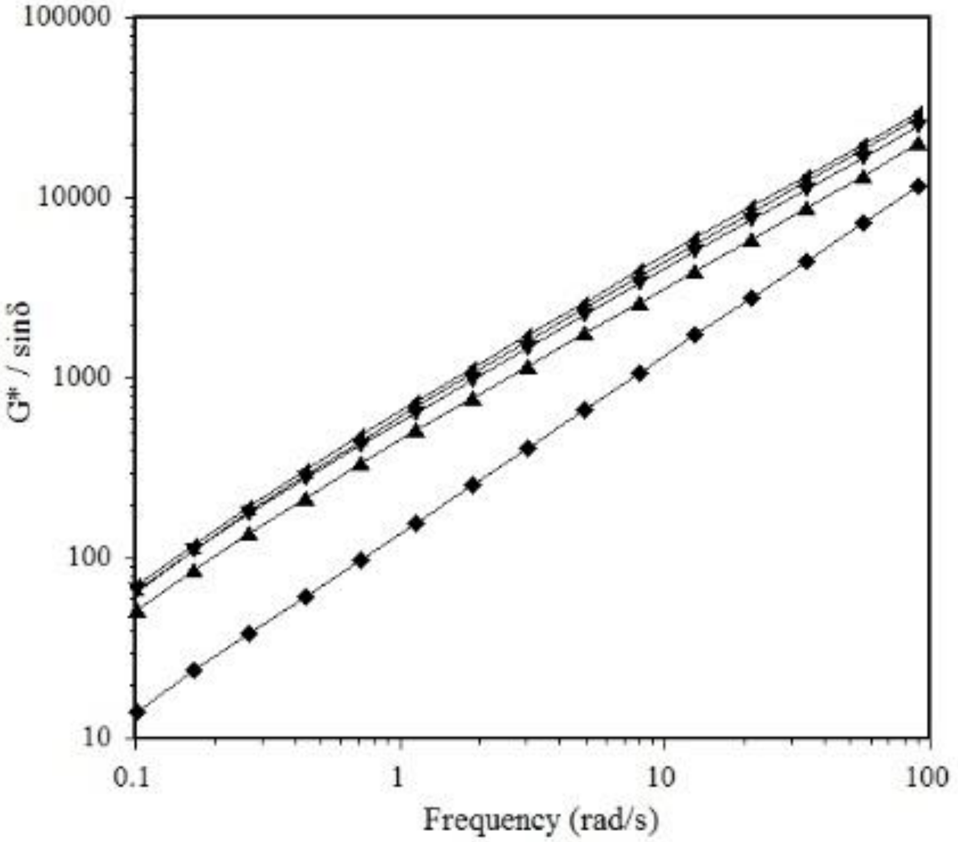


Figure 5.8 Effects of PPA and sulfur addition on rutting factor of NR-modified asphalt: (◆) Neat asphalt, (▲) NR/PPA/sulfur (3.2/0/0), (▼) NR/PPA/sulfur (3.2/2/0), (◣) NR/PPA/sulfur (3.2/2/0.3), (◢) NR/PPA/sulfur (3.2/2/0.5).

