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PHYSICAL PROPERTIES OF ASPHALT MODIFIED WITH POLYETHYLENE-*CO*-METHYL ACRYLATE AND ACIDS

Miss Rungnapa Chanathup

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
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By	Miss Rungnapa Chanathup
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Wimonrat Trakarnpruk, Ph.D.

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

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ได้ดัดแปรวัสดุยางมะตอยด้วยการเติมพอลิเอทิลีน-โค-เมทิลอะคลิเลตในปริมาณ 2-8 เปอร์เซ็นต์ โดยน้ำหนักและผสมกับกรดชนิดต่างๆ ได้แก่ กรดพอลิฟอสฟอริก กรดฟอสฟอริก และกรดซิตริก ในปริมาณ 1, 2 และ 3 เปอร์เซ็นต์โดยน้ำหนัก และใช้ภาวะในการผสม คือ 170 องศาเซลเซียส เป็นเวลา 2 ชั่วโมง พบว่า เมื่อเปรียบเทียบสมบัติทางกายภาพของวัสดุยางมะตอยที่ดัดแปรเหล่านี้กับวัสดุยางมะตอยที่ดัดแปลงด้วยสไตรีน-บิวทาไดอีน-สไตรีนในปริมาณ 4 เปอร์เซ็นต์โดยน้ำหนัก ซึ่งใช้เป็นวัสดุอ้างอิง สมบัติทางกายภาพของวัสดุยางมะตอยที่ดัดแปลงด้วยพอลิเอทิลีน-โค-เมทิลอะคลิเลต (4 เปอร์เซ็นต์โดยน้ำหนัก) ได้แก่ ค่าเพนิเทรชัน ค่าจุดอ่อนตัว ค่าดัชนีเพนิเทรชัน และค่าโมดูลัสเชิงซ้อน มีค่าใกล้เคียงกัน และเมื่อเติมกรดพอลิฟอสฟอริก กรดฟอสฟอริก และกรดซิตริก ในปริมาณ 1, 2 และ 3 เปอร์เซ็นต์โดยน้ำหนัก พบว่า ค่าเพนิเทรชัน ค่าความแตกต่างของจุดอ่อนตัว และค่าเสถียรภาพในการจัดเก็บลดลง ซึ่งแสดงถึงความแข็งแรง ความเข้ากันได้ของพอลิเมอร์ และการแยกชั้นระหว่างพอลิเมอร์และยางมะตอยในระหว่างการจัดเก็บลดลง ในขณะที่ค่าจุดอ่อนตัวสูงขึ้น ซึ่งแสดงว่าวัสดุยางมะตอยที่ดัดแปลงมีความไวที่ลดลงต่อการเปลี่ยนแปลงอุณหภูมิ นอกจากนี้ พบว่าค่าความหนืดสูงขึ้น แต่ไม่เกิน 3000 เซ็นติพอยส์ จึงง่ายต่อการผสมก่อนการใช้งาน ค่าความคืนตัวยืดหยุ่น และค่าโมดูลัสเชิงซ้อน พบว่าเพิ่มขึ้น ซึ่งแสดงถึงความสามารถในการต้านการเสียรูปจากการเกิดร่องล้อ และการแตกร้าวเมื่อมีการรับน้ำหนักจากการจราจร การเปลี่ยนแปลงสมบัติทางกายภาพดังกล่าวเป็นผลมาจากปฏิกิริยาระหว่างกรดและวงอะโรมาติกของแอสฟัลทีน ได้แก่ พันธะไฮโดรเจน และแรงไดโพล-ไดโพล มีผลทำให้ขนาดโมเลกุลของแอสฟัลทีนใหญ่ขึ้น ชนิดของกรดมีผลต่างกัน โดยประสิทธิภาพของกรดต่อการปรับปรุงสมบัติวัสดุยางมะตอยด้วยพอลิเอทิลีน-โค-เมทิลอะคลิเลตเป็นไปตามลำดับดังนี้ กรดพอลิฟอสฟอริก > กรดฟอสฟอริก > กรดซิตริก

สาขาวิชา.....ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์.....ลายมือชื่อนิสิต..
ปีการศึกษา.....................2547.....................ลายมือชื่ออาจารย์ที่ปรึกษา...............................

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KEY WORD: ASPHALT, POLYETHYLENE-*CO*-METHYL ACRYLATE

RUNGNAPA CHANATHUP: PHYSICAL PROPERTIES OF ASPHALT MODIFIED WITH POLYETHYLENE-*CO*-METHYL ACRYLATE AND ACIDS. THESIS ADVISOR: ASSOC. PROF. WIMONRAT TRAKARNPRUK, Ph.D., 71 pp. ISBN 974-53-1180-4

Asphalt was modified with polyethylene-*co*-methyacrylate in the range of 2-8 wt% and various kinds of acid: polyphosphoric acid, phosphoric acid and citric acid, in 1, 2 and 3 wt%, using mixing temperature of 170°C for 2 h. It was found that when comparing the physical properties of these modified asphalts with those of asphalt modified with styrene-butadiene-styrene (4 wt%) as reference material, some properties of the asphalt modified with 4 wt% polymer: penetration, softening point, penetration index and complex modulus are similar to those of the reference material. When polyphosphoric acid, phosphoric acid and citric acid was added in the amount of 1, 2 or 3 wt%, penetration value, variation of softening point and storage stability were decreased. These demonstrated the increase in strength and compatibility of the modified asphalts. The separation during storage between polymer and asphalt was decreased. The increase in softening point showed that the modified asphalt was less sensitive to the temperature change. In addition, the dynamic viscosity was found to increase, but not over 3000 centipoise. This makes the material easy to mix for use. The elastic recovery and complex modulus were increased, indicating the resistance in deformation due to the rutting and cracking from traffic loading. The change in physical properties resulted from the interaction between acid and aromatic ring of asphaltene: hydrogen bonding and dipole-dipole interaction. These resulted in the increase in molecular size of asphaltene. Different type of acid has different result. It was found that the efficiency of acid in improving polyethylene-*co*-methyacrylate asphalt's properties are in the order of polyphosphoric acid > phosphoric acid > citric acid.

Field of Study Petrochemistry and Polymer Science Student's signature.
Academic year 2004 Advisor's signature.

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ABBREVIATIONS

ASA	Amine Antistripping Agent
ASTM	American Society for Testing and Materials
CBp	Pyrolytic Carbon Black
C	Degree Celsius
DMA	Dynamic Mechanical Analysis
DSR	Dynamic Shear Rheology
EMA	Polyethylene-co-methyl acrylate
HP-GPC	High Performance Gel Permeation Chromatography
FTIR	Fourier Transform Infrared
HS	Hardening Susceptibility
Min	Minute
NMR	Nuclear Magnetic Resonance
PA	Phosphoric Acid
PE	Polyethylene
PG	Performance Grade
PI	Penetration Index
PP	Polypropylene
PPA	Polyphosphoric acid
SBS	Styrene-butadiene-styrene copolymer

CHAPTER I

INTRODUCTION

Asphalt is a product manufactured or refined from crude oil. These products have been derived from organic materials produced in processes that have spanned several million years in Earth’s history. The application of heat from the earth, biochemical and bacterial processes as well as pressure converted the organic materials into oil. The composition of this crude oil is very dependent on the source. There are approximately 1500 sources of crude in use in the world today from places as far apart as the North Sea, Middle East, South America, Asia, Micronesia and even Australia. Some have significant asphalt fractions, some have very little asphalt fractions. Asphalt is classified into the following three categories, aliphatic, cyclic and aromatic [1].

According to the complicated chemical structure, to determine the efficiency of asphalt from study its chemical property is difficult to perform thus the physical property has been studied instead. Thailand has to spend a lot of money on repairing the road pavement since natural asphalt is very sensitive to temperature and has low ductility property. With these reasons, the road pavements are bleeding, rutting at high temperature and cracking at low temperature which causes the pavement damage in short time. Therefore, for many years researchers have experimented with modified asphalt, mainly for industrial uses for example, adding asbestos, special fillers, mineral fibers, polymer and rubbers in order to enhance the performance of asphalt such as increase the viscosity, softening point, ductility and cohesion while decrease the temperature sensitivity.

Referring to the traditional colloidal approach, asphalt can be divided into three different groups. The first group corresponds to asphalts that behave like Newtonian fluids (viscosity is independent of the shear stress and the elastic effects are negligible); the second group contains asphalts which show elastic effects after the initial stage of deformation; the third group shows almost complete resilience after comparatively slight deformations. The three groups correspond to three colloidal models: sol (viscous), sol–gel (viscoelastic) and gel (elastic), respectively.

Polymers can be grouped into three main categories: thermoplastic elastomers (e.g. SBS copolymers), plastomers (e.g. EVA, and EBA random copolymers) and reactive polymers with maleic anhydride or epoxide function. Previous research reported that it was found difficult to disperse polymer molecule in the asphalt without segregation. For a polymer to be effective, it must be blended with the asphalt to improve resistance at high temperatures without making the asphalt too viscous at mixing temperatures or too brittle at low temperatures. If used in road asphalt, it should be capable of being processed by conventional equipment. In any cases, it must be available and not expensive, and physically and chemically stable during storage, application and service. Major problems are the solubility of polymer in asphalt and the stability of the modified product [2].

The use of polypropylene polymers and copolymers as modifiers for road asphalt appears promising. The problem of stability during storage for long periods at high temperatures can be solved by adding phosphorus compounds, especially polyphosphoric acid, which changes the asphalt structure from sol to gel. The stability of polymer-modified asphalts depends not only on the difference in density and viscosity between asphalt and polymer but also on asphalt structure.[2,3] It was also found that other types of acid such as maleic anhydride, succinic anhydride and dicarboxylic acids at low levels (< 0.1 M) are able to modify the viscoelastic properties of asphalts. The complex modulus, loss and storage modulus are increased as di-acid chain length increases [1].

This research aims to study the physical and rheological property of the modified asphalt using polyethylene-*co*-methyl acrylate and some of acids to study its compatibility and storage stability. The reason of choosing polyethylene-*co*-methyl acrylate is due to it is thermoplastic polymer which can withstand high temperature up to 350°C in addition to low cost [3]. Citric acid, phosphorus acid and polyphosphoric acid are chosen as the additive because of their ability in the oxidation reaction.

Objectives

1. To study the physical property and rheological characteristics of modified asphalt using polyethylene-*co*-methyl acrylate and acid.
2. To study the improvement of storage stability.

Scope of the investigation

The necessary procedures to achieve the goal are as follows:

1. Literature survey and in-depth study for this research work.
2. Design and preparation of apparatus and chemicals.
3. Mixing of asphalt with polyethylene-*co*-methyl acrylate, polyphosphoric acid, phosphoric acid and citric acid.
4. Testing of physical properties such as:
    - penetration
    - penetration index
    - softening point
    - elastic recovery
    - ductility
    - viscosity
    - weight loss
    - complex modulus
    - storage stability
5. Summarizing, discussing the results and writing the thesis.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Asphalt

2.1.1 Basic asphalt chemistry [1]

Asphalt composition is made up of polar and non-polar compounds in complex association. The asphalt structure and mechanical properties are determined by using the interaction of polar compounds. The chemistry of the asphalt produced depends on two main parameters, the crude source and the manufacturing process. The crude source is most influential for processes that involve no chemical modification of the final asphalt blend. In such systems the asphalt may be optimized for properties but not improved on. For systems where a chemical modification of the asphalt can be carried out or components from other feed sources can be introduced, an unsatisfactory asphalt may be made satisfactory. Asphalt can be conveniently viewed on two levels, molecular and intermolecular. The molecular level is important to determine the potential for structure formation and the inter-molecular level for the types of structuring that exist.

2.1.2 Elemental and molecular composition

Asphalts do contain trace amounts of metals, mainly vanadium and nickel. Table. 2.1 shows element composition of asphalts from several places.

Table 2.1 Elemental analysis of asphalt

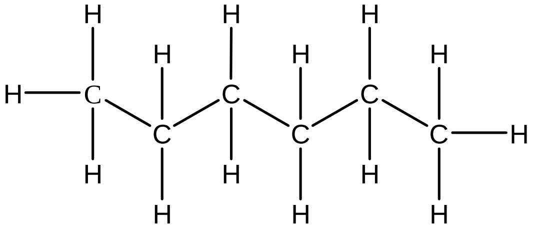
Element (wt%)	Mexican	Arkansas	Boscan	Calif
Carbon	88.77	85.78	82.9	86.77
Hydrogen	9.91	10.19	10.45	10.94
Nitrogen	0.28	0.26	0.78	1.10
Sulphur	5.25	3.41	5.43	0.99
Oxygen	0.77	0.36	0.29	0.20
Vanadium	180ppm	7ppm	1380ppm	4ppm
Nickel	22ppm	0.4ppm	109ppm	6ppm

Although all asphalts are predominantly carbon and hydrogen, most of the molecules contain at least one hetero (S, N, 0) atom. The hetero atoms are often present in sufficient amounts such that on average every molecule has one. These may be in the rings, in non ring components or as functional groups attached to compounds. These together with polar aromatic rings contribute polarity.

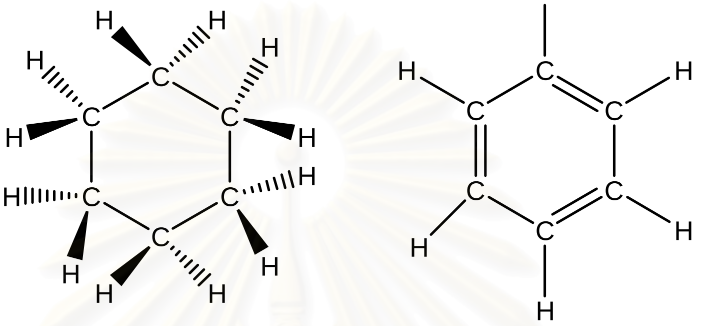
It is the arrangement of different elements or atoms into molecules that determines the interactions of these molecules and hence the physical properties. Because the hetero atoms often impart functionality and polarity they have a disproportionate effect on the properties. This includes effects such as aging, the more reactive the hetero atoms age faster.

The organic origin ensures a wide range of different molecules. These may be classified into the following three categories:

1. aliphatics
2. cyclics
3. aromatics



Aliphatic
(Hexane, C_6H_{14})



Cyclic
(Cyclohexane, C_6H_{12})

Aromatic
(Benzene, C_6H_6)

Fig.2.1 General type of molecules in asphalt.

These types of molecules, combined with the presence of hetero atoms determine the molecular interactions and hence the asphalt's properties. Carbon in aromatic ring systems is about 25-35 of the total carbon. The aromatic carbons are incorporated in condensed ring systems containing 1-10 rings. These ring systems may be associated with napthenic (saturated) ring systems and they both may have attachments of various branched and linear hydrocarbons. Carbon associated with napthenic ring systems are of the order of 15-30 of total carbon.

Non aromatic or napthenic hydrocarbons are present alone or as side branches (as above) and account for 35-60 of the carbon content. Other structures are present in different asphalts. The types of interactions available are: (see figure 2.2) pi- pi bonding (stacks of aromatic rings) polar or hydrogen bonding (polar interactions of hetero atoms) Van Der Waals forces (interactions due to aliphatic chains intertwining).

