แอสฟัลต์ดัดแปรด้วยพอลิเมอร์: ผลของจำนวนหมู่ฟังก์ชันของเบนซอกซาซีนต่อสมบัติของแอสฟัลต์ที่ดัดแปรด้วยพอลิเมอร์

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POLYMER-MODIFIED ASPHALTS: EFFECTS OF VARIED BENZOXAZINE FUNCTIONALITIES ON

POLYMER-MODIFIED ASPHALT PROPERTIES

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A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Engineering Program in Chemical Engineering

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งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาผลของจำนวนหมู่ฟังก์ชันของเบนซอกซาซีนต่อสมบัติของแอสฟัลต์ที่
ดัดแปรด้วยพอลิเมอร์ เพื่อปรับปรุงสมบัติทางกายภาพ, สมบัติทางเคมี, สมบัติทางความร้อน รวมไปสมบัติทางกล
ของแอสฟัลต์ โดยใช้เบนซอกซาซีนที่มีหมู่ฟังก์ชันต่างกันเป็นสารดัดแปร พอลิเบนซอกซาซีน เป็นพอลิเมอร์ใน
ตระกูลฟีนอลิก ที่มีสมบัติที่ดีหลายประการ เช่น สังเคราะห์ได้ง่าย ไม่มีผลพลอยได้จากการบ่ม มีความหนืดต่ำ ค่า
การดูดซึมน้ำต่ำ มีสมบัติทางกลที่ดี รวมไปถึงมีเสถียรภาพทางความร้อนสูง ในงานวิจัยนี้ใช้แอสฟัลต์เกรด 60/70
โดยเติมเบนซอกซาซีนในอัตราส่วน 0, 3, 6 และ 9 เปอร์เซ็นต์โดยน้ำหนัก ผสมโดยใช้เครื่องกวนที่ความเร็วรอบ
500 รอบต่อนาที จากนั้นนำไปบ่มที่อุณหภูมิ 190 องศาเซลเซียส เป็นเวลา 1 ชั่วโมง และศึกษาผลการปรับปรุง
สมบัติของแอสฟัลต์ที่ดัดแปรด้วยเบนซอกซาซีน พบว่า จุดอ่อนตัว (Softening point) เพิ่มขึ้น ในขณะที่ ค่าความ
แข็งในการเจาะทะลุ (Penetration) ลดลง และความหนืดของแอสฟัลต์ที่ดัดแปรด้วยเบนซอกซาซีนมีค่าเพิ่มสูงขึ้น
เมื่อเติมปริมาณของเบนซอกซาซีนเพิ่มขึ้น นอกจากนี้แล้วค่าการยืดดึง (Ductility) รวมไปถึงค่าความเหนียว และ ค่า
เทเนซิตี (Toughness and Tenacity) มีค่าเพิ่มสูงขึ้น ซึ่งแสดงให้เห็นถึงความเหนียวและความสามารถในการยึด
เกาะของแอสฟัลต์กับวัสดุมวลรวม และพบว่า มีค่าสูงขึ้นมากที่สุดที่อัตราส่วนของเบนซอกซาซีน 6 เปอร์เซ็นต์โดย
น้ำหนัก เมื่อเทียบกับแอสฟัลต์ปกติ ซึ่งจะเห็นได้ว่า ที่สัดส่วน 6 เปอร์เซ็นต์โดยน้ำหนักของเบนซอกซาซีนของแต่ละ
ฟังก์ชันนั้น สามารถปรับปรุงสมบัติของแอสฟัลต์ได้ดีที่สุด นอกจากนี้ค่าความต้านทานการเป็นร่องล้อ (G*/sin δ)
มีค่าเพิ่มสูงขึ้นจาก 1.3 kPa ของแอสฟัลต์ปกติ เป็น 2.6 kPa ซึ่งแสดงให้เห็นถึงความสามารถในการรับแรงที่ดีขึ้นมี
ความสามารถต้านทานการเป็นร่องล้อได้ดีขึ้น เมื่อพิจารณาการกระจายตัวของการผสมของเบนซอกซาซีนกับ
แอสฟัลต์ สมบัติทางเคมี, สมบัติทางความร้อน และ สมบัติทางกล เมื่อจำนวนหมู่ฟังก์ชันที่เพิ่มขึ้นที่ปริมาณการเติม
ของเบนซอกซาซีน 6 เปอร์เซ็นต์โดยน้ำหนัก พบว่าการกระจายของเบนซอกซาซีน กระจายตัวเป็นเม็ดเล็กๆอยู่
ภายในโครงสร้างของแอสฟัลต์ มีลักษณะการกระจายที่สม่ำเสมอและ มีปริมาณเพิ่มขึ้นตามจำนวนหมู่ฟังก์ชันของ
เบนซอกซีน จาก FTIR แสดงถึงการเปลี่ยนแปลงอย่างมีนัยสำคัญ ซึ่งแสดงการเกิดปฏิกิริยาทางเคมีระหว่างเบนซอก
ซาซีนกับแอสฟัลต์ นอกจากนี้ยังพบว่าแอสฟัลต์ดัดแปรด้วยเบนซอกซาซีนมีเสถียรภาพทางความร้อนที่สูงขึ้นโดยค่า
การสลายตัวทางความร้อนที่การสูญเสียมวล 5 เปอร์เซ็นต์ของแอสฟัลต์ที่ดัดแปรด้วยเบนซอกซาซีนมีค่าเพิ่มขึ้น
จาก 362 องศาเซลเซียส ของแอสฟัลต์ปกติเป็น 396 องศาเซลเซียส มอดุลสสะสมมีค่าเพิ่มสูงขึ้นและอุณหภูมิการ
เปลี่ยนสถานะคล้ายแก้ว (T_g) ของแอสฟัลต์ที่ดัดแปรด้วยเบนซอกซาซีนมีค่าสูงขึ้นจากแอสฟัลต์ปกติที่ -14.3 องศา
เซลเซียสเป็น 4.7 องศาเซลเซียส ซึ่งเพิ่มขึ้นตามจำนวนหมู่ฟังก์ชันของเบนซอกซาซีน จากการศึกษาการดัดแปร
สมบัติของแอสฟัลต์ด้วยเบนซอกซาซีนสามารถลดการเสียรูปการเกิดร่องล้อ (Rutting) การเกิดการแตกร้าว
(Cracking), การเยิ้ม (Bleeding) เพิ่มความสามารถยืดดึง (Ductility) ตลอดจนสามารถเพิ่มความเหนียวและค่า
เทเนซิตี (Toughness and Tenacity) ซึ่งจะช่วยเพิ่มความสามารถในการยึดเกาะของแอสฟัลต์ดัดแปรได้

ภาควิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต	....
สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อ อ.ที่ปรึกษาหลัก	....
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KEYWORDS: BENZOXAZINE RESIN / POLYMER MODIFIED ASPHALT / BENZOXAZINE FUNCTIONALITY / PAVEMENT

AMORNRAT SAENGPECH: POLYMER-MODIFIED ASPHALTS: EFFECTS OF VARIED BENZOXAZINE FUNCTIONALITIES ON POLYMER-MODIFIED ASPHALT PROPERTIES. ADVISOR: ASSOC. PROF. SARAWUT RIMDUSIT, Ph.D., 119 pp.

This research aims to study effects of benzoxazine functionalities on properties of asphalts modified bybenzoxazine resin. It could be seen that different functionalities of benzoxazine resin coulddevelop chemical, thermal and mechanical properties of asphalt. Polybenzoxazine, phenolic resin based polymer, processes some prominent properties such as easy synthesis, no by-products released upon curing process, low viscosity, low water absorption, and good mechanical properties as well as high thermal stability. Base asphalt (AC 60/70 penetration grade) was mixed with varied benzoxazine functionalities at various concentrations, i.e., 0, 3, 6 and 9 % by weight to prepare benzoxazine resins modified asphalt. The suitable mixing condition was obtained by mechanical mixing at 80 $^{\circ}$C for 1 hr at mixing speed of 500 rpm and then immediately cured at 190 $^{\circ}$C for 1 hr. Softening point and viscosity of benzoxazine resins modified asphalt increased whereas penetration depth decreased with increasing benzoxazine resins contents. In addition, the ductility, toughness, and tenacity significant were higher than unmodified asphalt. That could contribute to the improvement of aggregate retention and low temperature susceptibility. Thus, 6% by weight of benzoxazine resins used rendered the highest values. In addition, the rutting parameter ($G^*/\sin \delta$) increased from 1.3 kPa of neat asphalt to 2.6 kPa, representing resistance to permanent deformation. In consideration of the dispersity of two components in a mixture, chemical interaction, thermal and mechanical properties when the number of functional benzoxazine resins increased, morphology of benzoxazine resins modified asphalt showed that small particles of benzoxazine fraction dispersed in asphalt. From the results of FT-IR spectra, the regeneration of main bands of benzoxazine resins modified asphalt were identified and the significant variation was the peak intensity, which represents the chemical bonding between benzoxazine and asphalt matrix. Furthermore, the degradation temperature at 5 % weight loss of benzoxazine resins modified asphalt increased from 362°C of neat asphalt to 396 $^{\circ}$C with increasing functionality of benzoxazine resin. Also, the storage modulus increased and the glass transition temperature (T_g) of benzoxazine resins modified asphalt increased from -14.3 of neat asphalt to 4.7°C when functionality of benzoxazine resin increeased. The results could indicate that the benzoxazine resins were able to reduce rutting, cracking bleeding, andenhance the ductility as well as toughness and tenacity of asphalt mixtures, which was possible to promote the adhesion between modified asphalt and aggregate.

Department:	Chemical Engineering	Student's Signature -------------------------------
Field of Study:	Chemical Engineering	Advisor's Signature -------------------------------
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CHAPTER I

INTRODUCTION

1.1 GENARAL INTRODUCTION

Asphalt is an oil based substance consisting mainly of high molecular weight hydrocarbon molecules. It is a semi-solid, dark brown to black, thick, viscous mixture of heavy hydrocarbons material produced by removing the lighter fractions such as liquid petroleum gas, petrol and diesel from heavy crude oil during the refining process and natural asphalt. In addition, asphalt is a strong and durable adhesive that binds together a very wide variety of other materials without affecting their properties. It is also insoluble in water and can act as an effective waterproof and resists against most acids. Moreover, asphalt is a thermoplastic material and it becomes soft but it will harden as it cools [1, 2].

Asphalt has been used in several applications including preservatives, sealants, adhesives, waterproofing agents and it is also widely used for road pavement as a reliable weather resistant material. It is an ideal material for road pavement where low and high traffic conditions are desired. However, climate and traffic loading are key factors influencing permanent deformation of asphalt pavements like rutting, stripping, fatigue and cracking [3].