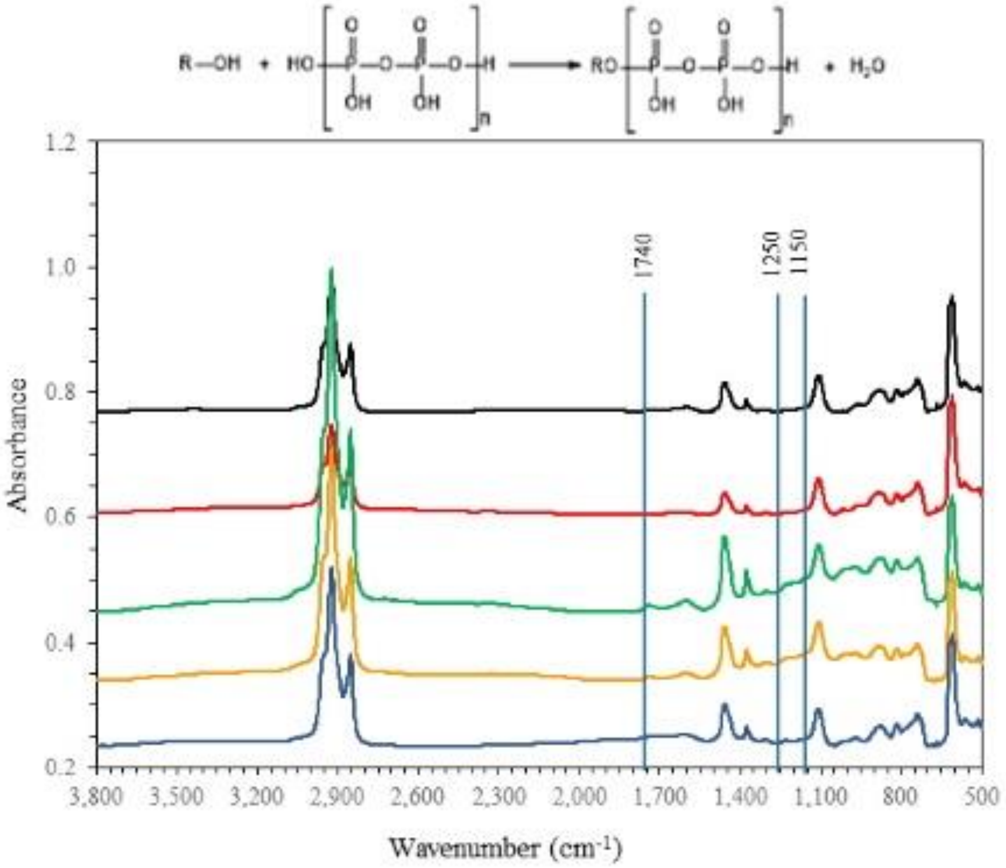


Figure 5.9 FTIR of the neat asphalt and its NR-modified asphalt: (⬛) Neat asphalt, (🟥) NR/PPA/sulfur (3.2/0/0), (🟩) NR/PPA/sulfur (3.2/2/0),

(🟨) NR/PPA/sulfur (3.2/2/0.3), (🟦) NR/PPA/sulfur (3.2/2/0.5).

Table 5.1 Effects of PPA and sulfur modifiers on softening point difference of NR-modified asphalt.

Modified asphalt samples	Softening point difference (°C)
NR/PPA/sulfur (3.2/0/0)	1.1
NR/PPA/sulfur (3.2/2/0)	0.3
NR/PPA/sulfur (3.2/2/0.3)	0
NR/PPA/sulfur (3.2/2/0.5)	0
NR/PPA/sulfur (3.2/2/0.7)	0
NR/PPA/sulfur (3.2/2/1.0)	0

Aluminum tube (before cut)

Aluminum tube was cut into three sections. The samples taken from the top and bottom sections were used to measure their softening points.

CHAPTER VI
CONCLUSIONS

An addition of NR in the form of latex was found to significantly increase softening point and reduce Brookfield viscosity of asphalt. On the other hand, penetration resistance of original asphalt substantially decreased with the NR addition. The use of PPA for long term stability enhancement purpose in asphalt was observed to further increase the softening point and Brookfield viscosity and reduce penetration resistance of original asphalt similar to the use of NR but to a lesser degree. At 3.2 wt% of NR and 2 wt% of PPA in the original asphalt, the softening point was increased from 46 to 60 ^{o}C, the penetration resistance was decreased from 67 to 51 mm and the Brookfield viscosity increased from 306 to 2,131 cP. Both NR and PPA were found to be highly compatible with the asphalt use and their combination is highly attractive for improving asphalt properties with minor effect on its processing behaviors. From micrograph, increasing sulfur in system shows better compatibility for asphalts, NR and PPA via a vulcanization process but sulfur content have to consider properly.