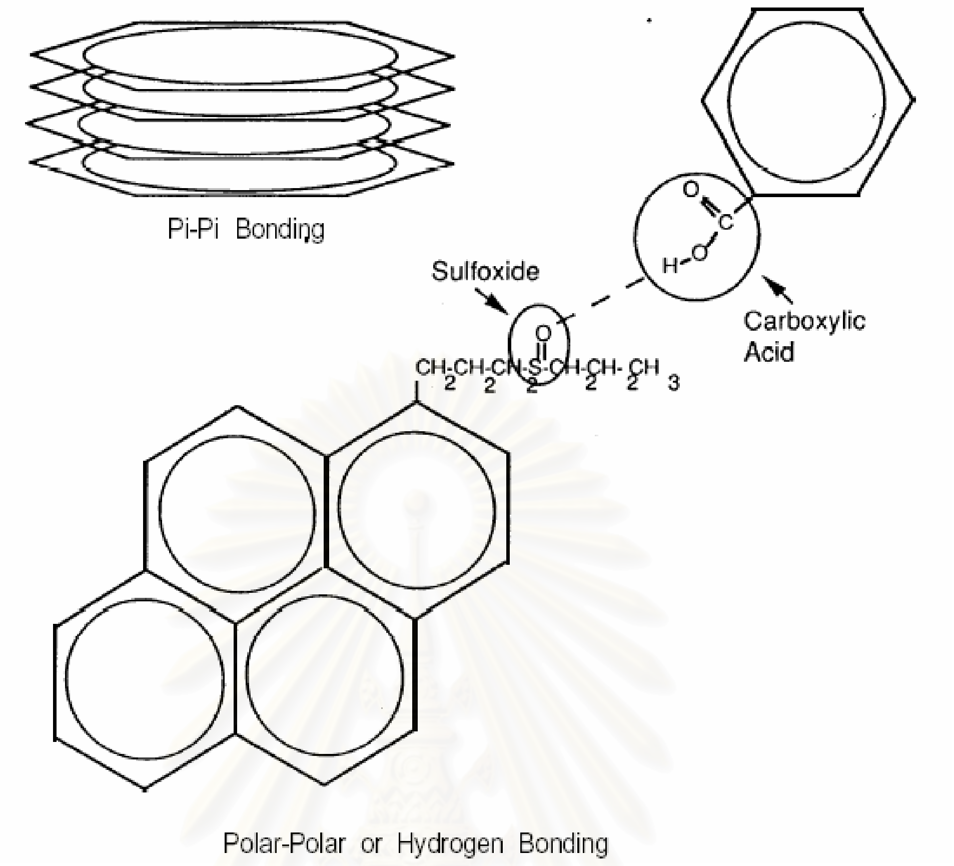


Fig. 2.2 Types of bonding in asphalt.

2.1.3 Asphalt Characterization [1]

2.1.3.1 Simple fractionation

Asphalts can be classified most simply as two major fractions, maltenes and asphaltenes.

Asphaltenes

Asphaltenes consist of highly condensed planar and heteroatom polar groups. The fraction is defined as the proportion of material precipitated when a straight chain alkane is added to the asphalt. They need not be high molecular weight but are the most polar of the fractions. It has been found that the asphaltenes are agglomerations of the most polar molecules in the asphalt and as such can only be dissociated from one another by dilution or some energy source such as heat or ion emission. When molecular weight is determined by field ionization mass spectroscopy of this fraction, the levels found are much lower than those traditionally recorded. This indicates that the asphaltenes are not large molecules but highly interactive polar molecules. The polarity of the asphaltene component is derived by the presence of hetero-atoms (S, 0, N). These are functionalized and the functional groups are the polar groups.

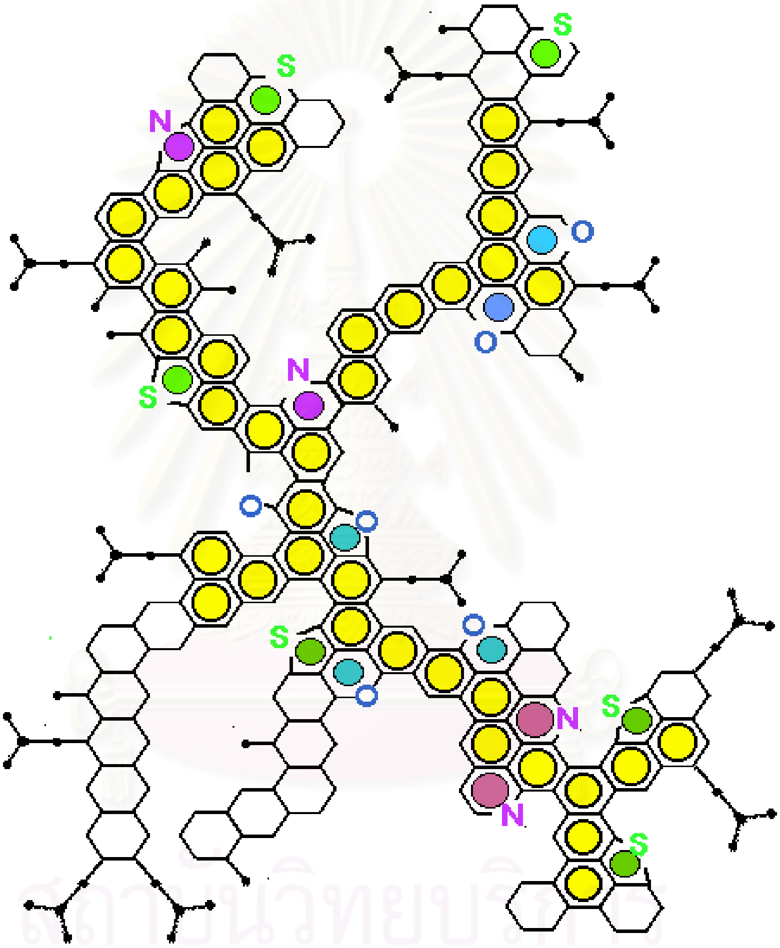


Fig.2.3 Molecular structure of asphaltene proposed for Maya crude (Mexico) by Altamirano, et al. [IMP Bulletin, 1986]

Maltenes

This is the remained portion of the asphalt. It consists of two fractions, oils and resins. Oils consist of n-, iso- and cyclo- paraffins and condensed napthenes with some alkyl aromatics. The aromatic portion is mostly naptho-aromatic hydrocarbons with three or four napthenic rings per molecule. The fraction is non-polar.

Resins are chemically very similar to the asphaltenes. That is they are a transition from oils to asphaltenes. The resins consist of mainly polycyclic molecules containing saturated aromatic and hetero-aromatic rings and hetero atoms in various functional groups, the resins are not as polar as the asphaltenes and hence are not as interactive.

2.1.3.2 Complex fractionations [4]

The fractionation techniques used in the last 50 years are:

Adsorption/ desorption
Chemical precipitation
Partitioning with partial solvents
Chemical reactivity
HPLC
GPC
Clay/ Gel

All of the fractionation techniques separate out the influential fractions in asphalt structuring and the compatibility of solvent type effects of the oil or neutral phases.

2.1.3.3 SHRP Fractionation

The Strategic Highway Research Program (SHRP) on fractionation of asphalts has refined the above concepts to separate out two important fractions, a solvent (oils) fraction and an associated fraction (asphaltenes / resins, polar materials). Size Exclusion Chromatography is the first step in fractionation. This is carried out in simple glassware columns packed with swollen beads. The pore structure of the gel beads determines the rate of flow through the column. The solvent phase flows straight through and the associated phase is slowed. The two fractions derived from this method are termed SEC I and SEC II.

The SEC I fraction is an associated phase, consisted of asphaltenes, resins which are polar materials. This phase gives the viscoelastic properties of asphalt. Viscoelastic properties can be observed by measurement of tan delta (ratio of viscous to elastic modulus). Gel type asphalts (elastic) thus have low values of tan delta and sol type asphalts (viscous) have high values of tan delta. In field terms a high SEC I fraction means greater structure, less thermal susceptibility and better performance at high temperatures.

The SEC II is the oil fractions in which the associated phases are dispersed. The better this fraction is as a solvent so it can give the less brittle of the asphalt.

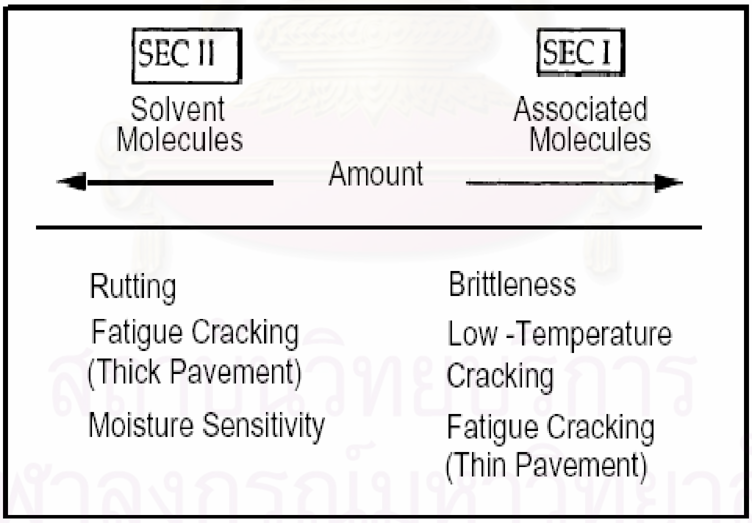


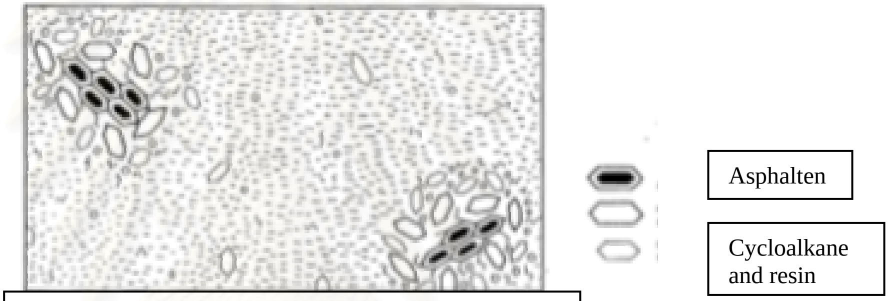
Fig. 2.4 Relationship of molecule type to asphalt performance.

2.1.4 Asphalt models

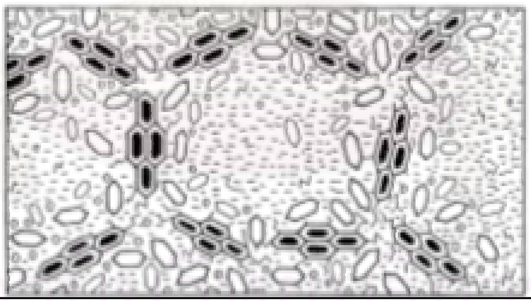
Asphalt models used to discuss the mechanical properties and physical behavior of asphalt in relation to different fractions are colloidal model and microstructure model.

2.1.4.1 Colloidal model

This is the traditional model where solid asphaltene particles are dispersed in the maltenes fraction. The asphaltene is the center of a micelle and these are peptized by the polar aromatic fractions absorbed from the maltenes. A sol type asphalt has the asphaltenes fully dispersed. In a gel type the micelles are not fully dispersed. Sol asphalts are Newtonian, gel asphalts are non-Newtonian. Real asphalts exhibit some character of both sol and gel. Generally most asphalts are Newtonian at temperatures higher than 60°C, at lower temperatures they exhibit non-Newtonian behaviour. The colloidal model is inadequate to explain the flow and elastic properties of asphalt under these conditions of setting.



Schemetic representation of “Sol” type bitumen



Schemetic representation of “Gel” type bitumen

Fig. 2.5 Colloidal model. [5]

2.1.4.2 Microstructural model

In this model (see Fig.2.6) asphalt is a continuum of polar and non- polar material i.e. a homogeneous, self compatible mixture consisting of a variety of molecular species that are mutually dissolved or dispersed. This creates areas of order or structure depending on the concentrations of polar material. The only differential between asphaltenes and resins is in polarity and thus the degree of potential associations. Thus structuring depends as much on asphaltene chemistry as concentration.

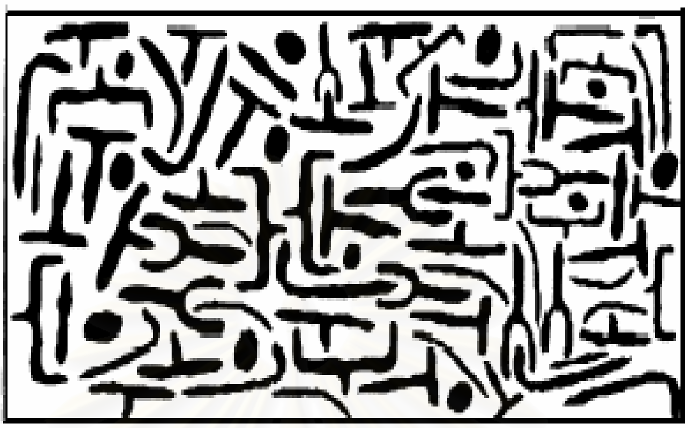


Fig.2.6 Microstructural model

2.2 The modification of asphalt [5]

In the last thirty years many researchers have looked at a wide spectrum of modifying materials for asphalts used in road construction. Table 1 details the majority of asphalt modifiers and additives that have been examined. For the modifier to be effective and for its use to be both practicable and economic, it must:

- be readily available.
- resist degradation at asphalt mixing temperatures.
- blend with asphalt.
- improve resistance to flow at high road temperatures without making the asphalt too viscous at mixing and laying temperatures or too stiff or brittle at low road temperatures.
- be cost effective.

The modifier, when blended with asphalt, should:

- maintain its premium properties during storage, application and in service.
- be capable of being processed by conventional equipment.
- be physically and chemically stable during storage, application and in service.
- achieve a coating or spraying viscosity at normal application temperatures.