Several additives have been used to increase the performance of asphalt binders. One of the most commonly used methods is to include certain additives into the asphalt so that its overall durability, elasticity, resistance against aging as well as service performance can be enhanced. Among those additives, polymeric modifier is considered as the most important additive. Polymer modified asphalts (PMA) are a major advancement in asphalt binder technology as these materials better satisfy the demands of increasing traffic volumes and thermal susceptibility [4-18]. Polymer used in asphalt technology may be listed in three main categories: plastomers, thermoplastic elastomers and reactive polymer [3, 4].

Firstly, plastomers can improve rutting resistance, but cannot improve low-temperature performance of asphalt such as polypropylene (PP), ethylene vinyl acetate (EVA), polyethylene terephthalate (PET) [7, 9, 11-12]. Secondly, thermoplastic elastomer can improve fatigue resistance and cracking resistance, but it has some limitation in improving properties against heat such as styrene butadiene styrene copolymer (SBS), styrene ethylene butylene styrene copolymer (SEBS), styrene-isoprene-styrene copolymer (SIS) [10, 13, 15-17].

Moreover, two classes of the polymers generally exhibit relatively low compatibility with asphalt [18]. To avoid these problems, a reactive polymer is incorporated in asphalt to impart rigidity, reduce deformations substantially under

load because it is consisting of reactive functional groups which are able to chemically interact with some components in asphalt materials [19, 20].

For example, epoxy resin is one popular thermosetting polymer used to modify asphalt for the steel deck pavement [21]. Epoxy resin was reported to help improve aging resistance, fatigue resistance and flow at medium or high temperatures. Moreover, it can also increase permanent deformation resistance at high temperature and can reduce temperature sensitivity of asphalt [21]. However, the use of some thermosets such as epoxy, which requires curing agent to start the curing process, might cause gelation of the resin during the asphalt compounding process. This problem can be circumvented by using thermally curable resin such as benzoxazine resin.

Benzoxaxine resin is a thermosetting polymer that offers several unique characteristics for use in polymer alloys or polymer composites including high glass transition temperatures, high mechanical properties, near-zero cure shrinkage, chemical resistance, good interfacial adhesion, low moisture uptake in hot or wet environments and low viscosity [22]. In addition, the curing reaction of benzoxazine resin demonstrates a self-polymerizing behavior that allows polymerization to occur without addition of either catalyst or curing agent (i.e. it is a one component resin system) and the heat of reaction is lower than epoxy [23]. In addition, benzoxazine functionalities have strong effects on its polymerization behaviors, thermo-

mechanical transition and properties of the resulting fully cured polybenzoxazine due to an enhancement on degree of crosslinking of the obtained polymers. It is expected that the use of benzoxazine resins of greater functionalities will further enhance the properties of benzoxazine-modified asphalts.

From our previous research, we have studied effects of di-functional benzoxazine resin as an asphalt modifier. From this study, the maximum service temperature from rutting parameter analysis of the unmodified asphalt is about 65°C whereas that of 9% weight benzoxazine modified asphalt is found to be greater with a value of 84°C. The results suggest a potential use of benzoxazine resin to improve road pavement properties [24].

Therefore, the aims of this study are to investigate and compare effects of benzoxazine resins of varied functionalities on properties of the modified asphalt. Major properties of benzoxazine-modified asphalts are to be characterized including rheology, morphology, thermal properties and mechanical properties. Finally, the potential chemical interaction of benzoxazine resin with asphalt will also be studied.

1.2 OBJECTIVES

1. To develop polymer modified asphalt using benzoxazine resins of varied functionalities as a modifier.

2   To investigate and compare effects of benzoxazine functionalities on rheological, physical, mechanical and thermal properties of polymer modified asphalt.

3   To evaluate potential chemical interaction of benzoxazine resin with asphalt.

4   To evaluate major characteristics for pavement application i.e. penetration resistance, viscosity, ductility, toughness, tenacity, softening point.

1.3. SCOPE OF THIS STUDY

1.   Synthesize benzoxazine resin with one, two, and three oxazine rings in their structures by solventless technology.

2. Prepare benzoxazine modified asphalt using benzoxazine resin contents from 0, 3, 6, and 9 % by weight.

3. Determine effects of types and contents of benzoxazine modifier on rheological, physical, mechanical and thermal properties of the obtained modified asphalts.

4. Evaluate potential chemical interaction of benzoxazine resin with asphalt.

5.   Evaluate major characteristics for pavement application i.e. penetration resistance, softening point, ductility, toughness, tenacity and Viscosity.

1.4. PROCEDURE OF THE STUDY

1. Study related research.

2. Synthesize chemical as modifiers

2.1 Synthesis of mono-functional Benzoxazine resin (Ph-a)

Phenol, p-formaldehyde and aniline at ratio 1:2:1 by molar were mixed in aluminum foil. First, the reaction was preheated to approximately 80 ℃ and then heated and stirred on 100 ℃ for 30 minutes. The mixture was obtained a liquid form.

2.2 Synthesis of bi-functional Benzoxazine resin (BA-a)

Mix bisphenol A, Paraformaldehyde and aniline at ratio 1:4:2 by molar were mixed in aluminum foil. It was stirred for 40 minute the temperature has been kept constant on 110℃. The mixture was obtained a pale yellow solid.

2.3 Synthesis of tri-functional Benzoxazine resin (Tris P-a)

Mix 1,1,1-Tris(4-hydroxyphenyl)ethane, Paraformaldehyde and aniline at ratio 1:6:3 by molar in aluminum foil. The process is same as bi-functional benzoxazine but the temperature was kept constant on 95-100 ℃ for 30 minute and then heat up to 130 ℃ for 30 minute. The mixture was obtained a pale yellow solid.

3. Modified asphalts

Asphalts grade 60/70 was mixed with benzoxazine resin and heated to $80\pm5^{\circ}$C by a stirrer at 500 rpm and mixed for 1 hour at the ratio of 0%, 3%, 6%, and 9% by weight. Then all samples were immediately cured at $190 \pm 5 \ ^{\circ}$C for 1 hr in an oven to crosslink the benzoxazine. The process of combination between polymer and asphalt is the same for all specimens.

4. Analysis of properties of the obtained benzoxazine-modified asphalts

- Chemical structure:

    - Fourier Transform Infrared Spectroscope (FTIR)

- Rheological properties:

    - Dynamic shear rheometer (DSR)

- Thermal properties :

    - Thermogravimetric analysis (TGA)

    - Differential scanning calorimeter (DSC)

- Thermomechanical properties :

    - Dynamic mechanical analysis (DMA)

- Physical properties

    - Morphology : Confocal laser scanning microscope (CLSM)

- Conventional test for asphalts.

    - Penetration

    - Softening point

    - Ductility

    - Toughness and Tenacity

    - Viscosity

5. Analyze and conclude the experimental results.

6. Prepare of the final report

CHAPTER II

THEORY

2.1 Asphalts

The term bitumen is used by European and Eastern countries, whereas the term asphalt is used by Americans. The sources of asphalt can be classified into two categories. First asphalt is obtained from petroleum crude oil. The second category includes the natural asphalt source [25]. Asphalt is an oil based substance consisting mainly of high molecular weight. It is a semi-solid, dark brown to black, thick, viscous mixture of heavy hydrocarbon materials, produced by removing the lighter fractions such as liquid petroleum gas, petrol, and diesel from heavy crude oil during the refining process or production of natural asphalt. Asphalt, which has thermoplastic nature, water resistance and adhesion toward most other substances, is a primary engineering material. Currently, there are many industries that use asphalt and products of the asphalt. Especially, building or traffic area uses asphalt in different form. Bitumen has uses that range from the construction of the pavements of roads, approximately 85% [26].

2.2 Chemical Composition of Asphalt

The chemical composition of asphalt is extremely complex and it varies widely according to the source of the crude oil from which the bitumen originates. In general, asphalt is a complex chemical mixture that is mainly composed of a large amount of hydrocarbons with minor amounts of structurally analogous heterocyclic species, some functional groups (heteroatom) containing sulfur, nitrogen and oxygen atoms and trace quantities of metals such as vanadium, nickel, iron, magnesium and calcium, which occur in the form of inorganic salts and oxides or in porphyries structures [2].

The most bitumen contains:

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

2.2.1 SARA classification of asphalt

Asphalt is usually classified based on its four major fractions namely, saturates, aromatics, resins, and asphaltenes [6]. Generally, these are commonly referred to by the SARA fractions. Originally, the classifications were carrying out by

column chromatography, using different adsorbing materials and solvents. Results of

SARA analysis of asphalt extracted by n-heptane solvents are shown in Figure 2.1.

```
                      ┌───────────┐
                      │  Asphalts │
                      └───────────┘
                          N-Heptane
         Soluble   ↓                    ↓   Insoluble
         ┌───────────┐            ┌──────────────┐
         │  Maltenes │            │  Asphaltenes │
         └───────────┘            └──────────────┘
              Liquid chromatography
         ↓                ↓              ↓
  ┌────────────┐   ┌────────────┐  ┌────────────┐
  │  Saturates │   │  Aromatics │  │   Resins   │
  └────────────┘   └────────────┘  └────────────┘
     N-hexane          Toluene      Methanol and
                                       Toluene
```
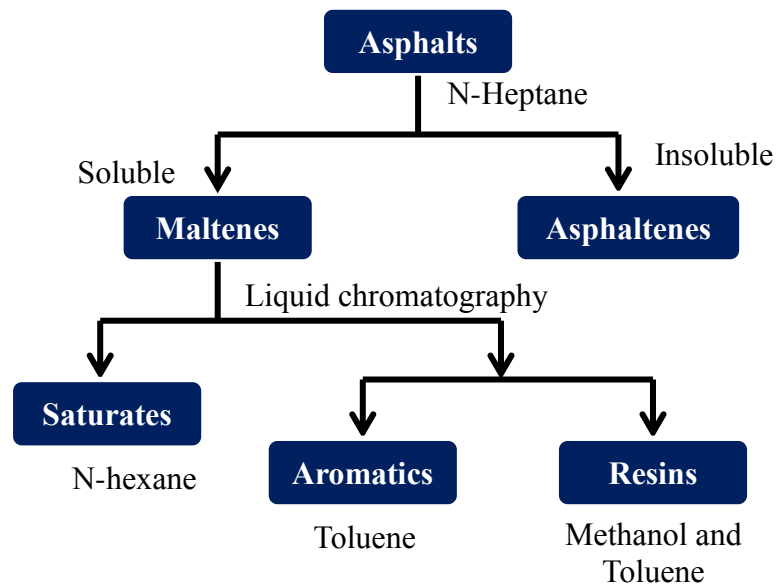
Figure 2.1 Schematic representation of the analysis for chemical composition of asphalt [2].

The technique used in SARA analysis is based on adsorbing the asphalt or its

fractions in a column packed with an activated adsorbent and then eluting a

particular fraction with a selective solvent in series. The fractions were then used for

further chemical analysis.