The effect of sulfur on high-temperature storage stability of the NR-modified asphalt series, the difference of softening point tended to decrease with increasing sulfur content in the system as a result of sulfur improved the compatibility of asphalts, NR and PPA via a vulcanization process. However, when the sulfur content increased to 0.3, it has no effect on the difference of softening point. The toughness and tenacity results show effect of added sulfur content in NR-modified asphalt consistent with storage stability test.

Therefore, from those results, it can be concluded that modified asphalt with NR/PPA/Sulfur at 3.2/2/0.3% is the best formula for NR-modified asphalt.

REFERENCES

[1] Zhang, F., Yu, J., and Wu, S. Effect of ageing on rheological properties of storage-stable SBS/sulfur-modified asphalts. J Hazard Mater 182(1-3) (2010): 507-17.

[2] Lu, X. and lsacsson, U. Influence of styrene-butadienestyrene styrene polymer modification on bitumen viscosity. Fuel 76 (1997): 1353-1359.

[3] Zhang, F. and Yu, J. The research for high-performance SBR compound modified asphalt. Construction and Building Materials 24(3) (2010): 410-418.

[4] Dong, D., Huang, X., Li, X., and Zhang, L. Swelling process of rubber in asphalt and its effect on the structure and properties of rubber and asphalt. Construction and Building Materials 29 (2012): 316-322.

[5] Zhang, F., Yu, J., and Wu, S. Influence of ageing on rheology of SBR/sulfur-modified asphalts. Polymer Engineering & Science 52(1) (2012): 71-79.

[6] Liu, S., Cao, W., Fang, J., and Shang, S. Variance analysis and performance evaluation of different crumb rubber modified (CRM) asphalt. Construction and Building Materials 23(7) (2009): 2701-2708.

[7] González, V., Martínez-Boza, F.J., Navarro, F.J., Gallegos, C., Pérez-Lepe, A., and Páez, A. Thermomechanical properties of bitumen modified with crumb tire rubber and polymeric additives. Fuel Processing Technology 91(9) (2010): 1033-1039.

[8] Nejad, F.M., Aghajani, P., Modarres, A., and Firoozifar, H. Investigating the properties of crumb rubber modified bitumen using classic and SHRP testing methods. Construction and Building Materials 26(1) (2012): 481-489.

[9] Jin, H., Gao, G., Zhang, Y., Zhang, Y., Sun, K., and Fan, Y. Improved properties of polystyrene-modified asphalt through dynamic vulcanization. Polymer Testing 21 (2001): 633-640.

[10] Wen, G., Zhang, Y., Zhang, Y., Sun, K., and Fan, Y. Rheological characterization of storage-stable SBS-modified asphalts. Polymer Testing 21 (2001): 295-302.

[11] Cortizo, M.S., Larsen, D.O., Bianchetto, H., and Alessandrini, J.L. Effect of the thermal degradation of SBS copolymers during the ageing of modified asphalts. Polymer Degradation and Stability 86(2) (2004): 275-282.

[12] Larsen, D.O., Alessandrini, J.L., Bosch, A., and Cortizo, M.S. Micro-structural and rheological characteristics of SBS-asphalt blends during their manufacturing. Construction and Building Materials 23(8) (2009): 2769-2774.

[13] Zhang, F., Yu, J., and Han, J. Effects of thermal oxidative ageing on dynamic viscosity, TG/DTG, DTA and FTIR of SBS- and SBS/sulfur-modified asphalts. Construction and Building Materials 25(1) (2011): 129-137.

[14] Specification for Natural Rubber Modified Asphalt Cement; Specification No. DH - SP 409/2013 Thailand, D.o.H.M.o.T., Editor. 2013.

[15] Sengoz, B. and Isikyakar, G. Analysis of styrene-butadiene-styrene polymer modified bitumen using fluorescent microscopy and conventional test methods. J Hazard Mater 150(2) (2008): 424-32.