Table 2.2 Some additives used to modify asphalt

Type of modifier	Example
Thermoplastic elastomers	Styrene–butadiene–styrene (SBS)
	Styrene–butadiene–rubber (SBR)
	Styrene–isoprene–styrene (SIS)
	Styrene–ethylene–butadiene–styrene (SEBS)
	Ethylene–propylene–diene terpolymer (EPDM)
	Isobutene–isoprene copolymer (IIR)
	Natural rubber
	Crumb tyre rubber
	Polybutadiene (PBD)
	Polyisoprene
Thermoplastic polymers	Ethylene vinyl acetate (EVA)
	Ethylene methyl acrylate (EMA)
	Ethylene butyl acrylate (EBA)
	Atactic polypropylene (APP)
	Polyethylene (PE)
	Polypropylene (PP)
	Polyvinyl chloride (PVC)
	Polystyrene (PS)
Thermosetting polymers	Epoxy resin
	Polyurethane resin
	Acrylic resin
	Phenolic resin
Chemical modifiers	Organo-metallic compounds
	Sulphur
	Lignin
Fibres	Cellulose
	Alumino-magnesium silicate
	Glass fibre

Table 2.2 (continued) Some additives used to modify asphalt

Type of modifier	Example
	Polyester
	Polypropylene
Adhesion improvers	Organic amines
	Amides
Antioxidants	Amines
	Phenols
	Organo-zinc/organo-lead compounds
Natural asphalts	Trinidad Lake Asphalt (TLA)
	Gilsonite
	Rock asphalt
Fillers	Carbon black
	Hydrated lime
	Lime
	Fly ash

As the asphalt is responsible for the visco-elastic behaviour characteristic of asphalt, it plays a large part in determining many aspects of road performance, particularly resistance to permanent deformation and cracking. In general, the proportion of any induced strain in asphalt that is attributable to viscous flow, i.e. non-recoverable, increases with both loading time and temperature. The effect of this is illustrated in Figs. 2.7(a) and (b). Figure 2.7(a) shows the response of an asphalt sample in a simple creep test. The strain resulting from the applied loading shows an instantaneous elastic response followed by a gradual increase in strain with time until the load is removed. The change in strain with time is caused by the viscous behaviour of the material. On removal of the load, the elastic strain is recovered instantaneously and some additional recovery occurs with time. This is known as ‘delayed elasticity’. Ultimately, a permanent residual strain remains, which is irrecoverable and is directly caused by viscous behaviour.

The response to a load pulse induced in an element of an asphalt due to moving traffic loads is shown in Fig. 2.7(b). Here it is not possible to distinguish between the two components of elastic response but the small permanent strain and larger elastic strain are shown. Although the permanent strain illustrated in Fig. 2.7(b) is small for a single pulse load, when many millions of load applications are applied to a pavement, a large accumulation will develop. It is this component that results in surface deformation. From the above, it is clear why more deformation occurs at high ambient temperatures and where traffic is slow moving or stationary.

One of the prime roles of an asphalt modifier is to increase the resistance of the asphalt to permanent deformation at high road temperatures without adversely affecting the properties of the asphalt at other temperatures. This is achieved by one of two methods, both of which result in a reduction in permanent strain. The first approach is to stiffen the asphalt so that the total visco-elastic response of the asphalt is reduced. The second option is to increase the elastic component of the asphalt thereby reducing the viscous component.

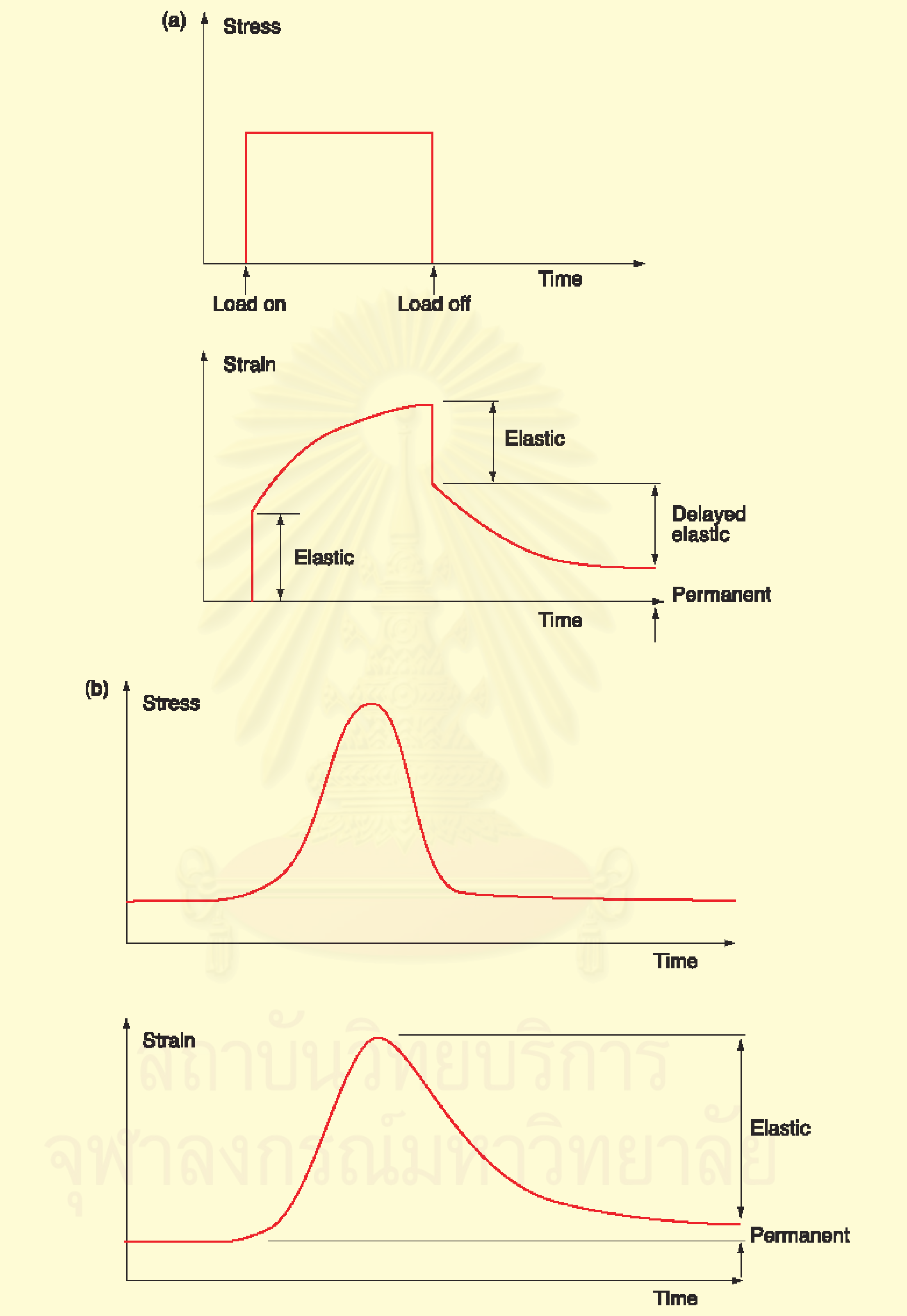
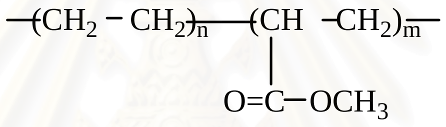


Fig. 2.7 Visco-elastic responses of an asphalt under (a) a static load and (b) a moving wheel load.

2.3 Ethylene-*co*-methyl acrylate

Ethylene-*co*-methyl acrylate copolymers (Fig. 2.8) show significantly better thermal and processing stability; they offer a number of technical advantages such as compatibility with a variety of engineering thermoplastics, including polyamides (PA), polyesters (PET, PBT), ABS and polycarbonate; and most importantly, they are highly cost-effective, being in an economic price range which yields better margins for processors and compounders. With the copolymers, compounders and processors can attain a moderate level of toughening and impact modification of engineering polymers at relatively low addition levels, thus ensuring that the base materials' processability does not suffer. The new copolymers are general-purpose tougheners, for use where a moderate level of modification is wanted.



$$-\left(CH_2-CH_2\right)_n-\left(\underset{\substack{| \\ O=C-OCH_3}}{CH}-CH_2\right)_m-$$

Fig. 2.8 Chemical structure of ethylene-*co*-methyl acrylate

2.3.1 Main features

Thermal stability

The copolymer resins have a substantially higher heat resistance than EVAs and other polar copolymers, whose lower thermal tolerance is often a major handicap when they serve as impact modifiers or as carrier resins for masterbatches. EVA, for example, starts to degrade around 220°C, whereas the EMAs remain stable up to 350°C in air, and EEAs are stable over 400°C in a nitrogen atmosphere. Fig.2.8 shows TGA curves (100% to 95% weight loss in air and N_2) for selected ethylene acrylate copolymers and an EVA resin for comparison.

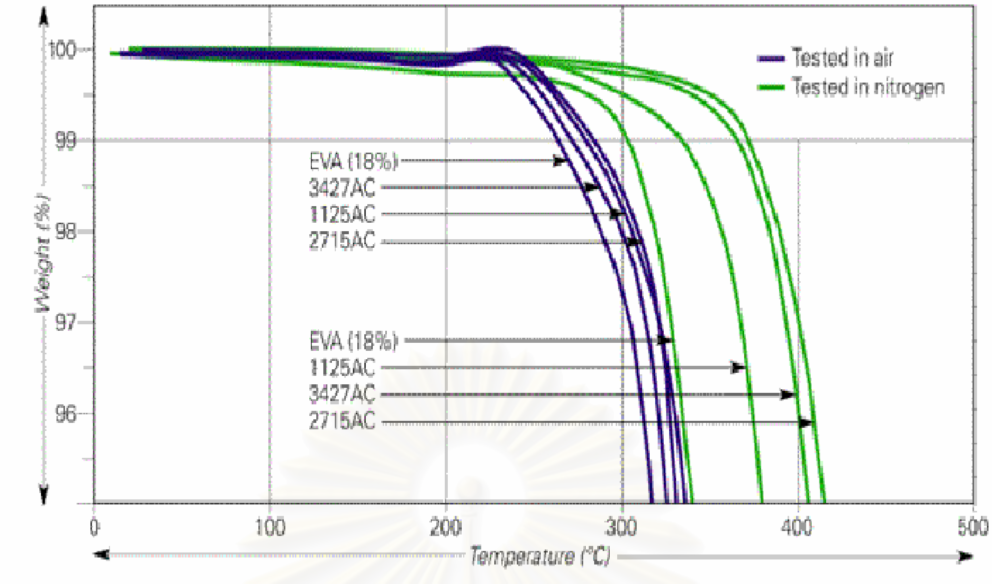


Fig.2.9 TGA curves (100% to 95% weight loss in air and N_2) for selected copolymers and an EVA resin for comparison.

High polarity

As a result of their high polarity, these copolymers are not only compatible with polyolefins, such as PP and PE, but also with a broad range of engineering plastics, including PA, PBT, PET and ABS.

Table 2.3 shows the general properties of ethylene-*co*-methyl acrylate. These properties are used as quality control in the manufacturing.

Table 2.3 Typical property data of ethylene-*co*-methyl acrylate

Property	**Typical Value**	**Units**	**Test Method**
MA-content	20	%	DuPont Method
Melt Flow Rate	190°C/2.16 kg	8.0 g/10 min	ISO 1133 / ASTM D1238
Density	942	kg/m^3	ISO 1183 / ASTM D792
Melting point by DSC	92	°C	ISO 3146 / ASTM D3418
Hardness, Shore A / D	87 / 28	–	ISO 868 / ASTM D2240
Tensile strength (500 mm/min)	11	MPa	ISO 527-2 / ASTM D638
Elongation at break (500 mm/min)	780	%	ISO 527-2 / ASTM D638
Tensile modulus (1 mm/min)	35	MPa	ISO 527-2 / ASTM D638

2.4 Acid chemistry for asphalt modification [6]

2.4.1 Introduction

Acid-base reactions follow predictable physical laws as defined by calculations for pH or pK. When a strong acid reacts with a strong base, the expected products are an ionic salt and water. One of the more compelling acid/base issues within Superpave is the question of whether modifiers used to make PG-graded binders will chemically react with an amine antistripping agent (ASA) added at the hot mix plant. If a reaction does occur, three potential problems could reduce performance of the mix. First, neutralization of an acid modifier might reduce the high temperature PG grade, reducing rutting resistance. Secondly, neutralization of the amine blocks the nitrogen electron pair, possibly impacting its antistripping ability. Finally, what effect might the resulting product salts have on mixture behavior, particularly with regard to moisture permeability or even emulsification of the asphalt in the presence of water, heat and repeated mechanical loading.

2.4.2 Natural acids in asphalt

Organic acids are found in most naturally occurring petroleum crudes, but their functionality and concentrations vary markedly. Asphalts distilled from heavy Venezuelan crudes frequently exhibit acid numbers of three or higher, whereas heavy crudes from the Middle East might have bitumen acid numbers below 0.5. During the oxidative aging process, significant amounts of sulfoxides and carboxylic acids are formed. The carboxylic acids are slightly water soluble, highly polar, and therefore tend to be the first molecules displaced from the aggregate surface when moisture is present.

2.4.3 Desalting-neutralizing natural acids with bases in the refining process

Refinery distillation towers operate at high temperatures, so corrosion is a serious problem. Processing acidic crudes requires expensive corrosion-resistant metallurgy in the column internals.

Another common alternative is to neutralize the crude with a strong base, such as sodium hydroxide or lime. The resulting water-soluble salts are then removed in a desalting unit before distillation. If the organic salts are not removed by desalting, these very polar molecules will not distill, and so remain in the asphalt. Salts from neutralization with sodium hydroxide are particularly notorious for causing stripping problems in asphalt mixes. This should not be surprising, since sodium salts are highly soluble in water, much more so than calcium salts if lime is used for neutralization. Hence, lime has become the neutralizing base of choice for many refiners.

2.4.4 Natural bases in asphalt

Asphalt also contains varying quantities of weak bases. Typical basic functionality includes indoles and quinolones. The basic compounds, when interacting through polar associations with their acidic counterparts, tend to form the molecular associations (asphaltenes) that are so important to the rheology of asphalt cement.

Amphoteric molecules (containing both acid and base functionality on the same molecule) could impact high temperature rheology in a manner far beyond what might be expected from their modest molecular weights [4].

2.4.5 Evaluating acid-base chemistry in asphalt

There are many tools available to qualitatively and quantitatively study acids and bases in asphalt. They are: non-aqueous titrations, fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), high performance gel permeation chromatography (HP-GPC), and ion exchange chromatography were then used to further characterize chemical functionality.

Lewis acids such as phosphorous pentoxide or ferric chloride have long been used as catalysts for air oxidation of roofing asphalts to assure the desired relationships between penetration and softening point. It has been known for some time that certain acids will harden asphalt. For example, asphalt rheology can be modified by bubbling hydrogen chloride gas through the bitumen, or by adding an aqueous acidic solution and then boiling off the water. The stiffening effect depends upon the amount of nitrogen bases 'available for conversion to hydrochloride salts or polymers [7].

2.4.6 Irreversible reactions

Certain strong acids irreversibly react with asphalt molecules. By adding sulfuric acid to asphalt in three different concentrations, asphalt is separated into acidic and basic components classified as pentane-asphaltenes, nitrogen bases that contained the nitrogen electron pair. It is also important to note that the organic sulfonates formed at each step in the sequential reactions are soluble and extracted into water. Such affinity for water would leave sulfonated asphalt very sensitive to moisture damage if the sulfonate salt remained in the mix [8].

2.4.7 Reversible reactions

Phosphoric acid (H_3P0_4) for modification of paving grade asphalts have been in force since the early 70th century. More recent patents on asphalt technology describe the use of acids in combination with polymers and other modifiers [9, 10, 11]. Although synthetic chemistry books describe irreversible reactions between phosphoric acid and aromatic rings, the chemistry of phosphoric acid in asphalt appears to be confined to reversible polar associations. Fig. 2.10 shows the interaction between polyphosphoric acids and polar molecule of asphaltene, two reactions occurred, esterification and acid base neutralisation.