2.2.1.1 Saturates [2]

Saturates are non-polar viscous oils with a similar molecular weight range to aromatics. The saturate fraction may contain saturated normal and branched-chain hydrocarbons, saturated cyclic hydrocarbons (naphthenic hydrocarbons). Sometimes, a small amount of mono-ring aromatic hydrocarbons may also be observed in this fraction; however, the properties of these mono-ring molecules are determined by attached saturated hydrocarbon side chains. Saturates generally constitute 5% to 20% of the total asphalt. The chemical structure of saturates is shown in Figure 2.2.
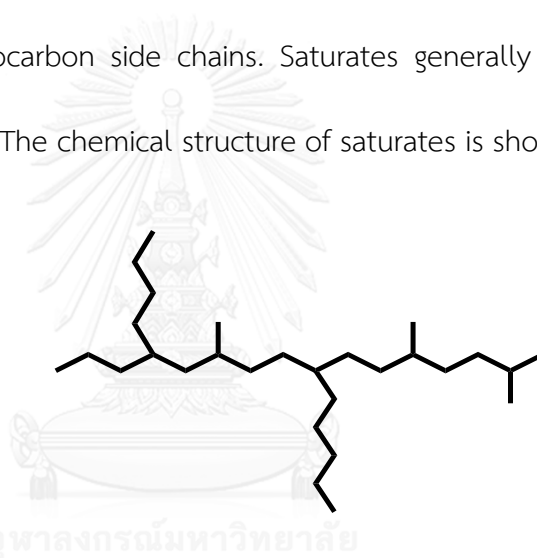
Figure 2.2 Chemical structure of saturates [2].

2.2.1.2 Aromatics [2]

Aromatics comprise the lowest molecular weight naphthenic aromatic compounds in the asphalt. They are dark brown viscous liquids that usually contain condensed nonromantic and aromatic ring systems and heteroatom sulfur, oxygen and nitrogen. Aromatics constitute 40% to 65% of the total asphalt and they represent the major proportion of the dispersion medium for the asphaltenes and

have a molecular weight in the range of 300 to 20,000. They give the adhesive properties of the bitumen. Their carbon skeleton is slightly aliphatic with lightly condensed aromatic. The chemical structure of aromatics is shown in Figure 2.3.
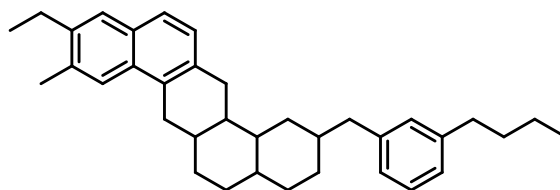
Figure 2.3 Chemical structures of aromatics [2].

2.2.1.3 Resins [2]

Resins are n-heptane soluble and are chemically similar to asphaltenes. They are dark brown solid or semi-solid and very polar in nature which makes them strongly adhesive. Resins are regarded as dispersing agents or peptizes for asphaltenes. Thus, the proportion of resins to asphaltenes can determine, to a degree, the solution (SOL) or gelatinous (GEL) character of the bitumen. The molecular weight ranges from 500 to 50,000. Resins work as stabilizers, which hold everything together in the bitumen. The chemical structure of resins is shown in Figure 2.4.
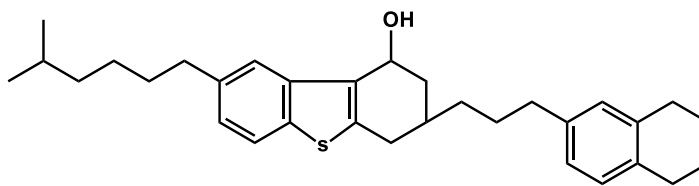
Figure 2.4 Chemical structures of resins [2].

2.2.1.4 Asphaltenes [2]

Asphaltenes are n-heptane insoluble black or brown amorphous solids containing, in addition to carbon and hydrogen, some nitrogen, sulfur and oxygen. The significant differentiating feature of this fraction is the preponderance of molecules with highly polarizable aromatic ring systems together with a high concentration of polar, heteroatom-containing functional groups.

Because of this, molecules in this fraction are strongly attached and are difficult to disperse even in polar solvents. The asphaltenes have a large effect on the rheological properties of bitumen. The increase of the asphaltenes content will lead to harder, more viscous asphalt with a lower penetration, higher softening point and consequently higher viscosity. Asphaltenes constitute approximately 5% to 25% of the asphalt. The chemical structure of asphaltene is shown in Figure 2.5.
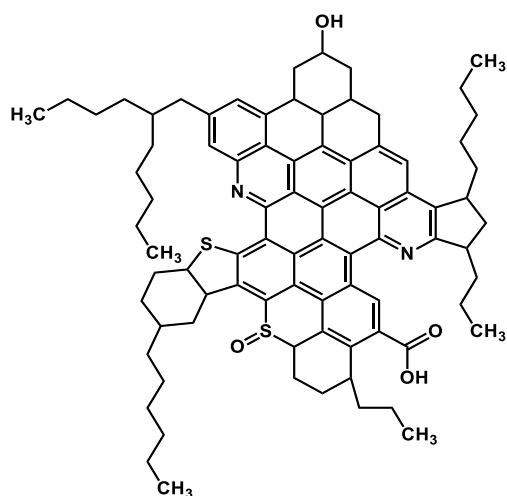
Figure 2.5 Chemical structure of asphaltene [2].

2.3 Microstructure of asphalt

The microstructure of asphalt is generally understood as multi-phase colloidal system. Asphalt classified into two categories sol-type bitumen and gel-type bitumen according to microstructure. In practice most asphalts are somewhere between these two states. A schematic representation of these two states is shown in Figure 2.6. In sol-type bitumens, asphaltene bitumens well dispersed within maltene continuum. In gel-type bitumen, the asphaltene micelles are not well dispersed and form large agglomerations. The degree of dispersion asphaltenes is controlled by the relative amounts of resins, aromatics and saturates.

As the ratio of aromatics increases, the dispersion of asphaltenes increases because of the aromatics form stabilizing layer around the asphaltene micelles.

The saturate oils have little solvent power in relation to the asphaltenes, so that as the saturate fraction increases, there is a great tendency for the asphaltenes to aggregate to form gel structure. However a high ratio of saturates tends to reduce viscosity because of their low molecular weight [2].
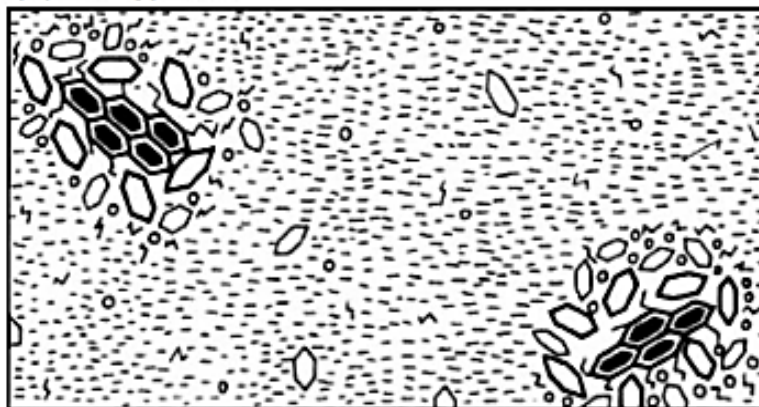
Figure 2.6 Schematic model representation of (a) sol-type bitumen, (b) gel-type of bitumen [2].

2.4 Viscoelastic Properties of Asphalts Material

Viscoelastic material defined as material, which store and dissipate mechanical energy in response by a mechanical stress. The asphalt cement is a viscoelastic materials and its mechanical behavior depend on both the temperature and the duration of loading. At low temperatures and short loading times asphalt cements behave as elastic solids, while at high temperatures and long loading times they behave as simple viscous liquids. At intermediate temperatures and loading times, the behavior is more complex.
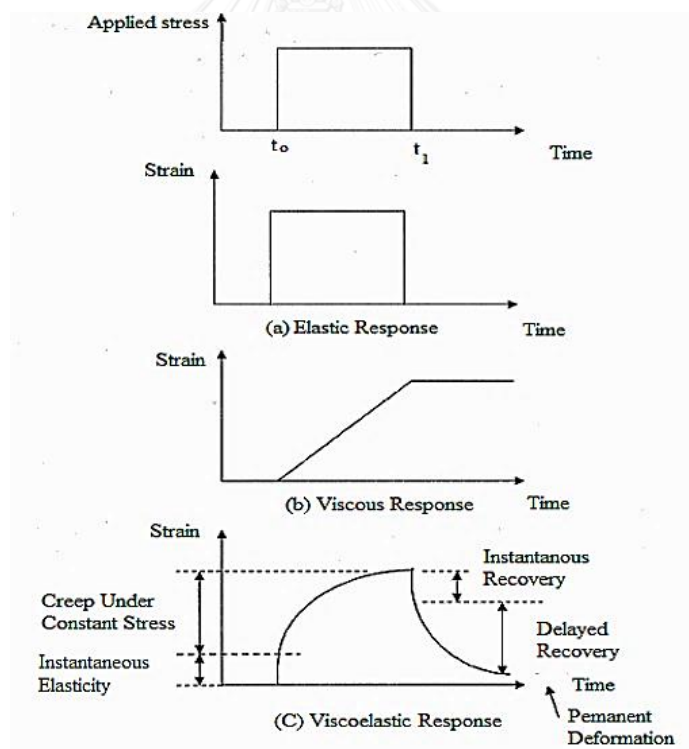
Figure 2.7 Response of elastic, viscous and viscoelastic material under constant stress loading [27].

The response of elastic, viscous and viscoelastic material under constant stress loading are presented in Figure (2.7). Figure 2.7 (a) shows that a constant load is applied to an elastic material, the strain of the material is proportional to the applied stress and when the applied stress is removed from the material, there is a complete recovery to the original position. Figure 2.7 (b) describes the behavior of a viscous material in which the strain of the material increases over time under constant stress. Figure 2.7 (c) demonstrates the behavior of a viscoelastic material in which a constant stress increases the strain over a long time and when the applied stress is removed, the material fails to attain its original position leading to permanent deformation [27].

2.5 Asphalt Rheology

Rheology is the study of material flow and deformation characteristics. In other words, rheology is the study of the relationship between stress and strain of materials. If a load is applied to a purely elastic material, the deformation produced will return to zero immediately after the removal of the stress. For a purely viscous material deformation increases as long as a stress is applied but this deformation remains at its maximum after removing the stress.

However, for a viscoelastic material such as asphalt, part of the deformation is recovered while part remains after removing the stress. The viscoelastic properties of asphalt are therefore a combination of those found for purely elastic and purely

viscous materials. Prior to any attempt to characterize the behavior of the bitumen, a thorough understanding of the structure and properties of its components is necessary [28].