[16] Vlachovicova, Z., Wekumbura, C., Stastna, J., and Zanzotto, L. Creep characteristics of asphalt modified by radial styrene–butadiene–styrene copolymer. Construction and Building Materials 21(3) (2007): 567-577.

[17] Polacco, G., Muscente, A., Biondi, D., and Santini, S. Effect of composition on the properties of SEBS modified asphalts. European Polymer Journal 42(5) (2006): 1113-1121.

[18] Khodaii, A. and Mehrara, A. Evaluation of permanent deformation of unmodified and SBS modified asphalt mixtures using dynamic creep test. Construction and Building Materials 23(7) (2009): 2586-2592.

[19] Ouyang, C., Wang, S., Zhang, Y., and Zhang, Y. Improving the aging resistance of styrene–butadiene–styrene tri-block copolymer modified asphalt by addition of antioxidants. Polymer Degradation and Stability 91(4) (2006): 795-804.

[20] Lu, X. and Isacsson, U. Modification of road bitumens with thermoplastic polymers. Polymer Testing (1999): 7786.

[21] Fu, H., Xie, L., Dou, D., Li, L., Yu, M., and Yao, S. Storage stability and compatibility of asphalt binder modified by SBS graft copolymer. Construction and Building Materials 21(7) (2007): 1528-1533.

[22] Masson, J.-F. Brief Review of the Chemistry of Polyphosphoric Acid (PPA) and Bitumen. Energy & Fuels (2008): 2637-2640.

[23] Lesueur, D. The colloidal structure of bitumen: consequences on the rheology and on the mechanisms of bitumen modification. Adv Colloid Interface Sci 145(1-2) (2009): 42-82.

[24] Yao, H., Dai, Q., and You, Z. Molecular dynamics simulation of physicochemical properties of the asphalt model. Fuel 164 (2016): 83-93.

[25] Navarro, F.J., Partal, P., Martínez-Boza, F., and Gallegos, C. Thermo-rheological behaviour and storage stability of ground tire rubber-modified bitumens. Fuel 83(14-15) (2004): 2041-2049.

[26] Read, J. and Whiteoak, D. The Shell Bitumen Handbook. Fifth ed.: Thomas Telford Publishing, 2003.

[27] Masson, J.-F., Price, T., and Collins, P. Dynamics of Bitumen Fractions by Thin-Layer Chromatography/Flame Ionization Detection. Energy & Fuels 15 (2001): 955-960.

[28] Carbognani, L., et al. Monitoring Bitumen Upgrading, Bitumen Recovery, and Characterization of Core Extracts by Hydrocarbon Group-type SARA Analysis. Petroleum Science and Technology 28(6) (2010): 632-645.

[29] Fan, T. and Buckley, J.S. Rapid and Accurate SARA Analysis of Medium Gravity Crude Oils. Energy & Fuels 16 (2002): 1571-1575.

[30] Raki, L., Masson, J.-F., and Collins, P. Rapid Bulk Fractionation of Maltenes into Saturates, Aromatics, and Resins by Flash Chromatography. Energy & Fuels 14 (2000): 160-163.

[31] Akmaz, S., Iscan, O., Gurkaynak, M.A., and Yasar, M. The Structural Characterization of Saturate, Aromatic, Resin, and Asphaltene Fractions of Batiraman Crude Oil. Petroleum Science and Technology 29(2) (2011): 160-171.

[32] Khan, S.A., Sarfraz, S., and Price, D. TLC-FID Calibration and Accurate Weight Determination of SARA Fractions in Heavy Crude Oil. Petroleum Science and Technology 30(23) (2012): 2401-2406.

[33] Groenzin, H. and Mullins, O.C. Asphaltene Molecular Size and Structure. The Journal of Physical Chemistry A 103 (1999): 11237-11245.