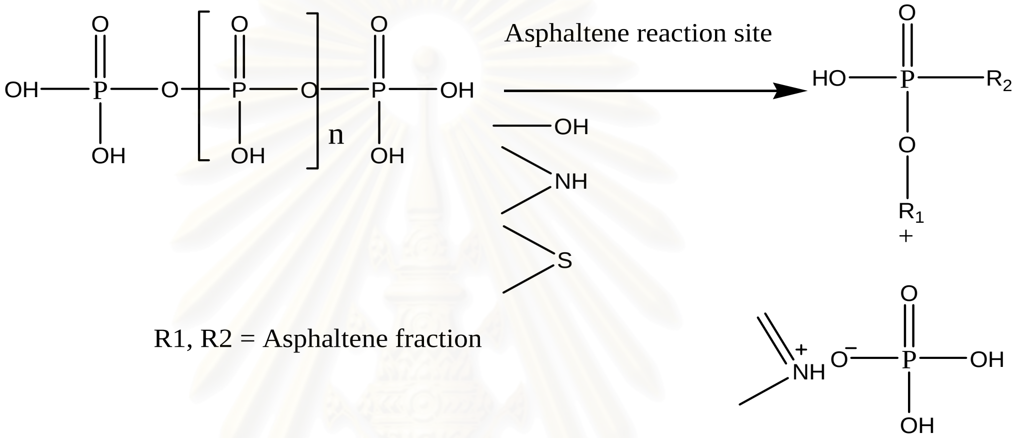


Fig. 2.10 Proposed reactions between polyphosphoric acid and asphaltene [12].

2.5 Literature reviews

Filippis *et al.* [13] studied the ageing resistance of asphalt by addition of phosphorous compounds such as phosphoric acid and polyphosphoric pentaoxide acid. The condition of mixing was about 200°C for 1 hour. It was found that the addition of phosphorus compound in the quantity of 1-5% by weight increased the softening point, viscosity and penetration index while penetration value decreased. The ageing resistance was improving when compared with that of the natural asphalt. The addition of phosphorus compound also affected to the chemical structure of asphalt, which being responsible for an increase in the average molecular weight and asphaltene content.

Giavarini *et al.* [14] studied the stability during storage of polypropylene and polyphosphoric acid-modified asphalt. The mixing condition was about 180°C. The acid (1-5% by weight) was then added and the mixture was stirred for 1 hour. After that, 2-10% by weight of polypropylene was added to the acid-treated asphalt, and then stirred again for an additional hour. The asphalt which was treated by 2% by weight of polypropylene and added 3% by weight of polyphosphoric acid resulted in reducing the segregation between the asphalt and polymers, examined from the difference of softening point between the upper and lower parts of the asphalt, the higher softening point, the lower penetration value with an increase in the penetration index. In addition, the adding of acid into asphalt also decreased phase angle while elasticity property increased.

Herrington *et al.* [7] studied the rheological property of asphalt modified with maleic anhydride compound, octadecanedioic acid ($HOOC(CH_2)_6COOH$), and carboxylic acid: maleic anhydride, glutaric acid ($HOOC(CH_2)_3COOH$) and decanoic acid ($CH_3(CH_2)_{10}COOH$) with the concentration less than 0.1 M. The reaction was carried out at 120-150°C for 1 hour. It was found complex modulus was increased and phase angle was decreased. Asphalt samples compounded with mono-carboxylic acid showed complex modulus lower than those with dicarboxylic acid. Acid containing longer chain showed lower complex modulus than that with shorter linkage.

Bonemazzi *et al*. [15] studied the structure change from viscous material to elastic material of the asphalt blended with olefinic copolymer and polyphosphoric acid. The reaction was carried out at 180°C for 1 hour. From the experiment it was shown that addition of 3% polyphosphoric acid into the asphalt without the addition of the copolymer, induced in 30°C increase of softening point, 80-100 unit decrease in penetration value. Penetration value is reported as the depth of the needle passing through the asphalt, where 1 unit is equal to 0.1 mm. Furthermore, the penetration index also increased from 0.8 to 4. The higher penetration index indicated the higher elastic property of the asphalt. In addition, when adding 3% polyphosphoric acid into the asphalt blended with 2% copolymer, it had the same effect on the softening point and penetration value as when adding 5% copolymer into the untreated asphalt.

Lu *et al.* [16] studied the rheology property and morphology of the polymer modified asphalts. The tested thermoplastic polymers are styrene-butadiene-styrene, styrene-ethylene-butylene-styrene, ethylene vinyl acetate and ethylene butyl acrylate in the amount of 3, 6 and 9%. Mixing was carried out at 180°C for 2 hours. The morphology of the modified binder was studied using fluorescence microscopy. The result indicated that 3% polymers were spread homogeneously in an asphalt phase while the mixtures containing higher polymer content (> 6%) were not homogeneous. It was found that polymer contents in the range of 3-9% resulted in almost the same complex modulus result which performed at 40°C to 130°C. At a given polymer content, the modified binders containing styrene-butadiene-styrene differ widely in their complex modulus from those containing ethylene vinyl acetate. Moreover, polymer modification increases the complex modulus and decreases the phase angle of asphalts.

Navarro *et al.* [17] studied the rheological characteristics of the modified asphalt by using ground tire rubber and styrene- butadiene-styrene. The mixing condition was at 180°C for 1.5 hours. From the study of storage modulus and loss modulus at -10°C and 75°C , it was found that the modified asphalt showed linear increase of both values at high temperature (75°C) and a decrease at low temperature (-10°C). In addition, 9% styrene-butadiene-styrene modified asphalt showed similar viscoelastic property to 3% polymer-modified asphalt.

Airey *et al.* [18] studied morphological, thermal and fundamental rheological characteristics of asphalt modified with ethylene vinyl acetate copolymer 3, 5 and 7% by weight. The reaction carried out at 170-185°C. It was found that the softening point raised from 48°C to 55°C, 61°C and 69°C, respectively. The penetration index increased from -1 to 0.08, 0.86 and 2.0 respectively. The ductility at 10°C decreased from 21 centimeters to 13, 8 and 5 centimeters, respectively. The viscosity are also increased. The complex modulus, deformation resistance ($G^*_{PMB}/G^*_{Asphalt}$) and the ductility was proportional to the amount of ethylene vinyl acetate.

Filippis *et al.* [2] studied the method to distinguish thermally cracked asphalt (VB) from straight-run distillation (SR) asphalt which are different on chemistry and structure. The asphaltene/resin ratio and basic/acid group of VB products are higher than SR products, when adding polyphosphoric acid into VB and SR. The mixing was performed at 100-400^{0}C until the sample was sufficiently fluid, two or three drops of H_3PO_4 was added and stirred for 2 min, the sample was kept at 120^{0}C for 3 min. The sample was dropped to a glass slide which can be absorbed under a microscope by transmitted light. It was found the formation insoluble material only when treating with VB, on the other hand SR no formation of visible insoluble material.

Chaala *et al.* [3] studied the rheological properties of asphalt modified with pyrolytic carbon black (CBp), a by product of scrap tyre pyrolysis, in amount of 5 to 30 % by weight The asphalt was heated to 100-110^{0}C before the CBp was added. Stirring was maintained until a homogenous mix was obtained. It was found that the temperature susceptibility of the asphalt is reduced and the storage modulus(G’) and loss modulus (G”) increase significantly for the mixture with 30 wt% of CBp. It was also found that softening point, penetration and viscosity are improved. The softening point increases with concentration of CBp, which makes penetrability of the sample decreases.

Lu *et al.* [19] studied the aging properties of styrene butadiene styrene (SBS) polymer modified asphalt, in amount of 3, 6 and 9% of SBS. The aging test of these materials was performed using the Thin Film Oven Test (TFOT). The sample was kept in an oven at 163^{0}C for 5 hours. After that, it were evaluated by using Dynamic Mechanical Analysis (DMA), Gel Permeation Chromatography (GPC) and Fourier Transform Infrared (FTIR) spectroscopy. The GPC analysis showed that the molecular weight of the SBS was decreased but increase of asphaltene content and bitumen molecular weight. Aging causes oxidation of bitumen which was indicated by FTIR analysis. The FTIR shows increasing of carbonyl and sulfoxides. The sulfoxide formation of the SBS polymer decreased, complex modulus was increased and phase angle was reduced through aging.

Yousefi *et al.* [20] studied the effects evaluation of the pyrolytic oil (H 18) on the properties of recycled polyethylene (RPE) modified asphalt. 1% RPE was mixed with 10% ethylene-polypropylne-diene-monomer (EPDM) and with plastomer

EXACT^{TM} 4041. In the first step, RPE and the modifiers were mixed at 180^0C and 60 rpm for 10 min, In the second step, the pyrolytic oil was added from 0-10% to the asphalt, the RPE and the modifiers in the first step and asphalt mixture in the second step were mixed at 160^0C for 2 hours. The rheological behaviors dynamic viscosity and dynamic complex modulus were almost the same. It was found that EPDM modified sample showed lower viscosity and modulus than other polymer modified asphalt. Addition of pyrolytic oil at 5 or 10% affects the rheological properties, resulting in an increase of viscosity and modulus in the low frequency region and an increase in the penetration.

Chipps *et al.* [21] studied a model for oxidative aging of rubber modified asphalt. The hardening susceptibility (HS) is the ratio of viscosity increase to FITR carbonyl growth. Low-cure blends were produced by mixing for 1 h at 500 rpm and 177^0C, long-term intermediate-cure blends were mixed for 12 h at 500 rpm and 191^0C and high-cure blends were blended for 6.5 hours at 4000 rpm at 232^0C. It was found that the low cure blends have low hardening rate, hardening susceptibility was decreased with increasing rubber content. Long-term blends showed no viscosity decrease during curing. It was also found that the hardening rate of high-cure blends decrease with increasing the rubber content. The hardening susceptibility of the high-cure material is lower than that of the long-term blends.

Gonzalez *et al.* [22] studied the rheological property of asphalt modified with 5% high density polyethylene, HDPE (Mw = 171500, Mw/Mn = 7.7 and density = 0.956 g/cm^3); low density polyethylene, LDPE (density = 0.924 g/cm^3); EPDM (Mw = 330000, Mw/Mn = 2.06, ethylene/propylene/ethylene norbornene ratio of 54/42/4) and their respective blend of EDPM with HDPE and LDPE in a 25 EDPM/ 75 HDPE , 25 EDPM/ 75 LDPE were mixed by using a twin screw at a rotating speed 50 rpm, 160^0C. The mixing condition of polymer and asphalt was at 180^0C and 1200 rpm for 6 hours. It was found from dynamic viscoelastic results that storage modulus and complex viscosity are enhanced when polymer is added, HDPE and HDPE/EPDM blends are the most effective. The storage modulus (G') loss modulus and complex viscosity decrease in the following order: HDPE/asphalt > HDPE-EPDM/asphalt > LDPE-EPDM/asphalt > EPDM/asphalt > LDPE/asphalt.

Kamiya *et al.* [23] studied compatibility role of styren-butadiene-styrene triblock copolymer in asphalt. The experimental results from DSC measurement indicated that maltene, the soluble fraction extracted from asphalt n-heptane, interacted preferentially with the polybutadiene unit (PB) of SBS, whereas asphaltene, insoluble fraction, predominated with the polystyrene (PS) unit. The components of asphaltene and maltene partially interacted with specific units of SBS, so that emulsifying effects of SBS resulted in phase inversion. Rheological and mechanical measurements demonstrated that viscosity, penetration and tensile strength of the composite were enhanced even at low SBS concentration (in range of 5-10%).

Lu *et al.* [24] studied the effect of polymer content/structure type on viscosity of styrene-butadiene-styrene (SBS) polymer modified asphalt. Results indicated that SBS polymer was not an inert additive. In addition, an increase in kinematic and dynamic viscosities of the modified asphalts was not directly proportional to polymer content; a marked viscosity increase was observed when the polymer content increased from 3 to 6% by weight of the blend. The base asphalts and modified asphalts containing 3% SBS were observed to be essentially shear rate independent, while those containing 6 or 9% SBS displayed shear-thinning behaviour. Compared to the modified asphalts with linear SBS, the modification with branched SBS demonstrated a higher degree of shear-thinning behaviour. These effects were dependent on ranges of shear rate and temperature.

Lepe *et al.* [25] studied the optimization of the mixing process condition and their influence on the mechanical properties of straight bitumen and modified binders with a number of polymers: high-density polyethylene (HDPE), density polyethylene (LDPE), SBS, ethylene-propylene-diene monomer (EPDM), their mixtures. Polymer addition to bitumen enhances the mechanical properties modified binder, depending on the polymer nature and mixing process. The LDPE/EPDM and HDPE/EPDM-modified binders, prepared in a rotor-stator device, showed a remarkable enhancement of the mechanical properties, as compared to those modified with LDPE, EPDM and SBS. Less promising results were usually obtained with a lab-scale mixer. These results were attributed to a more effective dispersion of the polymer with the rotor-stator device, which would favour the generation of polymer-rich microphase. The interactions among them may become sufficiently strong, yielding a plateau region in the mechanical spectrum. Blends of polyethylene and EPDM showed that the major component in the polymer blend mainly determinates the rheological behaviour of the binder, being the influence on the rheological behaviour of the interactions among the molecules of EPDM and LDPE less important than the interactions among the molecules of EPDM and HDPE.