2.5.1 The viscoelastic nature of asphalts

The DSR test is the most common test method to measure the stiffness and viscoelastic behavior of asphalt binder by applying dynamic shear loading (Figure 2.8). The complex shear modulus (G*) represents binder's stiffness. The DSR also measures the phase angle (δ) in order to determine the elastic response of the binder. The following equation is used to calculate G*.
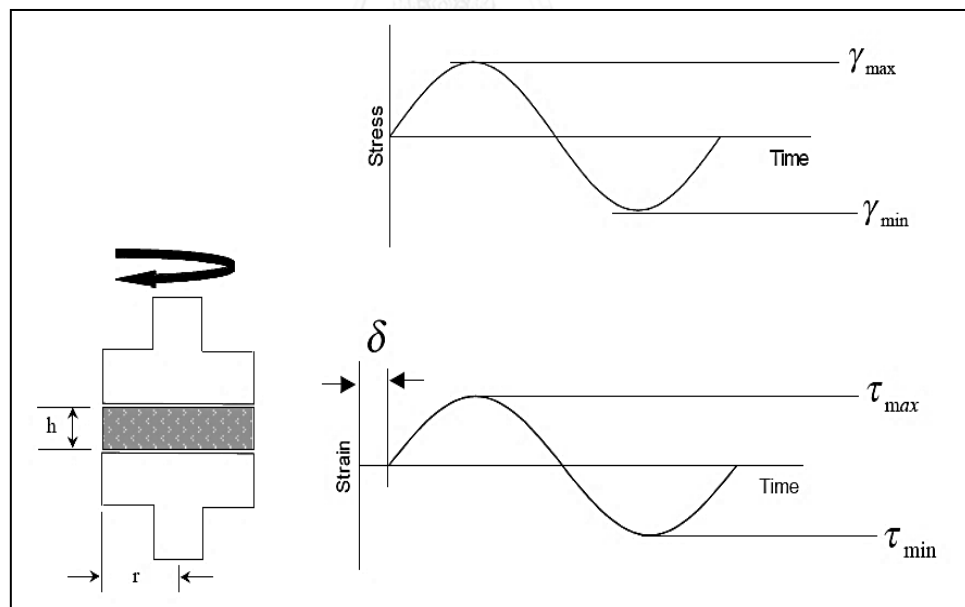
Figure 2.8 Dynamic oscillatory shear measurements using parallel plate geometry [29].

The applied stress and resulting strain are defined as follows:

$$\tau = \frac{2T}{\pi r^3} \tag{2.1}$$

$$\gamma = \frac{\theta r}{h} \tag{2.2}$$

The complex shear modulus, G* can then be calculated as follows:

$$G^* = \frac{\tau_{max} - \tau_{min}}{\gamma_{max} - \gamma_{min}} \tag{2.3}$$

Dynamic viscosity:

$$\eta^* = \frac{G^*}{\omega} \tag{2.4}$$

T	=	The applied torque (N. m)
r	=	The radius of the sample (m)
h	=	The thickness of the sample (m)
θ	=	The resulting deflection angle (rad)
γ	=	The resulting shear strain (%)
τ_{max}	=	Maximum applied shear stress
τ_{min}	=	Minimum applied shear stress
γ_{max}	=	Maximum resulting shear strain
γ_{min}	=	Minimum resulting shear strain
δ	=	Phase angle
ω	=	Angular frequency

Dynamic shear test may be conducted in two ways: controlled-stress and controlled strain. A controlled-stress test applies a sinusoidal varying stress and measures the magnitude and phase of the resulting strain. A controlled-strain test applies a sinusoidal varying strain to the sample and measures the magnitude and phase of the resulting stress.
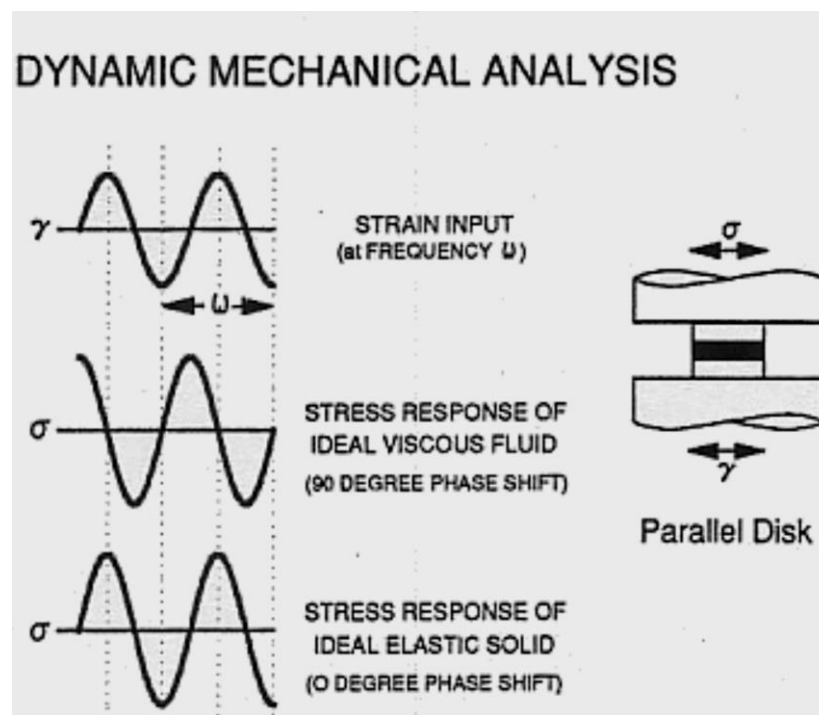
Figure 2.9 Dynamic shear analyses using parallel plate geometry [29].

The response to an applied shear strain is instantaneous and the resultant shear stress is in phase with the applied shear strain when the asphalt behaves as an elastic solid, whereas the resultant shear is 90° out of phase with the applied shear when the asphalts behaves as a viscous liquid.

The phase angle, **δ**, (Figure 2.9) varying between 0° and 90°, is the lag in the shear stress response compared to the applied shear strain, and therefore it is an important parameter to describe the viscoelastic behavior of asphalts.

In addition, the other three dynamic parameters: the storage modulus (elastic modulus), G', the loss modulus (viscous modulus), G", and the loss tangent, tan **δ**, are directly related to the complex modulus and the phase angle, and can be computed through a series of relatively simple equations given below:

Storage (Elastic) modulus

$$G' = G^* \cos \delta \tag{2.5}$$

Loss (Viscous) modulus:

$$G'' = G^* \sin \delta \tag{2.6}$$

$$\tan \delta = \frac{G''}{G'} \tag{2.7}$$

Rutting parameter:

$$\text{Rutting} = \frac{G^*}{\sin \delta} \tag{2.8}$$

Rutting parameter is a rheological parameter to analyze the properties of asphalt binders used in road pavement application which recommended by the Strategic Highway Research Program (SHRP) of the United State [29]. The relationships among complex shear modulus, storage modulus, loss modulus and phase angle can be shown schematically through a trigonometry of a right angle triangle as shown in Figure 2.10.
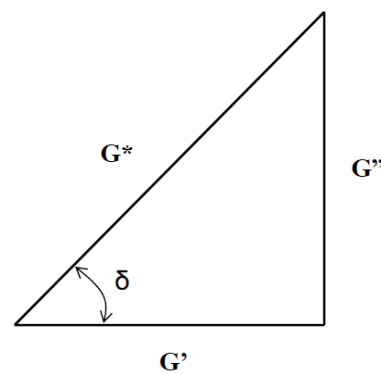
Figure 2.10 Relationship among dynamic complex modulus, storage modulus, loss modulus and phase angle [29].

The storage modulus, G', represents the in-phase component of complex modulus, whereas the loss modulus, G", represents the out-of-phase components of the complex modulus. It is noted that the elastic component of the response only represents part of the storage modulus, and the viscous response only represents part of loss modulus. Most real viscoelastic materials display a delayed elastic response, which is time dependent, but completely recoverable. They cannot be strictly interpreted as elastic and viscous modulus.

2.6 Common Permanent Deformation of Road Pavement

Pavement deterioration is the process by which defects develop in the pavement under the combined effects of traffic loading and environmental conditions.The four major categories of common asphalt pavement surface distresses are [30]:

1. Cracking

2. Surface deformation

3. Disintegration

4. Surface defects

2.6.1 Cracking

Fatigue cracking is commonly called alligator cracking. This is a series of interconnected cracks creating small, irregular shaped pieces of pavement. It is caused by failure of the surface layer or base due to repeated traffic loading (fatigue). Eventually the cracks lead to disintegration of the surface, as shown in Figure 2.11.
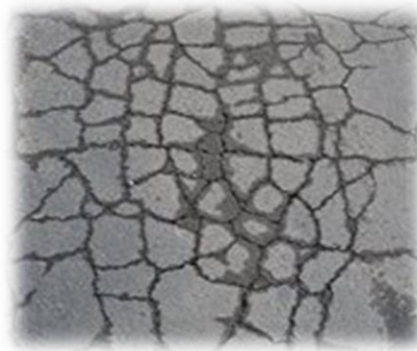
Figure 2.11 Fatigue cracking [31].

2.6.2 Surface deformation

Pavement deformation is the result of weakness in one or more layers of the pavement that has experienced movement after construction. The deformation may be accompanied by cracking. Surface distortions can be a traffic hazard. The basic type of surface deformation is rutting.

Rutting is the displacement of pavement material that creates channels in the wheel path. Very severe rutting will actually hold water in the rut. Rutting is usually a failure in one or more layers in the pavement. The width of the rut is a sign of which layer has failed. A very narrow rut is usually a surface failure, while a wide one is indicative of a subgrade failure. Inadequate compaction can lead to rutting. Figure 2.12 shows an example of rutting due to subgrade failure.

Figure 2.12 Rutting deformation [31].

2.6.3. Disintegration

The progressive breaking up of the pavement into small, loose pieces is called disintegration. If the integration is not repaired in its early stages, complete reconstruction of the pavement may be needed.

Potholes are bowl-shaped holes similar to depressions. They are a progressive failure. First, small fragments of the top layer are dislodged. Over time, the distress will progress downward into the lower layers of the pavement. Potholes are often located in areas of poor drainage, as seen in Figure. Potholes are formed when the pavement disintegrates under traffic loading, due to inadequate strength in one or more layers of the pavement, usually accompanied by the presence of water.

Figure 2.13 Potholes caused by poor drainage [32].

2.6.4. Surface defects

Surface defects are related to problems in the surface layer. The most

common types of surface distress are:

Figure 2.14 High severities raveling of asphalt surface [33].

1. Raveling

Raveling is the loss of material from the pavement surface. It is a result of insufficient adhesion between the asphalt cement and the aggregate. Initially, fine aggregate breaks loose and leave small, rough patches in the surface of the pavement. As the disintegration continues, larger aggregate breaks loose, leaving rougher surfaces. Raveling can be accelerated by traffic and freezing weather. Some raveling in chip seals is due to improper construction technique. This can also lead to bleeding. Repair the problem with a wearing course or an overlay.

2. Bleeding

Bleeding is defined as the presence of excess asphalt on the road surface which creates patches of asphalt cement. Excessive asphalt cement reduces the skid-resistance of a pavement, and it can become very slippery when wet, creating a safety hazard.