[34] Peramanu, S. and Pruden, B.B. Molecular Weight and Specific Gravity Distributions for Athabasca and Cold Lake Bitumens and Their Saturate, Aromatic, Resin, and Asphaltene Fractions. Industrial & Engineering Chemistry Research 38 (1999): 3121-3130.

[35] Paliukaitė, M., Vaitkus, A., and Zofka, A. Evaluation of bitumen fractional composition depending on the crude oil type and production technology. (2014).

[36] Suzuki, T., Itoh, M., Takegami, Y., and Watanabe, Y. Chemical structure of tar-sand bitumens by C and H n.m.r. spectroscopic methods. Fuel 61 (1982): 402-410.

[37] Corbett, L.W. Composition of asphalt based on generic fractionation, using solvent deasphaltening, elution-adsorption chromatography and densimetric characterization. Analytical Chemistry (1969): 576-579.

[38] Lin, J.-R., Lian, H., Sadeghi, K.M., and Yen, T.F. Asphalt colloidal types differentiated by Korcak distribution. Fuel 70 (1991): 1439-1444.

[39] Primio, R.d., Horsfield, B., and Guzman-Vega, M.A. Determining the temperature of petroleum formation from the kinetic properties of petroleum asphaltenes. Nature 406 (2000): 173–176.

[40] Koots, J.A. and Speight, J.G. Relation of petroleum resins to asphaltenes. Fuel 54 (1975): 179-184.

[41] Thanh, N.X., Hsieh, M., and Philp, R.P. Waxes and asphaltenes in crude oils. Organic Geochemistry 30 (1999): 119-132.

[42] Lian, H., Lin, J.-R., and Yen, T.F. Peptization studies of asphaltene and solubility parameter spectra. Fuel 73 (1994): 423-428.

[43] Laux, H., Rahimian, I., and Butz, T. Thermodynamics and mechanism of stabilization and precipitation of petroleum colloids. Fuel Processing Technology 53 (1997): 69-79.

[44] Rogel, E. Studies on asphaltene aggregation via computational chemistry. Colloids and Surfaces 104 (1995): 85-93.

[45] Robinson, H.L. A Rapra Review Report. in *Polymers in Asphalt*. 2004.

[46] Dupont company [Online]. 2016. Available from: http://www.dupont.com/products-and-services/construction-materials/asphalt-paving-systems/articles/modified-asphalt-for-engineers-specifiers.html [2016,November 28]

[47] Kraton Corporation [Online]. 2016. Available from: http://www.kraton.com/products/bitumen.php [2016,November 28]

[48] Sureshkumar, M.S., Filippi, S., Polacco, G., Kazatchkov, I., Stastna, J., and Zanzotto, L. Internal structure and linear viscoelastic properties of EVA/asphalt nanocomposites. European Polymer Journal 46(4) (2010): 621-633.

[49] Luo, W.-q. and Chen, J.-c. Preparation and properties of bitumen modified by EVA graft copolymer. Construction and Building Materials 25(4) (2011): 1830-1835.

[50] Bukowska, M. and Makaruk, L. Investigations on colloidal stability of asphalt-atactic polypropylene compositions. Fuel 67 (1988): 257-263.

[51] Korhonen, M. and Kellomaki, A. Miscibilities of polymers in bitumen and tall oil pitch under different mixing conditions. Fuel 75 (1996): 1727-1732.

[52] Giavarini, C., Filippis, P.D., Santarelli, M.L., and Scarsella, M. Production of stable polypropylene modified bitumens. Fuel 75 (1996): 681-686.

[53] Yeh, P.H., Nien, Y.H., Chen, J.H., Chen, W.C., and Chen, J.S. Thermal and Rheological Properties of Maleated Polypropylene Modified Asphalt. Polymer Engineering and Science (2005): 1152-1158.

[54] Polacco, G., Berlincioni, S., Biondi, D., Stastna, J., and Zanzotto, L. Asphalt modification with different polyethylene-based polymers. European Polymer Journal 41(12) (2005): 2831-2844.