Champion *et al*. [26] studied the morphology of difference types of the polymer: ethylene methyl acrylate (EMA), ethylene butyle crylate (EBA), ethylene vinyl acetate (EVA) and styrene butadiene styrene (SBS) by using cryo-scanning electron microscopies. The 4 to 6% blends for EMA and EBA-based blends gave the particles size about 2 and 25 µm respectively and 50 µm for SBS-based blend the particle size of SBS dependent on the amount of polystyrene.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Asphalt: Thai Petrochemical Industrial Co., Ltd.
2. Styrene butadiene styrene: Shell Co., Ltd.
3. Ethylene-*co*-methyl acrylate (Methyl acrelate: 20%): DuPont
4. Polyphosphoric acid (MW=258 g/mol) : Merck
5. Phosphoric acid(MW=98 g/mol): Merck
6. Citric acid: Merck

Table 3.1 The physical properties of asphalt

Properties	Results
Penetration at 25°C (0.1 mm)	65
Softening Point (°C)	49
Penetration Index	0.2
Ductility at 13°C before TFOT (cm)	>150
Ductility at 25 °C before TFOT (cm)	>150
Ductility at 13°C after TFOT (cm)	83
Ductility at 25 °C after TFOT (cm)	>150
Brookfield viscosity	
At 135°C, cP	356.5
At 165°C. cP	137.5
Flash point (°C)	336
Test on Residue from TFOT	
Weight loss (%)	0.1
Retained penetration at 25°C (%)	76.2

Table 3.2 The physical and chemical property of styrene butadiene styrene

Property	**Typical Value**	**Units**
Number average molecular weight	135,000	g/mole
Physical state	solid	-
Color	white	-
Density	880-950	kg/m^3
Specific gravity	<1	-

Table 3.3 The physical and chemical property of ethylene-*co*-methyl acrylate

Property	**Typical Value**	**Units**
MA-content	20	%
Melt Flow Rate	190°C/2.16 kg	8.0 g/10 min
Density	942	kg/m^3
Melting point by DSC	92	°C

Table 3.4 The physical and chemical property of polyphosphoric acid

Property	**Typical Value**	**Units**
Molecular weight	258	g/mole
Otho-phosphoric acid	82.5-83.5	%
Polyphosphoric acid	5	%
Density	2030-2060	kg/m^3
Viscosity @ 60°C	1000	mm^2/sec

Table 3.5 The physical and chemical property of phosphoric acid

Property	**Typical Value**	**Units**
Molecular weight	98	g/mole
viscosity@20°C	140	mm^2/sec
Vapor density(Air=1)	3.4	-
Specific gravity	1.685	-
Boiling point	158	°C
Melting point	42.3	°C

Table 3.6 The physical and chemical property of citric acid

Property	**Typical Value**	**Units**
Molecular weight	192	g/mole
Vapor density(Air=1)	<1	-
Specific gravity	1.665	-
Melting point	153	°C

3.2 Instruments and apparatus

1. Penetrometer: Stanhope Seta
2. Ball & Ring: Humboltd mfg. Co., Ltd.
3. Brookfield viscometer: model DV-II+
4. Thin film oven: Blue M
5. Dynamic shear rheology: Methrom
6. High shear mixer: Silverson lab mill

3.3 Experimental procedure

3.3.1 Preparation of asphalt mixture

The asphalt mixture was prepared by mixing asphalt with polyethylene-*c*o-methyl acrylate at the concentration ranging of 2, 4, 6 and 8% and added any one of acids such as polyphosphoric acid, phosphoric acid and citric acid at the concentration ranging 1% (polyphosphoric acid:0.004 mole, phosphoric acid:0.01 mole, citric acid:0.005 mole), 2% (polyphosphoric acid:0.008 mole, phosphoric acid:0.02 mole, citric acid:0.010 mole) and 3% (polyphosphoric acid:0.012 mole, phosphoric acid:0.03 mole, citric acid:0.015 mole) by weight of asphalt. The asphalt concentration relate to amount of polyethylene-*c*o-methyl acrylate and acid for example at the polyethylene-*c*o-methyl acrylate concentration ranging of 2 %, acid 1%, asphalt : 97%. A mixing condition was 170°C and maintained continuous stirring for 2 hours. The asphalt mixture was investigated the physical properties by measuring penetration, softening point, elastic recovery, ductility, viscosity, storage stability, thin film oven test and dynamic shear rheology. According to ASTM standard the reported result in this study are an average result from 3 times.

3.3.2 Testing procedures

3.3.2.1 Dynamic Shear Rheology [27]

(AASHTO TP5 Standard Test Method for Determining the Rheological Properties ofAsphalt Mixture Using a Dynamic Shear Rheometer (DSR))

The dynamic shear rheometer (DSR) is used to characterize the elastic behavior and consistency of asphalt mixtures at high and intermediate service temperature to make sure the asphalt will not become too soft and be susceptible to rutting.

The DSR measures the complex shear molulus (G*) and phase angle (3) of asphalt mixture at the desired temperature and frequency of loading. Complex shear modulus (G*) can be considered as the total resistance of the mixture to deformation when repeatedly sheared. Complex shear molulus (G*) consists of two components: (a) storage modulus G' or the elastic part, and (b) loss modulus W or the viscous part. The parameter phase angle is used as a measure of the relative elasticity of the asphalt [28,29].

The testing condition for this study is at temperature of 76°C. A small sample of asphalt is placed between two round plates with a 1 mm gap at a frequency of 10 rad/s. The lower plate is fixed, and the upper one turns back and forth (as shown in Fig. 3.1). This twisting action places a stress on the asphalt being tested. The reaction of a material to stress is strain, and the ratio of stress to strain yields a stiffness value. This specification requires a minimum stiffness of 1.00 kilo-Pascal (kPa) [30], which indicates this asphalt will not become too soft and rut at the test temperature of 76°C. The minimum stiffness value of 1.00 kPa remains constant, but the test is run at the high temperature for the performance grade (PG) being evaluated. Asphalt exhibits both of these types of response, depending on the temperature, and is known as a visco-elastic material. The DSR is capable of measuring the phase angle, ∂, and thereby helps identify the viscous and elastic components of the asphalt being tested.[31,32]

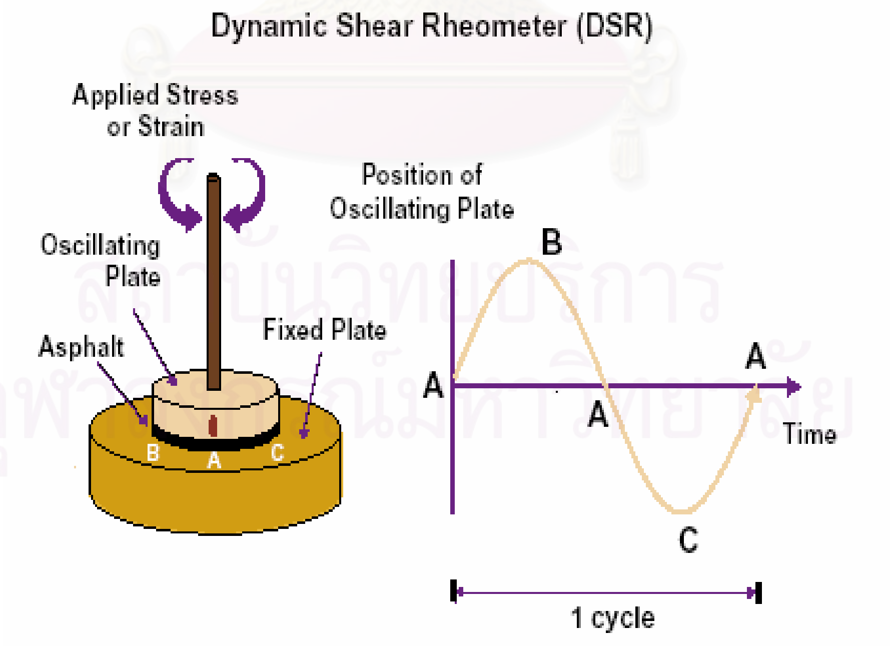


Fig. 3.1 Dynamic shear rheometer.

3.3.2.2 Penetration [33]

(ASTM D5: Standard Test Method for Penetration of Bituminous Materials)

Penetration test is the distance of needle that can pass into asphalt.

The consistency of asphalt is investigated by penetration test measurement. The penetration apparatus is shown in Fig. 3.2. Testing condition of penetration is at temperature of 25°C, a container of asphalt cement is brought into a thermostatically controlled water bath. The sample was placed under a needle of prescribed dimensions. The needle was loaded with a 100 g weight and is allowed to penetrate the asphalt cement sample for 5 seconds. The depth of penetration was measured in units of 0.1 min and was reported a penetration unit.

Fig. 3.2 Penetration apparatus.

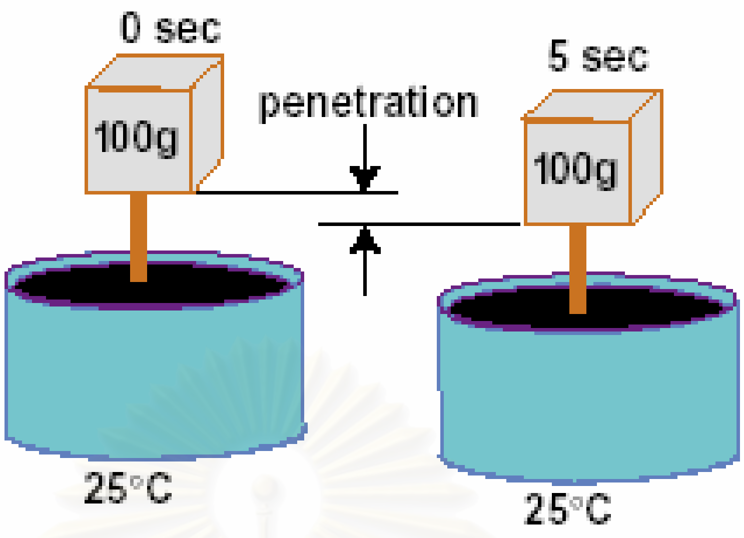


Fig. 3.3 Penetration test.

3.3.2.3 Softening point[34]

(ASTM D36: Standard Test Methodfor Softening Point of Bitumen (Ring-and-Ball Apparatus)

Softening point is the temperature which an asphalt attains a particular degree of softness under specified conditions of test

The softening point is investigated at the temperature susceptibility. Apparatus was shown in Fig. 3.5. The test was done by taking a brass ring filled with asphalt cement and suspending it in a beaker filled with water. Place the steel ball of specified dimensions and weight in the center of the ring as filled with the sample. The bath was heated at a controlled rate of 5°C/min. When the asphalt cement softens, the ball and asphalt cement shrinked toward the bottom of the beaker. Record the temperature at the instant when the softened asphalt sample shrinked the prescribed distance and touches the bottom plate.

Fig. 3.4 Ring and Ball.

Fig. 3.5 Softening point apparatus.

3.3.2.4 Elastic recovery [35]

(ASTM D5892, (6.2) Elastic recovery test method)

The elastic recovery is used to measure the recoverable strain after elongation by conventional ductility apparatus as outlined in the test method D113.

The test was performed at 25°C and with speed of 5 cm/min. The mold is similar in design to that described for use in the ductility test (see Fig. 3.6) except that the sides of the mold part a and a’ are straight. Elongate the asphalt mixture as prepared and condition as prescribed by test method D113 at the specified rate to 10 cm. Immediately cut the test specimen at the midpoint using scissors. Keep the test in water bath for 1 hour. After 1 hour, move the elongated into position until the two test specimen touch. Record the length of the test specimen as X. Percent recovery was calculated as:

$$\frac{10-X}{10} \times 100$$

Fig. 3.6 Mold-Elastic recovery.

3.3.2.5 Ductility [36]

(ASTM D113 Standard Test Method for Ductility of Bituminous Materials)

The ductility testing of asphalt material is to investigate the distance in centimetres, which asphalt material can be elongated before breaking (see Fig.3.7).

The sample was brought into the water bath at 13°C. The two ends of the sample were separated at the rate of 5 cm/min until the sample broke. To prevent floating or sinking of the stretched sample, salt was added to increase the specific gravity, and alcohol was added to decrease the specific gravity of the water.

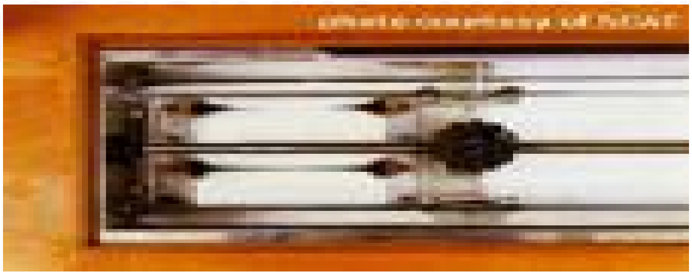


Fig. 3.7 Elongation of the asphalt material.

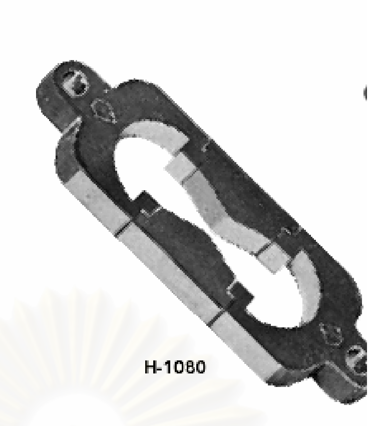


Fig. 3.8 Mold for ductility test.

3.3.2.6 Viscosity [37]

(ASTM D4402: Standard Test Method for Viscosity Determinations of Unfilled Asphalts Using the Brookfield Thermosel Apparatus)

Viscosity is used for measuring the flow of asphalt which can use for application in the plant.

The viscosity of asphalt is measured by Brookfield Thermosel Viscometer at elevated temperatures at 135, 145, 155 and 165°C. The shear rate was applied about 18.6 s, spindle no.21. A factor is applied to the torque dial reading to yield the viscosity of the asphalt in centipoises (cP).

Fig. 3.9 Brookfield viscometer.

3.3.2.7 Thin Film Oven Test [38]

(ASTM D754 Standard Test Method for Effects of Heat and Air on Asphaltic Materials)

Thin film oven test is used to determine the effects of heat and air on a film of semisolid asphalt materials.

The thin film oven test was conducted by placing a 50 g sample of asphalt cement in a cylindrical flat-bottom pan. The asphalt cement layer in the pan was about 3 mm deep. The pan containing the asphalt cement sample was transferred to a shelf in a ventilated oven maintained at 163°C (see Fig. 3.10). The shelf rotates at 5 to 6 revolutions per minute. The sample was kept in the oven for 5 hours, and then transferred to a suitable container for measuring softening point, penetration and ductility.

The average mass change of the material in all containers as mass percent of the original material was reported. A mass loss was reported as a negative number, while a mass gain was reported as a positive number. Penetration change was evaluated as the penetration of the residue expressed as the percentage of the original penetration.

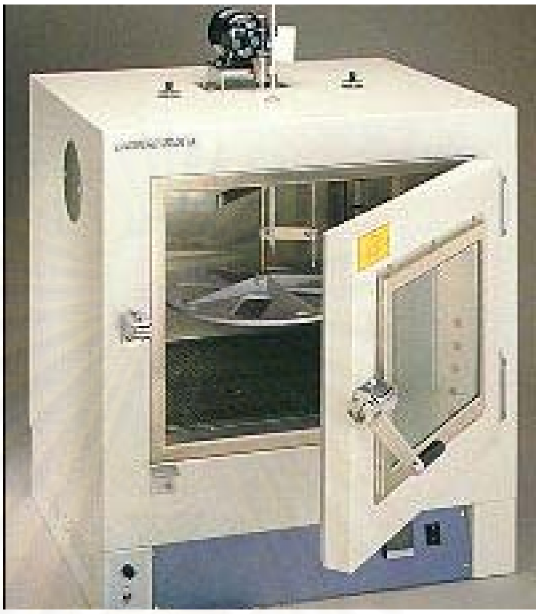


Fig. 3.10 Thin Film Oven Test.

3.3.2.8 Storage stability (separation test) [39]

(ASTM D5892, (6.1) Storage stability test method)

The separation of polymer and asphalt during storage at high temperature is evaluated by comparing the ring and ball softening point of the top and bottom samples taken from a conditioned sealed tube. The conditioning consists of placing a sealed tube of polymer modified asphalt in vertical position in a 163±5°C oven for 48 hours. At the end of the period remove the sample from the oven and place immediately in a freezer at -6.7±5°C for 4 hours. Remove sample from the freezer, cut the tube into three equal length section and place the top and bottom portions of the tube into separate beakers. Place the beaker into 163±5°C until the sample is sufficiently fluid. Thoroughly stirring, pour the top and bottom into the rings for ring and ball softening point test. The difference in °C between the softening point of respective top and bottom samples was reported.