This is caused by excessively high asphalt cement content in the mix, using asphalt cement with too low a viscosity, too heavy a prime or tack coat or an improperly applied seal coat. Bleeding occurs more often in hot weather when the asphalt cement is less viscous and the traffic forces the asphalt to the surface.

Figure 2.15 Bleeding of asphalt surface [33].

2.7 Aims of Polymer Modified Asphalts

The main reasons to modify asphalts with polymers could be summarized as follows [2, 26]:

− To obtain softer blends at low service temperatures and reduce cracking.

− To reach stiffer blends at high temperatures and reduce rutting.

− To reduce viscosity at layout temperatures.

− To increase the stability and the strength of mixtures.

− To improve the abrasion resistance of blends.

− To improve fatigue resistance of blends.

− To improve oxidation and aging resistance.

− To reduce structural thickness of pavements.

− To reduce life costs of pavements.

2.8 Classification of Asphalt Additives

Asphalt modifiers are divided to different main groups such as polymers (elastomeric, plastomeric and thermosetting), fillers, fibers, and waste material. These additives vary significantly in their physical and chemical characteristics and are expected to have widely variable effects on asphalt concrete pavement performance. Asphalt additives increase the stiffness of the mix at higher temperatures, decrease the stiffness at lower temperatures and increase the elasticity in the medium range temperatures. Types of asphalt additives showed in Table 2.1.

Table 2.1 Types of asphalt additives [2]

Type of Modifier	Purpose	Example
Filler	- Fill voids - Increase stability - Improve bond between aggregate and binder	- Lime - Portland Cement - Fly Ash
Elastomers	- Increase stiffness at higher temperature - Increase elasticity at medium range temperature to resist fatigue cracking. - Decrease stiffness at lower temperature to resist thermal cracking.	- Natural rubber - Styrene-butadiene-styrene (SBS) - Crum rubber (TR) - Styrene-butadiene-rubber (SBR)

Fiber	- Improve tensile strength - Improve cohesion - Allow for higher asphalt content within drain down	- Asbeston - Polyester - Fiberglass
Plastomers (Thermoplastics)	- Increase high temperature performance - Increase structural strength - Increase resistance to rutting	- Polyvinyl chloride (PVC) - Ethyl-vinyl-acetate (EVA) - Ethylene propylene (EPDM)
Thermosetting Polymers	- Very resistant to chemical attack - Less temperature susceptible - Higher flexibility - Cracking resistance - Better adhesivity	- Epoxy resin - Polyurethane resin - Acrylic resin - Phenilic resin
Waste Material	- Replace aggregate with cheaper product	- Recycle polymer

2.9 Polymer Modified Asphalt Binders

In recent years, an increase in traffic loading including, axle load, tire pressure, and number of passes, has shown some limitation in asphalt binder performance. Although asphalt binder has performed satisfactorily on a wide range of roads in the past, dramatic failures in hot-mix asphalt (HMA) have been reported. This may be related to the binder, the mix design, and the aggregate. One solution for limiting

these failures is the use of polymers as modifiers for asphalt binder in pavements exposed to severe climatic conditions and increasingly heavy truck traffic [34].

Figure 2.16 Hot mix asphalt construction [35].

The idea that polymers will result in better long-term performance of the binder is a too simple view of a very complex situation. Unless rheologists can define the suitable type of polymer for each application and the suitable extent of the modification, actual effects of polymer on binder performance would be left to chance. The use of polymer modified binders is increasing rapidly throughout the world.

Polymer-modified asphalts (PMA) derive their technological and conceptual origin from the need for enhancing the performance and durability of asphaltic materials as well as their adhesion to mineral aggregates. PMAs are produced by mixing asphalt and polymer (usually 3–7% by weight); they were developed because conventional flexible pavements had become inadequate in the last few decades

because of a dramatic increase in traffic intensity and load, which shortened their in-service life, thereby increasing the frequency of road maintenance and re-paving required. Modification is normally achieved through simple mechanical dispersion of the polymer in molten asphalt under high shear.
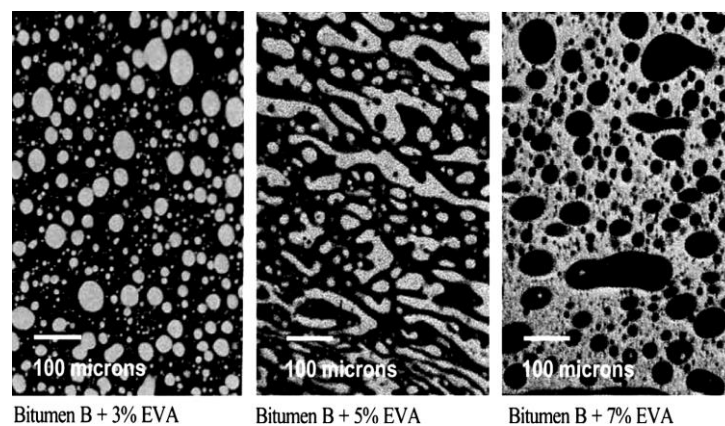
Figure 2.17 Fluorescent images of EVA modified bitumen with various contents (by weight) of EVA [3].

Approximately 75% of all modifiers are elastomeric, 15% are plastomeric, and the remaining 10% are either rubber or miscellaneous under these three categories. The polymers used in asphalt technology may be listed according to their importance in three main categories [4]:

➢　Thermoplastic elastomers (TPE)

➢　Plastomers

➢　Reactive polymer

The longer life and better quality of PMA-based pavements usually lead to both economical and safety requirements that overcome the initial investment, which is higher with respect to the use of conventional unmodified binders. Since the introduction of PMA in the paving industry, researchers have attempted to use almost all available polymers as asphalt modifiers, including thermoplastics and elastomer [3, 14].

The mechanism of resistance to deformation is different between elastomers and plastomers. The load-deformation behavior of elastomers is similar to that of a rubber band, i.e., increasing tensile strength with increased elongation and ability to recover to the initial state after removal of load. Under a given load, elastomers deform faster than plastomers, gain more strength during elongation, and recover elastically after withstanding large strains. On the other hand, exhibit high early strength but are less flexible and more prone to fracture under high strains than elastomers.
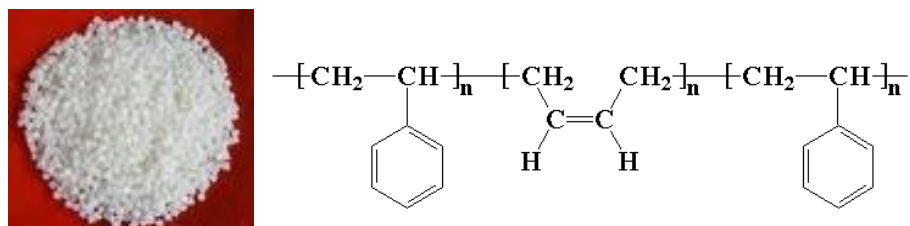
Figure 2.18 Structure of styrene–butadiene–styrene (SBS) [36].

Examples of polymers widely used in flexible pavements are the thermoplastic rubbers, styrene-butadiene-styrene (SBS), an elastomer, and ethylene vinyl acetate (EVA), a plastomer. However, the produced PMA should satisfy a long list of requirements including appropriate mechanical properties, storage stability and high-temperature viscosity compatible with the traditional road-building processes and apparatus, and reasonable cost.

Researchers attempted various ways to remove these drawbacks. Some technical developments for removing drawbacks such as saturation, sulfur vulcanization, adding antioxidants, using hydrophobic clay minerals, functionalization and application of reactive polymers [3].The added functional groups are usually expected to interact with some components of bitumen in various ways such as forming hydrogen bonds or chemical bonds, which may improve the compatibility to some extent.

For instance, functionalized SBS copolymers by respectively adding amino and carboxylic acid groups during synthesis these functional groups could improve the compatibility of SBS copolymers with bitumen without significant influences on their other properties. Meanwhile, other resarchers functionalized polymer modifier by grafting. Maleic anhydride (MAH), methacrylic acid and glycidyl methacrylate (GMA), which are structured in Figure 2.19, were respectively attempted to graft some

currently used polymer modifiers and they were all found to be able to improve the

storage stability of the PMA even with some other enhanced properties [37, 38].
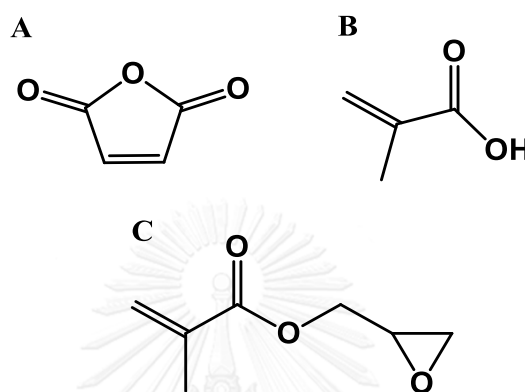
Figure 2.19 Structures of: (A) maleic anhydride (MAH); (B) methacrylic acid; and (C)
glycidyl methacrylate (GMA). [3]

2.10 Modified Asphalts by Thermosetting

Currently, several resrecahs have been studied using themosetting polymers

to modified asphalt including epoxy resin , polyurethane resin, acrylic resin and

phenolic resin [2]. Thermosetting polymers have potential applications such as

adhesives, coatings, and electric and electronic materials that originate from their

network structures. These structures are responsible for dimensional stability,

chemical resistance, and improved thermal properties.

2.10.1 Benzoxazine resin

Benzoxazine-based materials have recently been developed as a new type phenolic system in order to overcome various short-comings of conventional phenolic resins. Phenolic resins are presented in many industrial application and products such as fiber-forced composites, scratch resistant coatings. Although these systems have significant features that including high strength level of thermal and mechanical behaviors, flame retandancy and resistance against various solvents, there are some noticeable problems.

For instance, these conventional materials are brittle, have poor shelf life, acid or base catalysts are often used for the preparation of resin. Using of catalysts in this case leads to corrode the processing equipment, release by products (such as water, ammonia compounds) and formation of micro voids during curing.

First synthesis of benzoxazines was reported by Holly and Cope in 1940s by using condensation reaction of primary amines with formaldehyde and phenol [23]. But the potential use of benzoxazines has been recognized recently. So these materials have an increasing concern in many applications due to the fact that become a new type of thermoset phenolic resins with attractive features as follow:

(i)   Near zero volumetric change upon curing.

(ii)   Low water absorption.

(iii)   High glass transition temperature

(iv)   Good mechanical properties.

(v)   Good interfacial adhesion

(vi)   No strong acid catalysts required for curing.

The structure of phenol and amine can be altered, designed and functionalized to synthesize benzoxazine monomers to offer a wide range of applications. But, the slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor solubility of the precursors are the major disadvantages associated with this procedure.