[55] Habib, N.Z., Kamaruddin, I., Napiah, M., and Tan, I.M. Rheological Properties of Polyethylene and Polypropylene Modified Bitumen. International Journal of Civil and Environmental Engineering (2011): 96-100.

[56] Tanaka, Y. Structural characterization of natural polyisoprenes: solve the mystery of natural rubber based on structural study. Rubber Chemistry and Technology (2001): 355-375.

[57] Polymerprocessing.com [Online]. 2001. Available from: http://www.polymerprocessing.com/polymers/NR.html [2016,November 28]

[58] Vichitcholchai, N., Panmai, J., and Na-Ranong, N. Modification of Asphalt Cement by Natural Rubber for Pavement Construction. Rubber Thai Journal (2012): 32-39.

[59] Khadivar, A. and Kavussi, A. Rheological characteristics of SBR and NR polymer modified bitumen emulsions at average pavement temperatures. Construction and Building Materials 47 (2013): 1099-1105.

[60] Yousefi, A.A. Rubber-modified Bitumens. Iranian Polymer Journal 11 (2002): 303-309.

[61] Jeffersonlab [Online]. 2016. Available from: http://education.jlab.org/itselemental/ele016.html [2016,November 28]

[62] Weng, G., Huang, G., Lei, H., Qu, L., Nie, Y., and Wu, J. Crack initiation and evolution in vulcanized natural rubber under high temperature fatigue. Polymer Degradation and Stability 96(12) (2011): 2221-2228.

[63] Ray, S. and Ray, S.K. Separation of organic mixtures by pervaporation using crosslinked rubber membranes. Journal of Membrane Science 270(1-2) (2006): 132-145.

[64] Yadollahi, G. and Sabbagh Mollahosseini, H. Improving the performance of Crumb Rubber bitumen by means of Poly Phosphoric Acid (PPA) and Vestenamer additives. Construction and Building Materials 25(7) (2011): 3108-3116.

[65] Tang, N., Huang, W., Zheng, M., and Hu, J. Investigation of Gilsonite-, polyphosphoric acid- and styrene–butadiene–styrene-modified asphalt binder using

the multiple stress creep and recovery test. Road Materials and Pavement Design (2016): 1-14.

[66] Tayfur, S., Ozen, H., and Aksoy, A. Investigation of rutting performance of asphalt mixtures containing polymer modifiers. Construction and Building Materials 21(2) (2007): 328-337.

[67] Road Science [Online]. 2016. Available from: http://www.roadscience.net/services/distress-guide [2016,November 28]

[68] Isacsson, U. and Zeng, H. Relationships between bitumen chemistry and low temperature behaviour of asphalt. Construction and Building Materials 11 (1997): 83–91.

[69] Jahromi, S.G., Vossough, S., Andalibizade, B., and Smith, B.J. RETRACTED: Fracture mechanism in bitumen, modified bitumen and asphalt mixes. Construction and Building Materials 29 (2012): 142-148.

[70] Moreno, F. and Rubio, M.C. Effect of aggregate nature on the fatigue-cracking behavior of asphalt mixes. Materials & Design 47 (2013): 61-67.

[71] Khan, R., Grenfell, J., Collop, A., Airey, G., and Gregory, H. Moisture damage in asphalt mixtures using the modified SATS test and image analysis. Construction and Building Materials 43 (2013): 165-173.

[72] Petersen, J.C. and Glaser, R. Asphalt Oxidation Mechanisms and the Role of Oxidation Products on Age Hardening Revisited. Road Materials and Pavement Design 12 (2011): 795-819.

[73] de Sá Araujo, M.d.F.A., Lins, V.d.F.C., Pasa, V.M.D., and Leite, L.F.M. Weathering aging of modified asphalt binders. Fuel Processing Technology 115 (2013): 19-25.

[74] Edwards, Y., Tasdemir, Y., and Isacsson, U. Rheological effects of commercial waxes and polyphosphoric acid in bitumen 160/220 – high and medium temperature performance. Construction and Building Materials 21(10) (2007): 1899-1908.