CHAPTER IV

RESULTS AND DISCUSSION

The modification of asphalt with polyethylene-*co*-methyl acrylate (EMA) and each of the three acids, polyphosphoric acid, phosphoric acid and citric acid was performed by directly mixing the asphalt with EMA and acids. Physical properties were determined by following tests:

1. Consistency of polymer modified asphalt were investigated by using parameter as follows;
    - Dynamic shear rheology
    - Penetration
    - Penetration index (PI)
2. Temperature susceptibility was investigated by using parameter as follow;
    - Softening point
3. Compatibility was investigated by using parameter as follow;
    - Variation of softening point
4. Elasticity was investigated by using parameter as follow;
    - Elastic recovery
    - Penetration index (PI)
5. Ductility of asphalt was investigated by using parameter as follow;
    - Ductility
6. Proper of mixing condition was investigated by using parameter as follow;
    - Viscosity
7. Stability was investigated by using parameter as follow;
    - Storage stability

4.1 Selection of proper concentrations of EMA and acid

In this study, asphalt modified with 4% SBS by weight was prepared and used as the reference sample, because nowadays it is regularly used for road pavement. This quantity of SBS can improve the physical properties to meet the road specification requirement.

Preliminary tests were conducted by modifying the asphalts with polymer (EMA) and polyphosphoric acid (PPA). The quantity of EMA ranging on 2, 4, 6 and 8% by weight of asphalt, and PPA in the range of 1, 2 and 3% by weight of asphalt were evaluated. The proper concentration of EMA and acid in the modified asphalt was selected from the formula which showed properties similar to the reference SBS modified asphalt. Data are shown in Tables 4.1-4.4.

Table 4.1 Physical properties of asphalt modified with 2% EMA and different amount of PPA

Physical properties	4%SBS	%EMA-%PPA			
		2-0	2-1	2-2	2-3
Penetration (0.10 mm)	53	52	45	38	37
Softening point (°C)	63.4	50.1	59	74	78
Penetration index	2.50	-1.06	0.59	2.80	3.30
Ductility@13°C (cm)	62.0	32.0	12.0	10.0	8.5
Elastic recovery @ 25°C (%)	85	46	65	72	74
Storage stability 163°C, 48 h (°C)	22.1	24.8	20.6	3.3	1.6
Brookfield viscosity (cP) -135°C	878.0	483.0	615.0	750.0	1043.0
- 145°C	575.0	308.0	393.0	485.0	692.5
- 155°C	387.5	215.0	268.0	338.0	432.5
- 165°C	257.5	163.0	198.0	238.0	312.5
Variation of softening point (°C) (Before TFOT-After TFOT)	5.3	5.5	3.7	1.2	-0.4
Retain penetration (%)	74	77	76	74	73
Dynamic shear modulus (G*/sinδ) (KPa) (spec.> 1 KPa)	4.59	2.61	4.02	5.37	9.85

Table 4.2 Physical properties of asphalt modified with 4% EMA and different amount of PPA

Physical properties	4%SBS	%EMA-%PPA			
		4-0	4-1	4-2	4-3
Penetration (0.10mm)	53	51	38	35	34
Softening point (°C)	63.4	54.7	71.5	79.3	83.0
Penetration index	2.50	-0.02	2.40	3.00	3.80
Ductility@13 °C (cm)	62.0	26.0	12.0	10.0	8.7
Elastic recovery @ 25°C (%)	85	63	76	79	80
Storage stability 163°C, 48 h (°C)	22.1	25.0	20.4	3.6	1.2
Brookfield viscosity (cP) -135°C	878.0	598.0	963.0	1515.0	2025.0
- 145°C	575.0	390.0	633.0	975.0	1158.0
- 155°C	387.5	270.0	420.0	650.0	813.0
- 165°C	257.5	190.0	290.0	445.0	598.0
Variation of softening point (°C) (Before TFOT-After TFOT)	5.3	5.7	4.1	2.1	0.2
Retain penetration (%)	74	73	71	71	68
Dynamic shear modulus (G*/sinδ) (KPa) (spec.> 1 KPa)	4.59	3.30	5.07	8.11	12.76

Table 4.3 Physical properties of asphalt modified with 6% EMA and different amount of PPA

Physical properties	4%SBS	%EMA-%PPA			
		6-0	6-1	6-2	6-3
Penetration (0.10mm)	53	44	39	38	36
Softening point (°C)	63.4	68.3	80.0	82.4	83.0
Penetration index	2.50	2.30	3.70	3.90	4.00
Ductility@13 °C (cm)	62.0	22.7	10.7	10.0	7.0
Elastic recovery @ 25°C (%)	85	80	82	86	89
Storage stability 163°C, 48 h (°C)	22.1	26.4	22.4	2.4	0.2
Brookfield viscosity (cP) -135°C	878.0	987.5	1698.0	1973.0	2313.0
- 145°C	575.0	752.5	1128.0	1425.0	1725.0
- 155°C	387.5	512.5	782.5	958.0	1127.0
- 165°C	257.5	425.0	572.5	698.0	847.0
Variation of softening point (°C) (Before TFOT-After TFOT)	5.3	7.3	4.8	2.2	0.4
Retain penetration (%)	74	70	69	66	64
Dynamic shear modulus (G*/sinδ) (KPa) (spec.> 1 KPa)	4.59	4.95	7.59	9.92	15.60

Table 4.4 Physical properties of asphalt modified with 8% EMA and different amount of PPA

Physical properties	4%SBS	%EMA-%PPA			
		8-0	8-1	8-2	8-3
Penetration (0.10mm)	53	40	37	36	35
Softening point (°C)	63.4	80.2	83.5	84.5	87
Penetration index	2.50	3.90	4.00	4.10	4.30
Ductility@13°C (cm)	62.0	20.6	8.9	6.0	6.0
Elastic recovery @ 25°C (%)	85	84	86	88	88
Storage stability 163°C, 48 h (°C)	22.1	26.9	22.3	0.9	0.3
Brookfield viscosity (cP) -135°C	878.0	1685.0	2162.5	2787.5	3215.0
- 145°C	575.0	1135.0	1572.5	1687.5	1825.0
- 155°C	387.5	808.0	1097.5	1295.0	1345.0
- 165°C	257.5	583.0	702.5	897.5	978.0
Variation of softening point (°C) (Before TFOT-After TFOT)	5.3	8.4	5.3	2.7	1.4
Retain penetration (%)	74	68	68	67	66
Dynamic shear modulus (G*/sinδ) (KPa) (spec.> 1 KPa)	4.59	7.34	20.64	32.50	48.63

From Table 4.1-4.4, when compare the physical properties between the reference material and the asphalts modified with EMA (2-8%) and PPA (1-3%), it was found that the asphalt mixed with 4% EMA and 1-3% PPA gave similar physical properties to the reference material. The properties such as penetration, softening point, penetration index and dynamic shear modulus are shown in Table 4.2. SBS gave more elastic recovery result elasticity than EMA because SBS is thermoplastic elastomer but EMA is thermoplastic polymer material. Each property will be discussed in details as below.

4.2 Effect of PPA concentration on physical properties

4.2.1 Dynamic shear rheology

The physical behaviour of the modified asphalt was examined further by dynamic shear rheometry (DSR). The advantage of this technique, over traditional viscosity and penetration measurements, is that it allows measurement of physical properties at low strains and short loading times (frequencies), close to those likely to be experienced in the field due to traffic. The small deformations involved allow characterization of the material without destruction of internal structure. Figure 4.1 shows the G* of EMA- and PPA-modified asphalt.

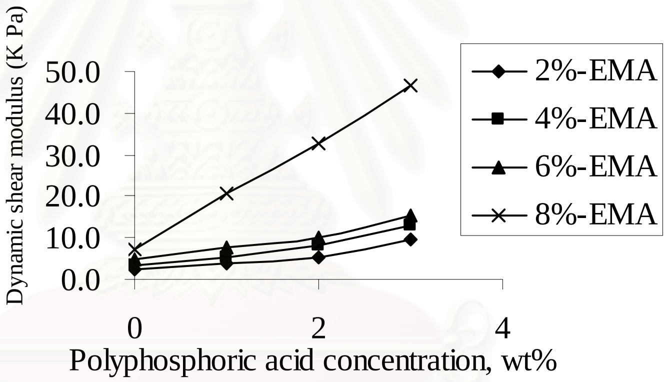


Fig. 4.1 Effect of EMA and PPA concentration on dynamic shear modulus

G* values are seen to increase with increasing of EMA and PPA concentrations. For 8% EMA sample, when increasing PPA concentration, the G* values sharply increase. The additives modified asphalt behaves like elastic solid at intermediate temperature, possibly as a result of the formation of (or enhancement of existing) transient networks of asphalt species, linked by hydrogen bonding and dipole-dipole interaction [7]. The EMA modified asphalt by adding PPA changed type of the structure from sole to gel type that asphalt behaves more elastic and stiffness.

The proposed reaction between polyphosphoric acid and asphaltene was shown in the figure 2.10 and the gel type of asphalt was shown in figure 2.5.

4.2.2 Penetration

The penetrability of either EMA modified asphalt with and without PPA is shown in Figure 4.2. It is seen that the penetrability of EMA modified asphalt decreases when increasing EMA concentration. It was found that the penetrability of asphalts modified with 2 and 4% EMA by weight dramatically decrease with increasing PPA concentration. On the other hand, the penetrability of asphalts modified with 6 and 8% EMA by weight slightly decrease with increasing EMA and PPA concentration, this indicates that the consistency of asphalt increases due to two factors. One is the maltene penetrated into EMA and it swells and disperses thoroughly in asphalt phase. Another factor is the interaction between PPA and polar molecule of asphaltene which makes the molecule of asphaltene larger with higher molecular weight. [1] As a result, the needle penetrates into modified asphalt less. A lower penetration means high resistance to deformation in the road pavement. It should be mentioned that in the previous report, it was found that increasing of polyphosphoric acid (1-5% by weight) in the polymer modified asphalt mixture can reduce the penetration value [14, 15].

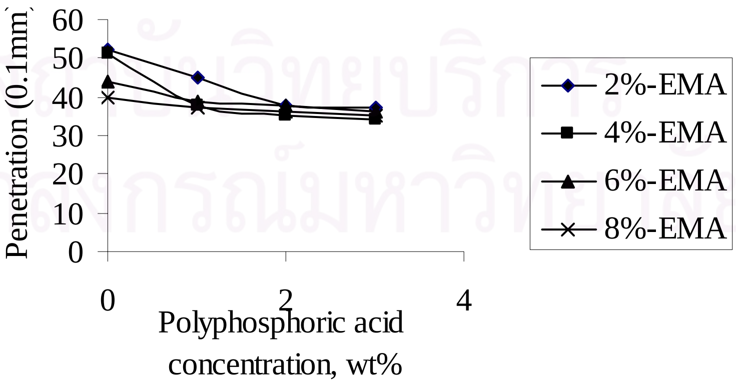


Fig. 4.2 Effect of EMA and PPA concentration on penetration

A relative aging of asphalt is indicated by using the percentage of retained penetration. It is measured by penetration before and after thin film oven test as equation below.

$$\%\ \text{Retained penetration} = \frac{\text{penetration after TFOT}}{\text{penetration before TFOT}} \times 100$$

It is seen that retained penetration decreases when the concentration of EMA and PPA was increased. When the asphalt was aged in the thin film oven at 163°C within 5 hours, some oils was evaporated and crosslinking occurred, heating caused the polymer effectively disperse in asphalt phase so the needle penetrated into asphalt less after Thin Film Oven Test (TFOT) compared to that before TFOT.

For general road pavement aging performance, low percentage of the retained penetration gives a good rutting resistance and also increasing stiffness.

Asphalt can be evaluated its relative temperature susceptibility by using the penetration index (PI) as equation below. [7]

$$PI = \frac{20U-300V}{U+30V}$$

Where $U = (\log 4)*(T_{RB}-T_P)$

$V = (\log 800-\log P_T)$

T_{RB} = The value of softening point (°C)

T_P = The temperature of penetration test (°C)

P_T = The value of penetration at temperature of penetration test

The PI of asphalt modified with EMA and PPA acid is shown in Figure 4.3. EMA has significantly improved temperature susceptibility. The PI increases with increasing concentration of EMA and acid. The reduced temperature susceptibility typically shows a rubbery elastic behavior. The asphalts modified with 2% and 4%

EMA at 0% level of acid has PI lower than zero, which indicates high temperature susceptibility. It was previously reported that the addition of polyphosphoric acid to asphalt in the amount of 1-5% by weight can increase the penetration index (PI) under mixing condition at 200°C for 1 hour.[1]

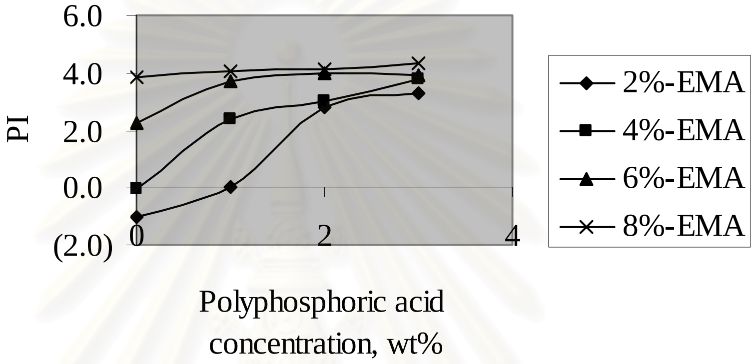


Fig. 4.3 Effect of EMA and PPA concentration on penetration index

4.2.3 Softening point

The softening point of asphalt modified with EMA is shown in Figure 4.4. It is seen that the softening point increases with increasing of the concentration of EMA and PPA. However, it increases little for 8% EMA. On the other hand, for those of 2%, 4% and 6% EMA, the softening point increases dramatically. As a result, the asphalts modified with EMA and PPA show high temperature susceptibility at high concentration of EMA and PPA. The dispersion of polymer in the asphalt phase and interaction of PPA to asphaltene is effected. In the previous study it was found that the softening point increases with increasing of polyphosphoric acid (1-5% by weight) in the polymer modified asphalt. [14, 15]

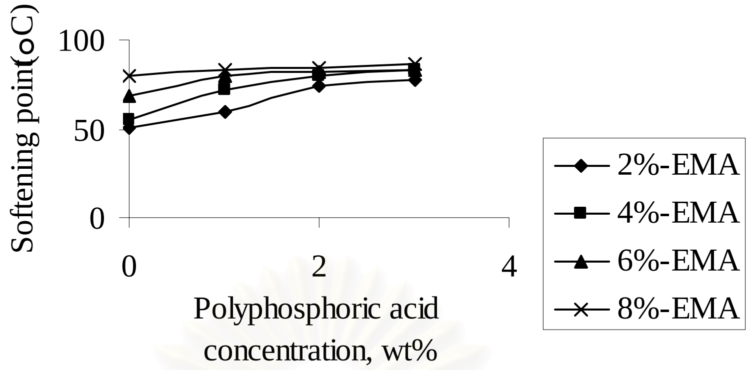


Fig. 4.4 Effect of EMA and PPA concentration on softening point

4.2.4 Variation of softening point

The difference of softening point value before and after performing Thin Film Oven Test can be used to indicate the compatibility of modified asphalt materials. The variation of softening point values of EMA modified asphalt is shown in Figure 4.5.