The use of an organic solvent also increases the cost of the products and causes environmental problems. Furthermore, the solvent residue in the precursors also leads to problems during processing of the benzoxazine resins. To overcome these shortcomings, solventless synthesis in the melt state was developed [39]

In this study will use a benzoxazine resin which various functional consist of mono-functional, di-functional and tri-functional based on multifunctional phenols on the final properties of the asphalt. Benzoxazine resin can be classified into a mono-functional, a di-functional type, and tri-functional depending on the type of phenol derivative.

2.10.2 Mono-functional benzoxazine monomers

Condensation reaction of primary amines with formaldehyde and substituted phenols for the synthesis of well-defined benzoxazine monomers was reported. According to the reported procedure, this reaction was performed in a solvent in two-steps. It was found that the benzoxazine ring reacts preferentially with the free ortho positions of a phenolic compound and forms a mannich bridge. The synthetic procedure of the mannich condensation for benzoxazine synthesis in a solvent proceeds by first addition of amine to formaldehyde at lower temperatures to form an N,Ndihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the elevated temperature to form the oxazine ring [40].

2.10.3 Bi-functional and multi-functional benzoxazine monomers

Curing of mono-functional benzoxazines with phenol resulted in the formation of only oligomeric structures with average molecular weight around 1000 Da. Actually, there is no convincing evidence reported for the thermal dissociation theory, though it was mentioned in the literature. Moreover, it was reported that the reduction of reactivity is due to the hydrogen bonding formation. Such phenomenon was observed in the temperature range below where reverse mannich reaction occurs in benzoxazine chemistry [40]. To overcome this limitation, a new class of bi-

functional or multifunctional benzoxazine monomers have been developed, and their curing into phenolic materials with the ring opening reactions being initiated by dimers and higher oligomers in the resin composition. The precursor that used varied [1-59] phenol, formaldehyde and aniline were polymerized as shown in Figure 2.20.
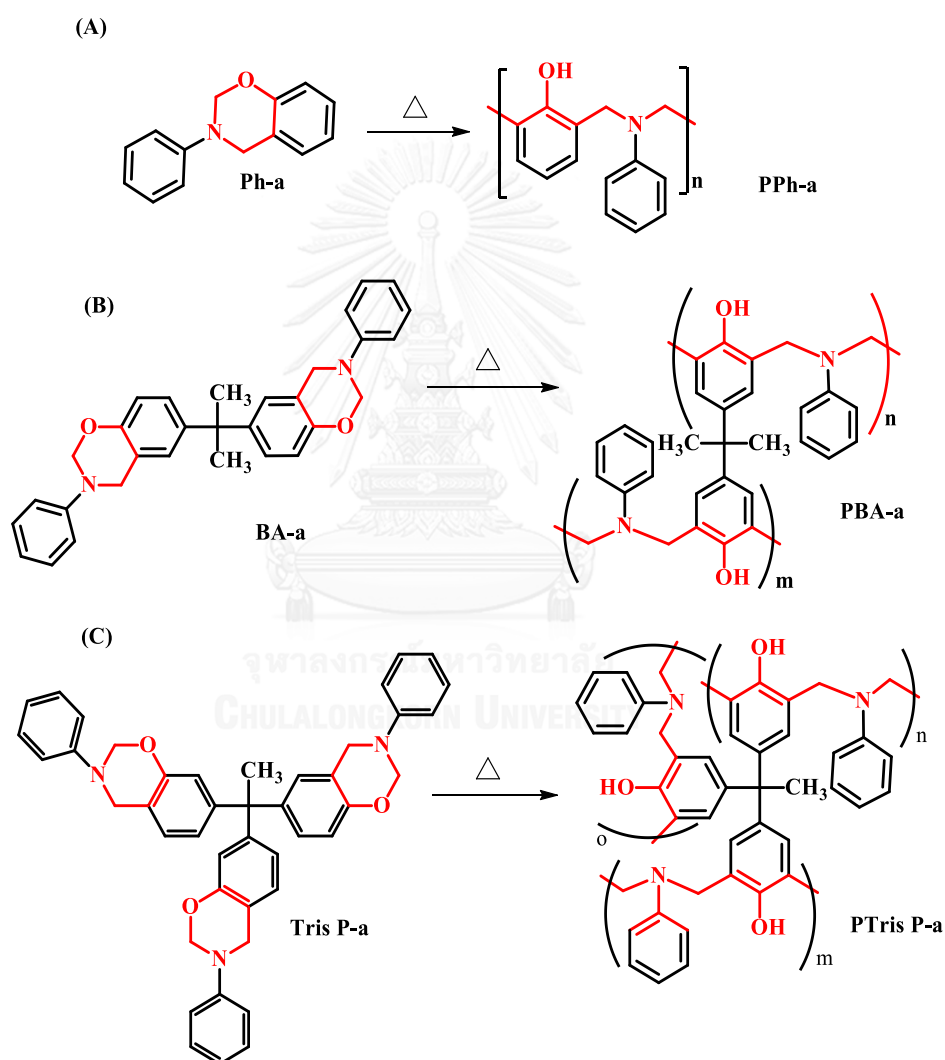
Figure 2.20 Ring opening polymerization of Ph-a (A) BA-a (B), and Tris P-a monomers(C) [23, 59].

CHAPTER III

LITERATURE REVIEWS

A. Oumpancharoen and S. Rimdusit, 2013 [24] studied Benzoxazine-modified asphalt for pavement applications. Asphalt grade 60/70 was mixed benzoxazine resin (Figure 3.1) and heated to 80±5 ℃ by a stirrer at 500 rpm for 1 h at the ratio of 0-9 % weight. Also, the effects of curing temperature at 150-190 ℃ on rheology, physical and mechanical properties.
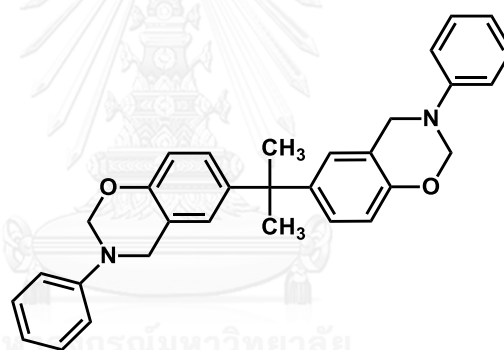
Figure 3.1 Bi-functional benzoxazine BA-a [24].

The DSC thermogram illustrated that proper curing conditions can provide highest temperature and mechanical properties as 190 ℃ for 1 hour when compare with neat asphalt. In addition, the degradation temperature at 800 ℃ when benzoxazine contents increased can be develop.

Figure 3.2, the rheological properties revealed viscosity at 60 °C, storage and

loss moduli are increased when polymer contents increased.
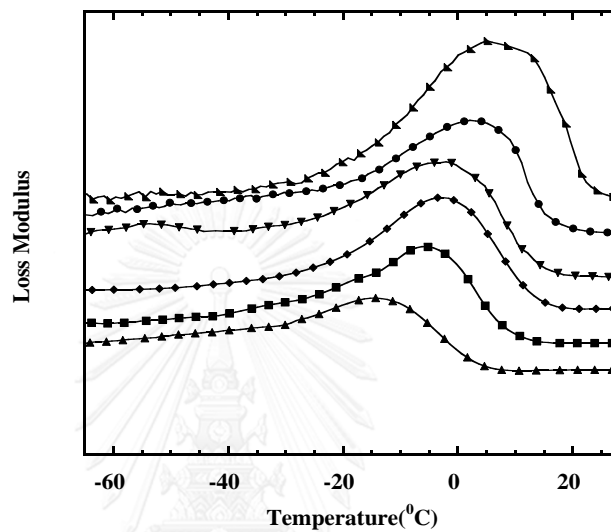
Figure 3.2 Overlay plot of DMA thermograms of loss modulus of benzoxazine-
modified asphalt: (▲) neat asphalt, (■) 1wt%, (♦) 3wt%, (▼),5wt%,(●) 7wt%, (◤)
9wt% [24].

Furthermore, the maximum temperature is considered with rutting parameter

which increasing benzoxazine contents can influence higher maximum temperature

increased, shown in Figure 3.3. Moreover, the softening point and penetration index

were increased while penetration values were decreased upon benzoxazine contents

increased.
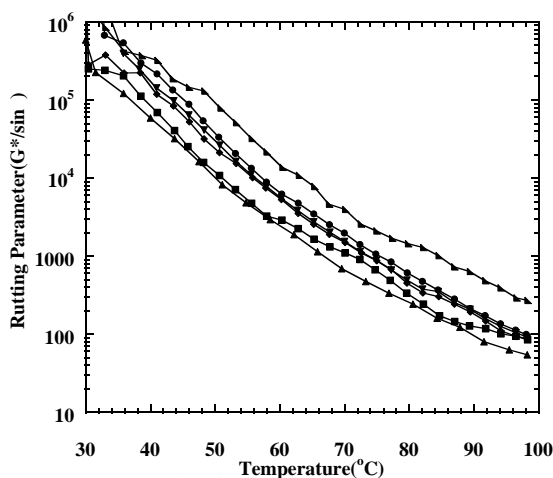
Figure 3.3 Rutting parameter of benzoxazine-modified asphalt: (▲) neat asphalt,(■)1wt%, (♦) 3wt%, (▼) 5wt%, (●) 7wt%, (◤) 9wt% [24].

J. Yu, et al, 2009 [5] studied laboratory investigation of the properties of asphalt modified with epoxy resin. In this work, asphalt 60/80 pen grade was mixed at 170±5 °C with 3% by weight of SBS for 60 min. After that, the epoxy resins with curing agent were added into the blend of and mixed by stirrer 500 rpm for 30 min. Epoxy-asphalt with 10, 20, 30, 40 and 50 % epoxy resin including curing agent were characterized (the ratio of curing agent to epoxy resin was 7.5 : 10 by % weight).
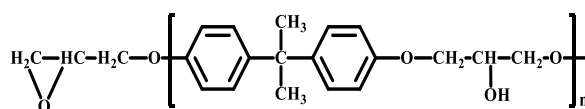
Epoxy resin: MTHPA:
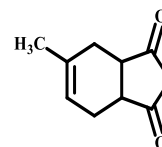
The molecule structure of epoxy resin and acid anhydride.
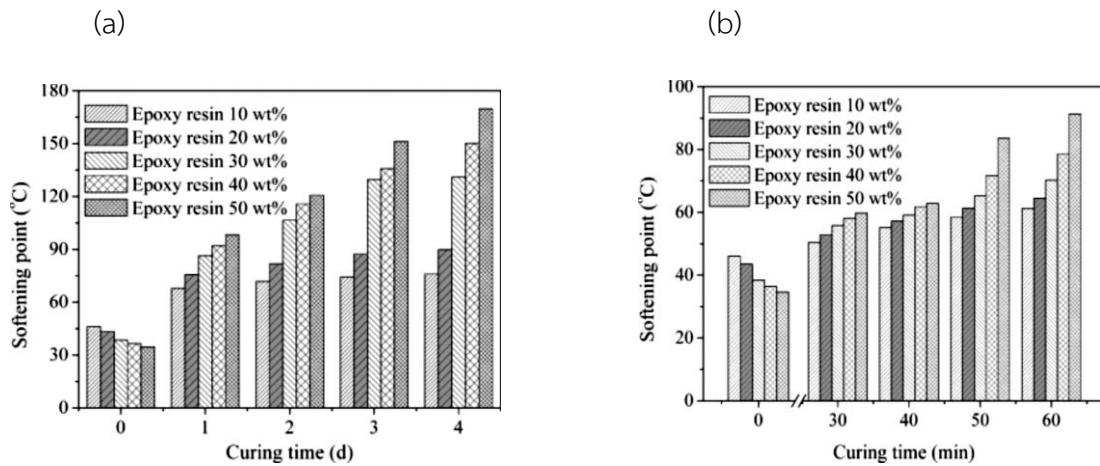
Figure 3. 4 Effect of curing temperature on softening point at 120 $^{\circ}$C (a) and 60 $^{\circ}$C (b) [5].