[75] Edwards, Y., Tasdemir, Y., and Isacsson, U. Rheological effects of commercial waxes and polyphosphoric acid in bitumen 160/220—low temperature performance. Fuel 85(7-8) (2006): 989-997.

[76] Filippis, P.D., Giavarini, C., and Scarsella, M. Improving the ageing resistance of straight-run bitumens by addition of phosphorus compounds. Fuel 74 (1995): 836-841.

[77] Bonemazzi, F. and Giavarini, C. Shifting the bitumen structure from sol to gel. Journal of Petroleum Science and Engineering 22 (1999): 17-24.

[78] Chen, J.S. and Huang, C.C. Fundamental characterization of SBS-modified asphalt mixed with sulfur. Journal of Applied Polymer Science 103(5) (2007): 2817-2825.

[79] Dehouche, N., Kaci, M., and Mokhtar, K.A. Influence of thermo-oxidative aging on chemical composition and physical properties of polymer modified bitumens. Construction and Building Materials 26(1) (2012): 350-356.

[80] Fang, C., Yu, R., Liu, S., and Li, Y. Nanomaterials Applied in Asphalt Modification: A Review. Journal of Materials Science & Technology 29(7) (2013): 589-594.

[81] Ghaly, N.F. Effect of Sulfur on the Storage Stability of Tire Rubber Modified Asphalt. World Journal of Chemistry (2008): 42-50.

[82] Liu, J., Yan, K., You, L., Ge, D., and Wang, Z. Laboratory performance of warm mix asphalt binder containing polyphosphoric acid. Construction and Building Materials 106 (2016): 218-227.

[83] Parvez, M.A., Al-Mehthel, M., Wahhab, H.I.A.-A., and Hussein, I.A. Utilization of Sulfur and Crumb Rubber in Asphalt Modification. Journal of Applied Polymer Science (2014).

[84] Zhang, F. and Hu, C. The research for SBS and SBR compound modified asphalts with polyphosphoric acid and sulfur. Construction and Building Materials 43 (2013): 461-468.

[85] Masson, J.-F. and Collins, P. FTIR Study of the Reaction of Polyphosphoric Acid and Model Bitumen Sulfur Compounds. Energy & Fuels (2009): 440-442.

[86] Olabemiwo, O.M., Esan, A.O., Adediran, G.O., and Bakare, H.O. The performance of Agbabu natural bitumen modified with polyphosphoric acid through

fundamental and Fourier transform infrared spectroscopic investigations. Case Studies in Construction Materials 5 (2016): 39-45.

[87] MartÃ-nez-Estrada, A., ChÃ¡vez-Castellanos, A.E., Herrera-Alonso, M., and Herrera-NÃ¡jera, R. Comparative study of the effect of sulfur on the morphology and rheological properties of SB- and SBS-modified asphalt. Journal of Applied Polymer Science 115(6) (2010): 3409-3422.

[88] Wang, C. and Zhang, J. Evaluation of Rutting Parameters of Asphalt Binder Based on Rheological Test. International Journal of Engineering and Technology 6(1) (2014): 30-33.

[89] Noria Corporation, Practicing Oil Analysis March 2002: Fourier Transform Infrared Spectroscopy [Online]. 2016. Available from: http://www.machinerylubrication.com/Read/305/fourier-transform-infrared-spectroscopy [2016,November 26]

APPENDIX

VITA

Mr. Wachira Saowapark was born in Trang, Thailand. He received the Bachelor's Degree of Engineer with a major in Chemical Engineering from the Faculty of Engineering, Prince of Songkla University in 1994 and Master's Degree of Chemical Engineering from the Faculty of Engineering, Chulalongkorn University in 2002.

Some part of this work was selected to oral presentation in the The 22nd Regional Symposium on Chemical Engineering 2015 which was held during September 24-25, 2015 at Novotel Bangkok Suvarnabhumi Airport hotel, Thailand.