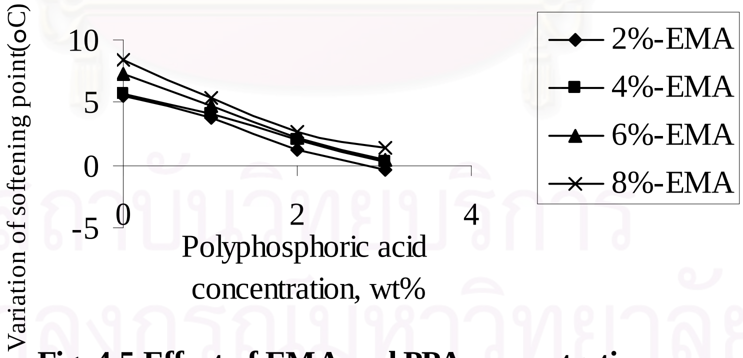


Fig. 4.5 Effect of EMA and PPA concentration on variation of softening point

The value slightly increases when increasing of EMA concentration. When increasing PPA concentration it dramatically decreases. PPA Addition to EMA modified asphalt gives a good compatibility of polymer modified asphalt. Since crosslinking between PPA and polymer occurs, the polymer becomes completely networked in asphalt before aging in Thin Film Oven Test.

In Thai industrial standard good compatibility of modified asphalt materials is required and it should be in a range of -4 to +6. [39]

4.2.5 Elastic recovery

Figure 4.6 shows the curve of elastic recovery, it is seen that the elastic recovery values of EMA modified asphalt dramatically increase when increasing EMA concentration from 2% to 4% by weight of asphalt. but slightly increases for 6% to 8% EMA concentration. It indicates that for high polymer concentration, it is hard to disperse thoroughly into asphalt phase due to the limitation of maltene phase.

The present result is consistent with previous report. When increase the polymer content (3-9% by weight): styrene butadiene styrene, ethylene vinyl acetate, ethylene butyl acrylate in asphalt, it gave good elasticity [16]. It was also reported that adding polyphosphoric acid (1-5% by weight) together with polypropylene (2-10% by weight), at mixing condition at 180°C for 1 hour can increase the elasticity properties [14].

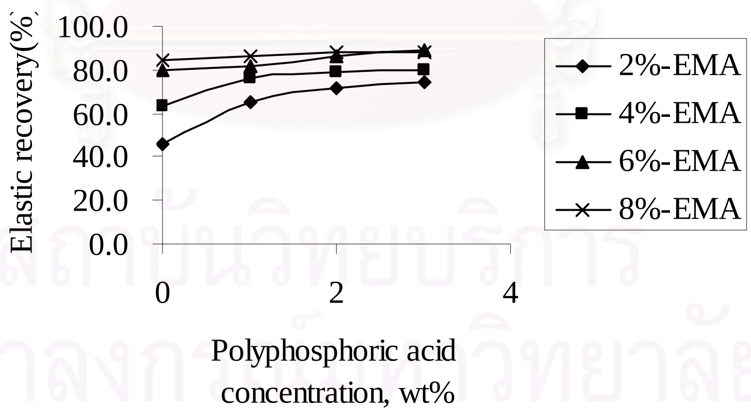


Fig. 4.6 Effect of EMA and PPA concentration on elastic recovery

4.2.6 Ductility

The values of ductility of EMA modified asphalt at 13°C is shown in Figure 4.7.

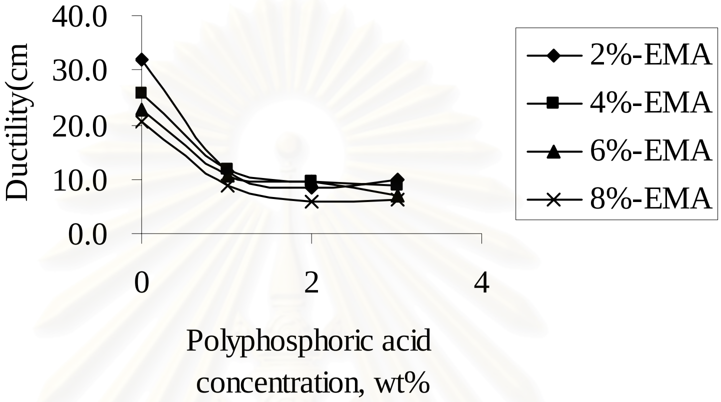


Fig. 4.7 Effect of EMA and PPA concentration on ductility

The ductility slightly decreases with an increase of EMA concentration. When increasing PPA concentration, it was found that the ductility dramatically decreased inthe range of 0-1% PPA, and slightly decreased in the range of 2-3% PPA. Acid addition increased brittleness and hardness of asphalt as a result of interaction between PPA and polar molecule in asphaltene fraction that becomes larger.

4.6.7 Viscosity

The viscosity is used to evaluate the proper mixing condition on hot mixed application. General specification proper viscosity should not over 3000 cP at mixing temperature. The elevated temperatures in this study are at 135, 145, 155 and 165°C. The shear rate was applied about 18.6 s, using spindle no.21.

Figures 4.8-4.11 show the Brookfield viscosity of asphalts modified with 2-8% EMA and each mixture added with the PPA concentration from 1% to 3%.

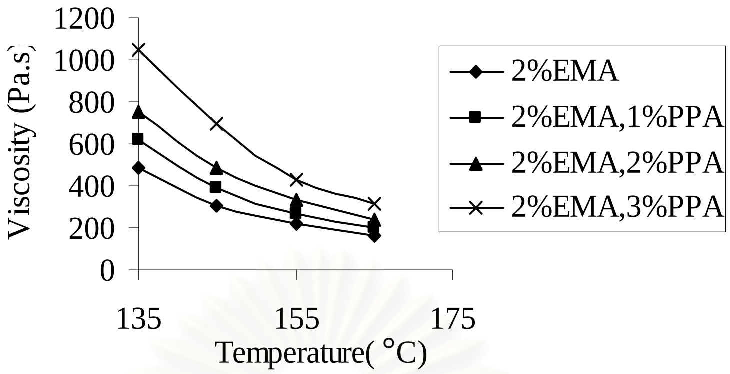


Fig. 4.8 Effect of 2% EMA and PPA concentration on viscosity

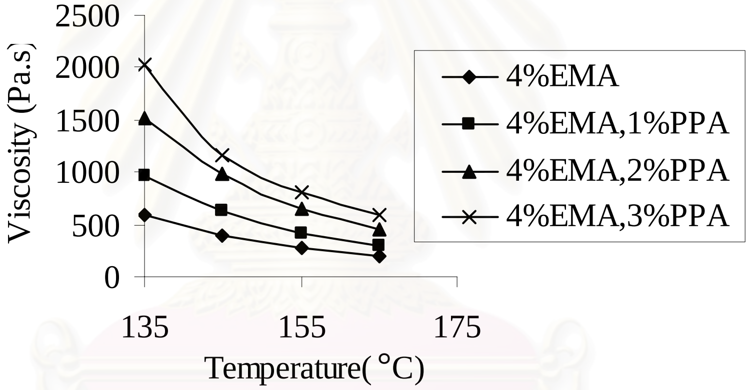


Fig. 4.9 Effect of 4% EMA and PPA concentration on viscosity,2

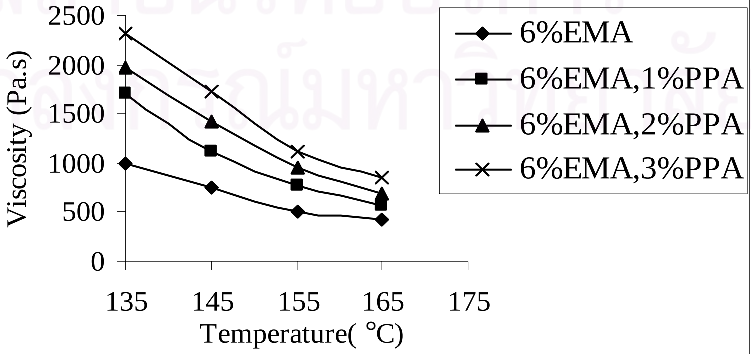


Fig. 4.10 Effect of 6% EMA and PPA concentration on viscosity

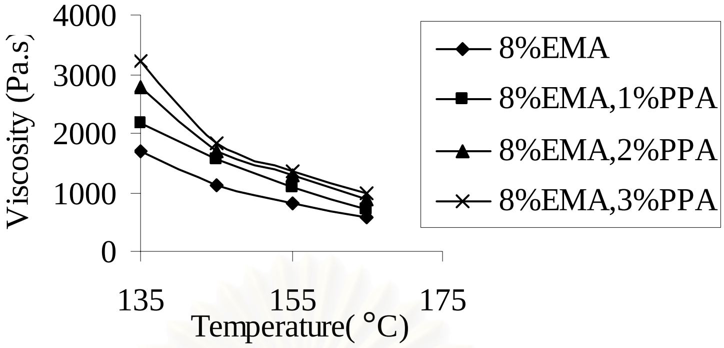


Fig. 4.11 Effect of 8% EMA and PPA concentration on viscosity

For the same proportion of asphalt mixture it was found that when increasing temperature the viscosity value dramatically decreases.

When increasing the EMA and PPA concentrations, the curves show dramatically increase in viscosity. The viscosity result of 6% EMA-0%PPA give a similar result to 2% EMA-3% PPA, this shows that by adding acid , EMA amount can be reduced. Therefore it can save cost of the production by addition of acid.

During mixing at high temperature, hot asphalt penetrates the polymer particles and the polymer become solvated and/or swollen. The addition of polyphosphoric acid can increase the viscosity , due to the interaction between polar molecule of asphalt and PPA which results in higher viscosity [1,16].

4.2.8 Storage stability

Figure 4.12 shows the curve of storage stability.

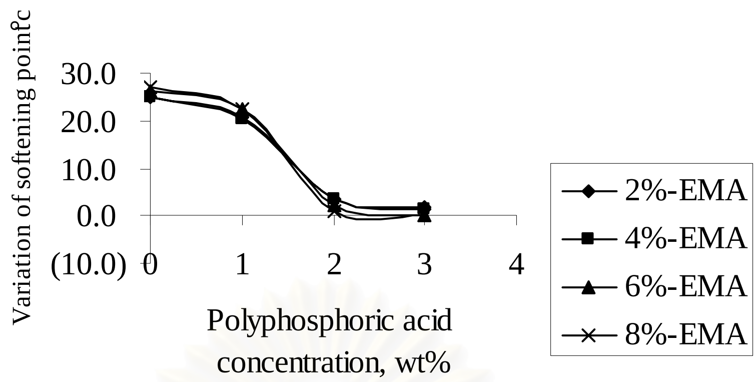


Fig. 4.12 Effect of EMA and PPA concentration on storage stability

It is seen that the storage stability slightly decreases with an increase of EMA concentration.

The values of the variation of softening point was used to indicate the storage stability suddenly decreases when increasing the PPA concentration and remains unchanged for concentration above 2%. Addition of PPA results in a good stability of asphalt when stored at high temperature. This can be explained by the reaction of PPA and polar molecule of asphalt. When viscosity of asphalt and polymer are similar, the segregation during storage of the modified asphalt will not be developed. The result in this study is similar to previous study that indicated the stability during storage can be improved with polypropylene modified asphalt which was added polyphosphoric acid (1-5% by weight) [14].

From investigation of the physical properties of EMA- and acid-modified asphalt using various concentrations, it can be concluded that the EMA and PPA could improve some physical properties of the modified asphalt, summarized as follows:

- Dynamic shear modulus increases, that is resistance to deformation is improved.
- Penetration value decreases, that is the consistency of asphalt is improved.
- PI value increases, that is the elasticity property is improved

- Softening point increases, that is the temperature susceptibility is improved.
- Elastic recovery increases, that is elasticity property is improved.
- Ductility increases with increasing of both EMA and PPA concentrations, that is elongation viscosity is improved.
- Storage stability increases, that is storage stability is improved.

4.3 The physical properties comparison of phosphoric acid (PA) and citric acid

In this study, besides polyphosphoric acid (PPA), two other acids were used and compared to the PPA. From the proper concentration determined from the previous experiments (Table 4.2), the concentration of EMA was fixed at 4%, and acid concentration was varied to 1-3%.

The data of their physical properties are shown in Tables 4.5-4.6. The curves are plotted in Figs. 4.13-4.22.

Table 4.5 Physical properties of asphalt modified with 4% EMA and different amount of PA

Physical properties	%EMA-%PA		
	4-1	4-2	4-3
Penetration (0.10mm)	42	36	34
Softening point (°C)	69.5	76.5	81.0
Penetration index	2.40	3.00	3.50
Ductility@13 °C (cm)	13.0	11.3	9.6
Elastic recovery @ 25°C (%)	63	67	71
Storage stability 163°C,48 h (°C)	21.6	4.4	2.4
Brookfield viscosity (cP) -135°C	673.0	818.0	1022.5
- 145°C	423.0	598.0	797.5
- 155°C	305.0	413.0	642.5
- 165°C	248.0	318.0	467.5
Variation of softening point (°C) (Before TFOT-After TFOT)	6.1	5.1	2.6
Retained penetration (%)	76	75	74
Dynamic shear modulus (G*/sinδ) (KPa) (spec.> 1 KPa)	5.11	8.71	10.22

Table 4.6 Physical properties of asphalt modified with 4% EMA and and different amount of citric acid

Physical properties	%EMA-%citric acid		
	4-1	4-2	4-3
Penetration (0.10mm)	49	47	42
Softening point (°C)	57.0	60.0	64.5
Penetration index	0.40	0.90	1.50
Ductility@13 °C (cm)	27.8	24.0	19.0
Elastic recovery @ 25°C (%)	61	65	67
Storage stability 163°C,48 h (°C)	22.6	11.6	7.2
Brookfield viscosity (cP) -135°C	583.0	593.0	708.0
- 145°C	395.0	400.0	460.0
- 155°C	268.0	273.0	308.0
- 165°C	190.0	193.0	213.0
Variation of softening point (°C) (Before TFOT-After TFOT)	12.5	12.0	9.4
Retained penetration (%)	64.4	65.8	68.2
Dynamic shear modulus (G*/sinδ) (KPa) (spec.> 1 KPa)	3.85	4.00	4.25

Figure 4.13 shows dynamic shear modulus. It was found that the dynamic shear modulus increased in the order: PPA > PA > citric acid. It should be mentioned that monocarboxylic acid was reported to show lower complex modulus than dicarboxylic acid. [7]

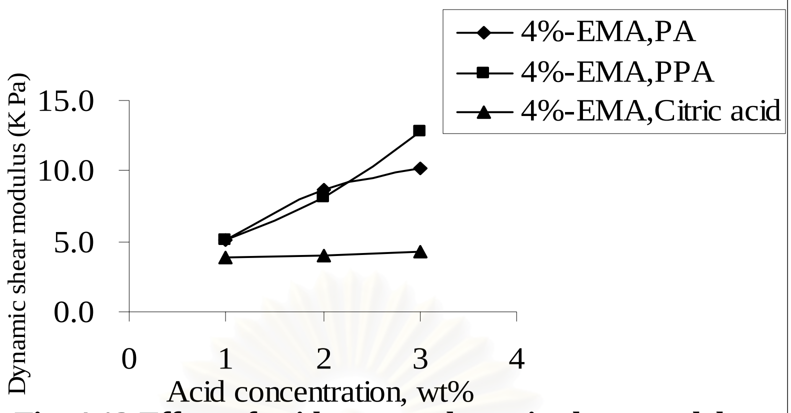


Fig. 4.13 Effect of acid type on dynamic shear modulus

Figures 4.14-4.15 show penetration and penetration index (PI). It was found that the penetration decreased in the order: PPA > PA > citric acid. PI value increased in the order: PPA > PA > citric acid. This result agrees with the previous report [9,14].