The effects of epoxy resin contents, ratio of curing agent to epoxy resin and curing temperature on properties of epoxy asphalt were investigated. The effect of curing temperature and time on property of epoxy asphalt was assessed by softening point. The curing conditions are as following:

(1) The sample was test directly when it was prepared

(2) The sample was test after different curing time at 120 $^{\circ}$C.

(3) The sample was test after different curing time at 60 $^{\circ}$C.

Results indicated that epoxy resin and epoxy asphalt showed similar curing efficiency. Epoxy asphalts can be cure at 120 or 60 ℃ (Figure 3.5) and its viscosity at 120 ℃ can meet the demands of asphalt mixture mixing and paving.
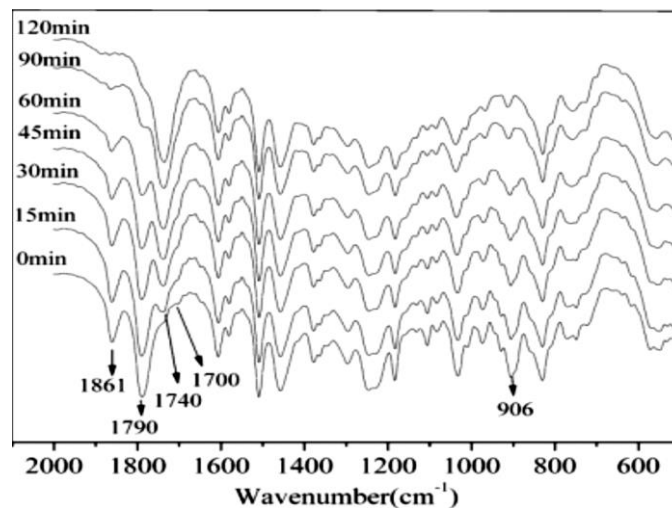
Figure 3.5 FTIR spectra of epoxy asphalt for different curing time at 120 $^{\circ}$C [5].

The chemical reaction of epoxy resin in epoxy asphalt is slow and reaction occurs not only with the curing agent but also carboxylic acid in epoxy asphalt as shown in Figure 3.5, gives FTIR spectra of modified asphalt with 40 % epoxy resin during curing at 120 $^{\circ}$C. Epoxy asphalt that cured at the beginning also showed a tiny peak around 1700 cm^{-1}, which should be attributed to carbonyl or carboxylic of asphalt. The most important of these peaks is that of the epoxy band at 906 cm^{-1}. Thus, the change of epoxy group peak was followed at 120 $^{\circ}$C. After cure reaction began, the peak value of characteristic acid anhydride bands at 1861 cm^{-1} and 1790 cm^{-1} and the epoxy resin characteristic band at 906 cm^{-1} decreased with curing time,

and a new band at 1740 cm^{-1} appeared, which was attributed to ester carbonyl of cured product.

Figure 3.6 gives the mechanical properties revealed that the tensile strength increased significantly when the contents of epoxy resin were more than 30 wt %, which is attributed to the formation of continuous networks structure in epoxy asphalt. But the elongation at break of epoxy asphalt decreased as the epoxy resin concentration increased.
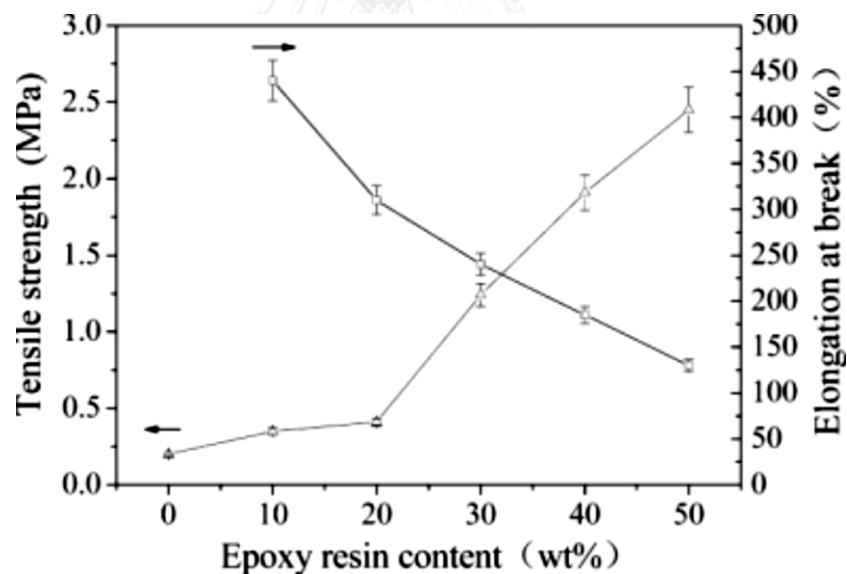
Figure 3.6 Effect of epoxy resin content on mechanical property [5].

C. Peiliang et al, 2010 [19] studied effect of epoxy resin contents on the rheology propoties of epoxy-asphalt blends. Asphalt 60/80 pen grade was mixed at 170±5 ℃ with 3% by weight of SBS for 60 min. After that, epoxy resin with curing

agent were added into blend and mixed by stirrer 500 rpm for 30 min. Epoxy-asphalt with 10, 20, 30, 40 and 50 % epoxy resin including curing agent was characterized. The molecular structure of epoxy resin and curing agent are shown in Figure 3.4. In this study, the effects of epoxy resin contents on rheological properties of epoxy-asphalt binders were tested using dynamic shear rheometer compared to original asphalt binder. The complex modulus of epoxy-asphalt containing 20 wt % epoxy resin is order of magnitude higher than the original ones is displayed in Figure 3.7.
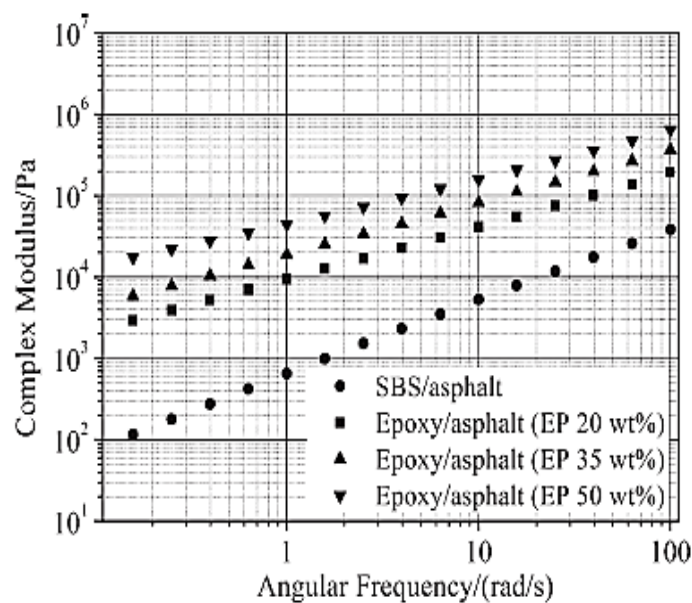
Figure 3.7 Effects of frequency on the G* of asphalt and epoxy-asphalt at 60°C [19].

Epoxy resin also affects phase angle significantly, and the higher the epoxy resin contents the higher effect. Moreover, the increased rut resistances at high

temperature Figure 3.8 shown the maximum temperature of original asphalt is ~75℃

whereas for epoxy-asphalt binder containing 20 wt % epoxy resins the value is 96℃.
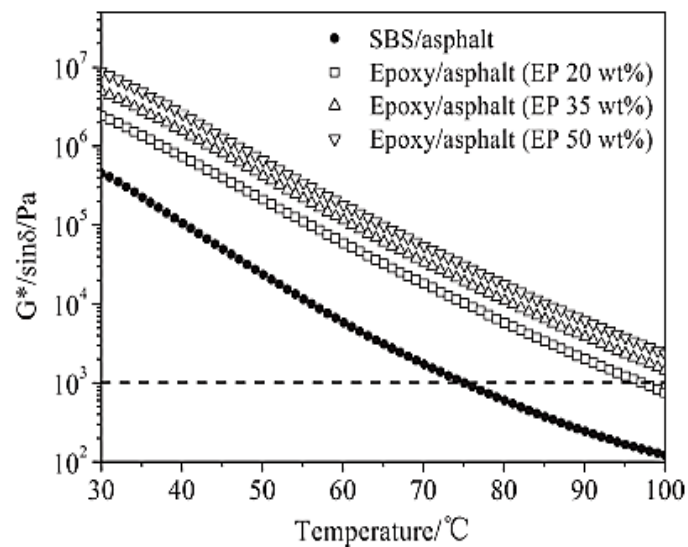
Figure 3.8 Relation of temperature and G*/sin δ at 10 rad/ sec asphalt and epoxy-
asphalt [19].