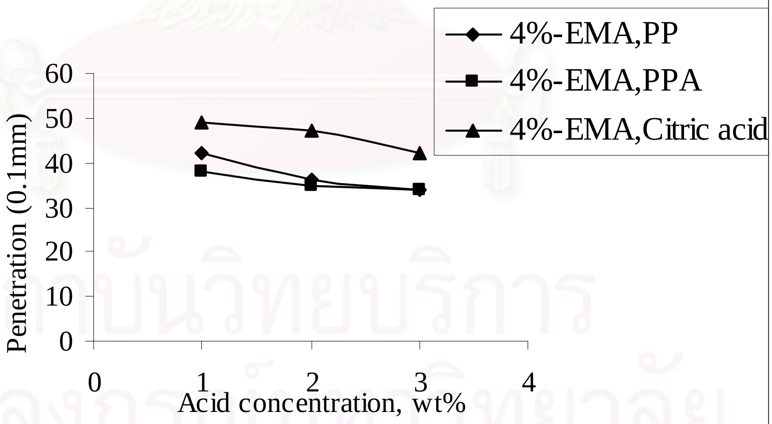


Fig. 4.14 Effect of acid type on penetration

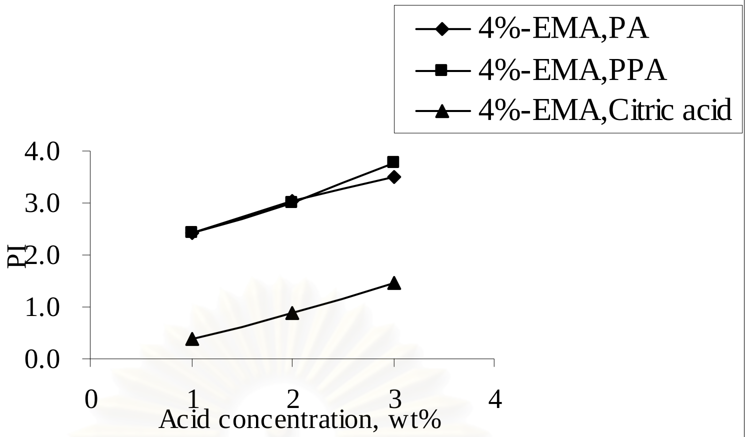


Fig. 4.15 Effect of acid type on penetration index

Figure 4.16 shows softening point before TFOT. It was found that the softening point increased in the order: PPA > PA > citric acid.

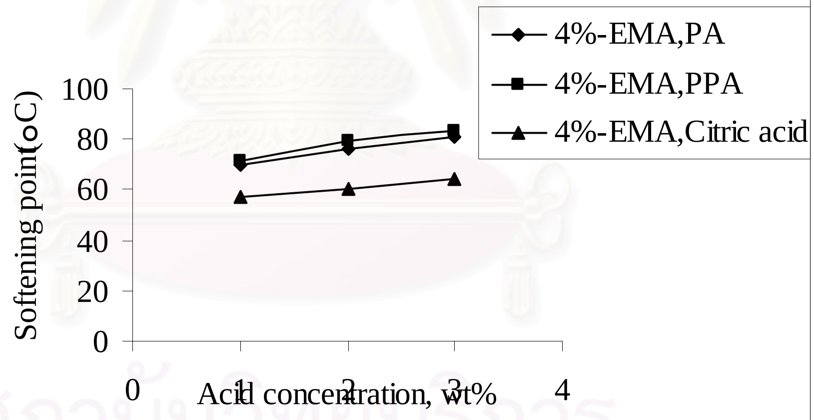


Fig. 4.16 Effect of acid type on softening point

Figure 4.17 shows elastic recovery. It was found that the elastic recovery increased in the order: PPA > PA > citric acid.

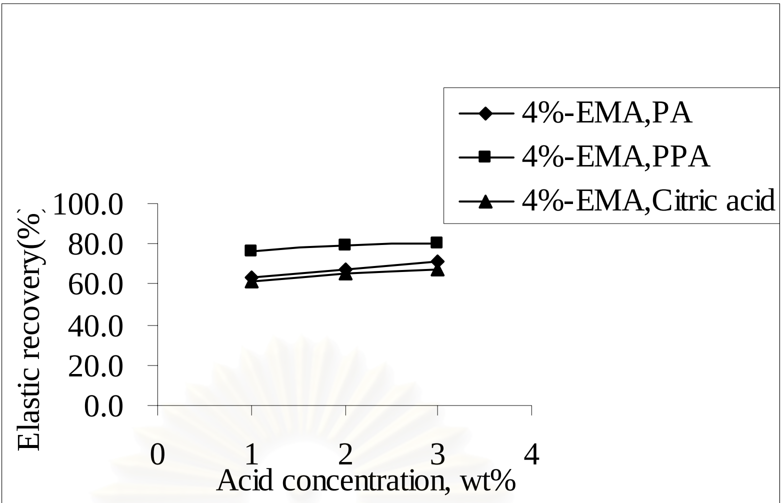


Fig. 4.17 Effect of acid type on elastic recovery

Figures 4.18-4.20 show dynamic viscosity of the modified asphalt with diffrerent acid. It was found that at the same mixture the viscosity increased in the order: PPA > PA > citric acid.

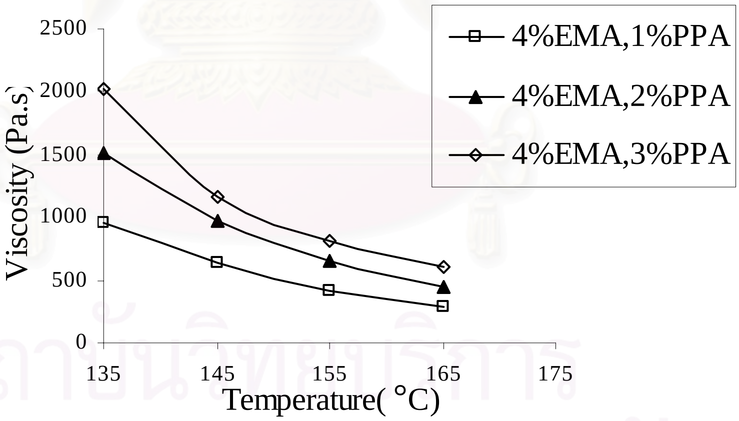


Fig. 4.18 Effect of EMA and PPA concentration on viscosity

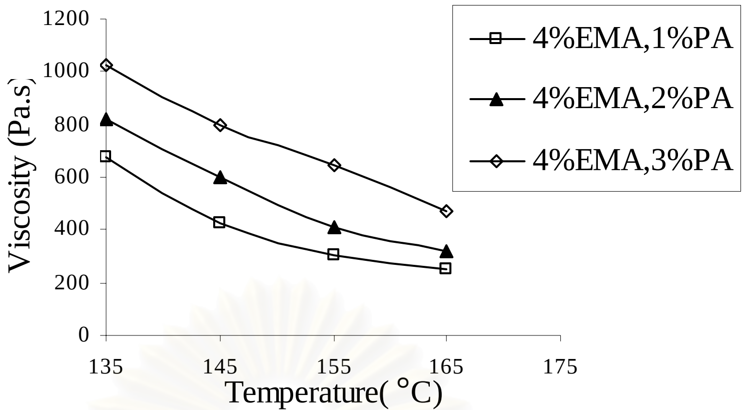


Fig. 4.19 Effect of EMA and PA concentration on viscosity

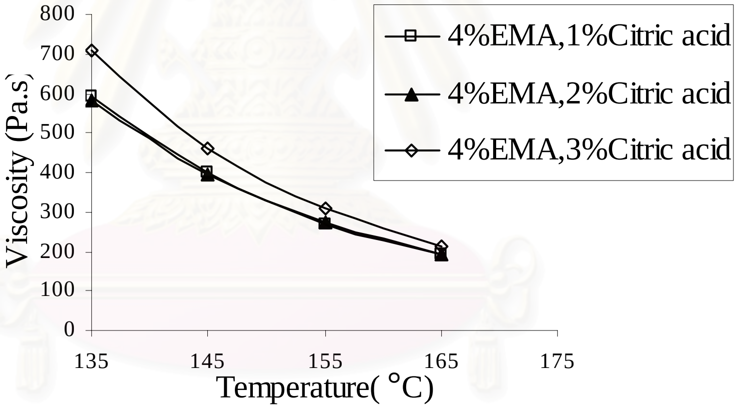


Fig. 4.20 Effect of EMA and Citric acid concentration on viscosity

Figure 4.21 shows ductility. It was found that the ductility increased in the order: PPA > PA > citric acid.

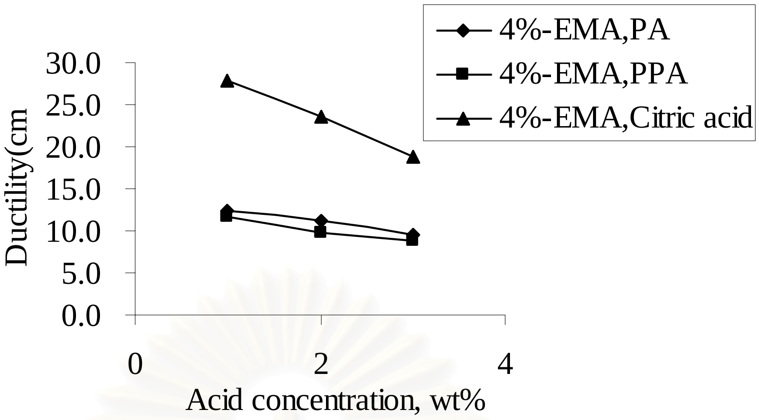


Fig. 4.21 Effect of acid type on ductility

Figure 4.22 shows storage stability. It was found that the storage stability increased in the order: PPA > PA > citric acid.

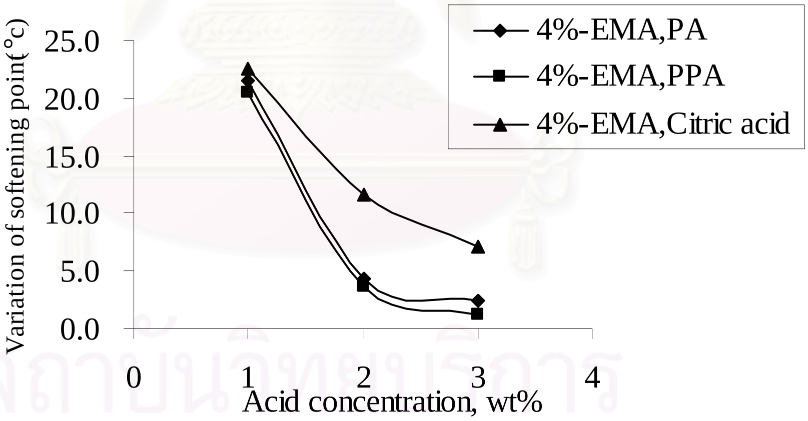


Fig. 4.22 Effect of acid type on storage stability

From the above results obtained in this work, it can be concluded that at 4% EMA by weight, the acid treatment was responsible for the improvement in some physical properties. Polyphosphoric acid (PPA) is better than phosphoric acid and citric acid.

CHAPTER V

CONCLUSION

Asphalt was modified with polyethylene-*co*-methyl acrylate (EMA) and some additives: polyphosphoric acid (PPA), phosphoric acid (PA) and citric acid at different level of concentration. Their physical and rheology properties have been investigated. The results are summarized below.

When compare the asphalts modified with varying amount of EMA, with the reference sample (4% SBS-modified asphalt), it was found that the 4% EMA-modified asphalt give the similar properties to the reference, such as penetration, softening point, penetration index and dynamic shear modulus.

For 4% EMA-modified asphalt, it was found that penetration decreased with an increasing of acids concentration. Adding PPA in 1, 2 and 3% by weight resulted in a more decrease of penetration than adding PA and citric acid.

A similar trend occurred in penetration index. It increased for samples modified with PPA. Penetration index of asphalts modified with phosphoric acid increased while penetration index of asphalts modified with citric acid increased lower than PPA and phosphoric acid.

Softening point increased with an increase of EMA and acid concentration. When adding three types of acids (1, 2 and 3% by weight), it was found that asphalts modified with PPA gave a higher elastic recovery than asphalts modified with phosphoric acid and citric acid. The softening point of asphalts modified with PPA increased most to 71.5°C, 79.3°C and 83.0°C respectively.

Variation of softening point decreased with an increase of EMA and acid concentration. The asphalts modified with PPA give a lower variation of softening point than those with phosphoric acid and citric acid.

Softening point indicates the temperature susceptibility, increasing of softening point shows lower temperature susceptibility. Lower variation of softening point shows good compatibility of EMA and asphalt. The more compatibility is requirement of the standard specification in the road pavement industry.

Elastic recovery was increased with increasing of EMA and acid concentration. PPA can form larger asphaltene molecule than phosphoric acid and citric acid. The higher elastic recovery is a good quality when aging in long period, as it reduces cracking deformation.

Viscosity increased with increasing of EMA and acid concentration. The viscosity of asphalts modified with PPA increased more than those of asphalts modified with phosphoric acid and citric acid. PPA caused asphaltene molecule become larger, resulting in higher viscosity. Viscosity not more than 3000 cP, is suitable for use in the plant as it is easily pumped.

The storage stability of asphalts modified with PPA is better than phosphoric acid and citric acid as the molecule of asphalt becomes larger, causing the viscosity higher. Therefore, the separation of phase between asphalt and polymer did not occur.

The dynamic shear modulus result indicates that EMA and acids increased elasticity, stiffness at the testing temperature. It was found no cracking. Dynamic shear modulus increased with an increasing of EMA and acids concentration.

The results from this work demonstrated that PPA improved the physical properties of asphalt more effectively. This is due to the interaction between phosphorous and the aromatic structure of asphaltene, H-bonding and dipole-dipole interaction. This involves a change towards a gel structure of colloidal system (large molecule of asphaltene and high molecular weight). It seems that the type of acid has affected the molecule of asphalt. Phosphoric acid was shown to be able to improve the properties but with less effect than PPA. On the other hand, citric acid, the lowest molecular weight in this work which possessing three carboxylic groups has the least effect. The effectiveness of acids to improve the EMA-modified asphalt are in the order: PPA > PA > citric acid.

Suggestion for future work

To further improve the properties of polymer modified asphalt, especially ductility and elastic recovery properties, higher percentage of ethylene monomer should be mixed. Meanwhile, some other types of additives, such as sulphur might be attempted to crosslink the asphalt and polymer.

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