Kang et al, 2015 [21] studied rheological behaviors of epoxy asphalt binder in

comparison Y of base asphalt binder and SBS modified asphalt binder. The structure

of SBS shown in Figure 3.9 and epoxy resin, curing agent, shown in Figure 3.4.
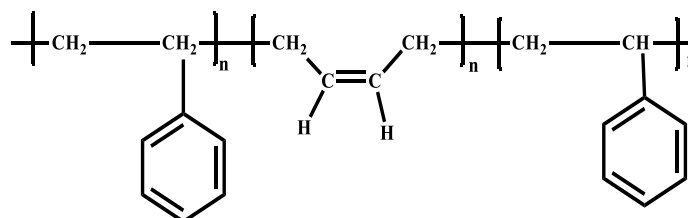
Figure 3.9 The structure of Styrene-butadiene-styrene (SBS)

Complex modulus of base asphalt (the black), SBS modified asphalt (the blue) and epoxy asphalt (the red) is covered 8, 7 and 3 orders of magnitude from -30°C to 120 °C, respectively. Thus, both base asphalt and SBS modified asphalt experience the whole process from hard solid to viscous elastic liquid, and eventually to viscous (Newtown) liquid, but epoxy asphalt retains solid state from beginning to end.
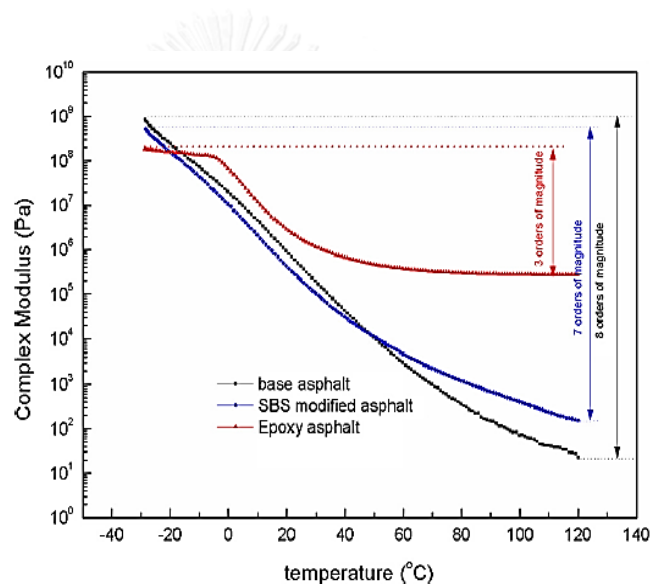
F**igure 3.10** Complex modulus with temperature curves of base, SBS and epoxy asphalt [21].

When comparing the first two binders, the thermal stability of SBS modified asphalt is better than that of base asphalt because the higher modulus is in the range of 50 °C to 120 °C and the lower modulus is at temperatures of below 50°C as shown in the Figure 3.10.

Furthermore, the result of creep and recovery test were more suitable for characterization of anti - rutting ability of asphalt binders than rutting factor, G^* / sin δ. Creep and recovery experiments show that epoxy asphalt was completely elastic after 100 loading–unloading circles, which implies that epoxy asphalt has a remarkable anti-rutting potential, on the contrary, base asphalt binder and SBS modified asphalt binder are in the state of newton liquids under the same experimental conditions as shown in Figure 3.11.
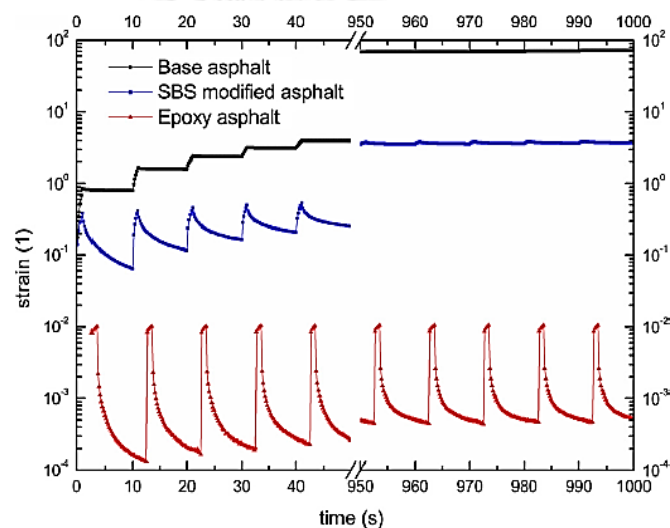
Figure 3. 11 Creep and recovery curves of base, SBS and epoxy asphalt
(60 °C, 300 Pa) [21].

V. Bulatović et al, 2014 [37] studied rheological properties of bitumen modified with ethylene butylacrylate glycidylmethacrylate. This article presents the characterization of properties of two bitumen sources (BIT 70/100,B1 and BIT 50/70,B2) modified with two types of reactive polymers, both are ethylene

butylacrylate glycidylmethacrylate, Elvaloy AM and Elvaloy 4170 with a different

percentage of reactive functional group, glycidylmethacrylate, GMA 1.6 and 1.9% by

weight. The reactive polymer modifications increase the complex modulus and the

complex viscosity of both bitumens, mainly at high temperature, while very little

change is noted at lower temperature that indicate a reactive polymer gives stiffness

and enough rigidity to the bitumen so that it does not flow at high temperatures.

The addition of reactive polymers to both bitumens reduces the phase angle, and

Elvaloy PMBs show better elasticity at higher temperatures.
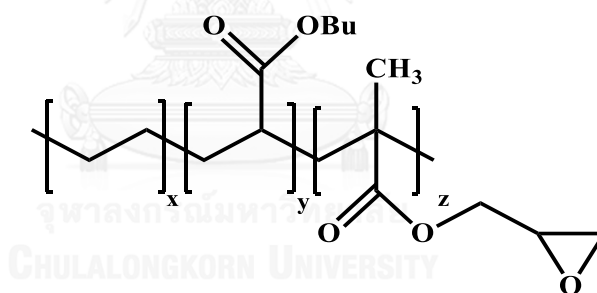
Figure 3.12 The structure of ethylene butylacrylateglycidylmethacrylate (EBAGMA)
[37].

The effect of reactive polymers, Elvaloy AM and Elvaloy 4170, on the

conventional properties of the base bitumens are shown in Table 3.1

.

Table 3.1 Conventional properties of BITs and Elvaloy PMBs.

Properties	B1	B2	B1/AM 1.6	B1/AM 1.9	B1/4170 1.6	B1/4170 1.9	B2/AM 1.6	B2/AM 1.9	B2/4170 1.6	B2/4170 1.9
Before RTFOT										
Penetration (25°C, 1/10 mm)	71.1	62.9	64.6	66.7	60.6	62.7	55.4	55.4	54.8	
Softening point (°C)	46.7	48.6	55.5	55.0	57.2	66.0	55.2	57.0	59.6	
Penetration index, PI (−)	−1.24	−1.03	0.77	0.72	0.95	2.77	0.27	0.67	1.18	
Elastic recovery (%)	−	−	68.0	69.0	72.5	74.5	68.5	72.0	72.5	
After RTFOT										GEL
Penetration (25°C, 1/10 mm)	44.0	38.7	38.2	40.8	38	GEL	34.0	36.0	35.9	
Softening point (°C)	51.1	54.7	59.0	59.2	64.0	GEL	61.0	65.5	67.7	
Penetration index, PI (−)	−1.22	−0.67	0.19	0.38	1.12	GEL	0.32	1.26	1.69	
Elastic recovery (%)	−	−	70.0	62.5	70.5	GEL	60.0	61.0	68.5	

All Elvaloy PMB samples have higher critical temperatures, i.e. better resistance to permanent deformation. Elvaloy PMBs with BIT 50/70 have higher critical temperatures compared to PMBs with BIT 70/100.

In addition, Figure 3.13 showed all the samples investigated in this study were homogeneous and there was no difference in the softening point value between the top and the bottom of the tube. Due to a chemical reaction between the polymer and the bitumen, the phase separation was avoided. From the results, we can conclude that all Elvaloy PMB samples improved their storage stability because of the chemical reaction between the polymer and bitumen as shown in Figure 3.14.
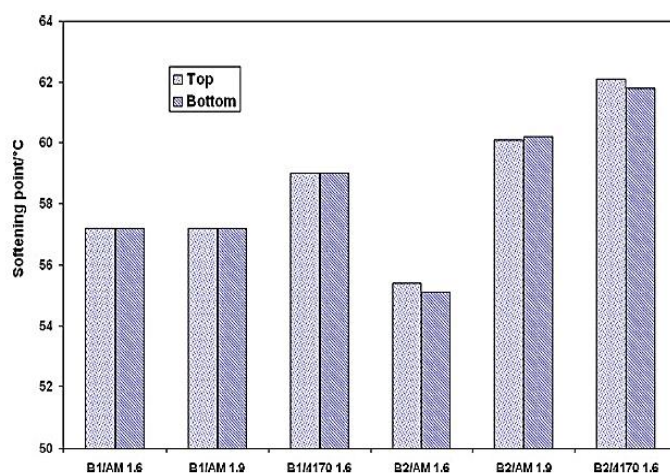
Figure 3.13 Storage stability of all Elvaloy PMB samples

In IR spectra of Elvaloy PMB (B1/AM 1.6), the bands characteristic of the epoxy groups at 943, 907, and 849 cm^{-1} disappear, while the intensity of the band at 1163 cm^{-1} is decreased. This indicates that the epoxide ring is open and chemical reactions between the carboxylic acid group in asphaltenes from BIT and Elvaloy occur. The same reaction is present in all investigated Elvaloy PMBs.
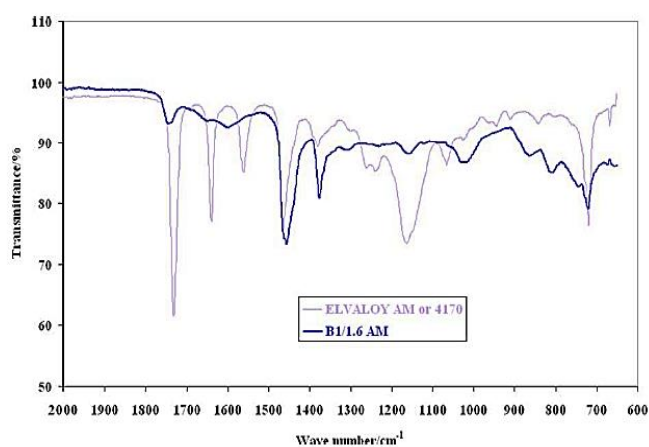
Figure 3.14 FT-IR spectrum for bitumen modified with ELVALOY.

CHAPTER IV

EXPERIMENT

4.1 Materials

The base asphalt with 60/70 penetration grade was kindly supported by IRPC Co., Ltd. Table 4.1 shows the properties of asphalt 60/70. Phenol (Sigma Aldrich, 99%), bisphenol-A (PTT Phenol Co., Ltd., polycarbonate grade), 1,1,1 tris(4-hydroxyphenyl)ethane (Sigma Aldrich 99%), para-formaldehyde (Merck Company, AR grade), aniline (Panreac Quimica SA Company, AR grade) which were used without purification.

Table 4.1 Specification of asphalt penetration grade 60/70.

Property	Data
Penetration, 25°C	68 °C
Softening point (°C)	46 °C
Ductility (cm), 25°C	100 cm

4.2 Benzoxazine Resin Preparations

4.2.1 Synthesis of mono-functional Benzoxazine resin (Ph-a)

Phenol, paraformaldehyde and aniline were mixed at ratio of 1:2:1 by molar. First, the reaction was preheated to approximately 80 °C and then heated and stirred mechanically at 100 °C for 30 minutes. The Ph-a monomer was obtained as yellow fluid. The chemical structures of Ph-a monomer is shown in Figure 4.1.

4.2.2 Synthesis of bi-functional Benzoxazine resin (BA-a)

Bisphenol-A, paraformaldehyde and aniline were mixed at ratio of 1:4:2 by molar and stirred for 30 minutes at the temperature 110 °C. The BA-a was obtained as pale yellow solid. The BA-a monomer was obtained as yellow fluid. The chemical structures of BA-a monomer is shown in Figure 4.2.
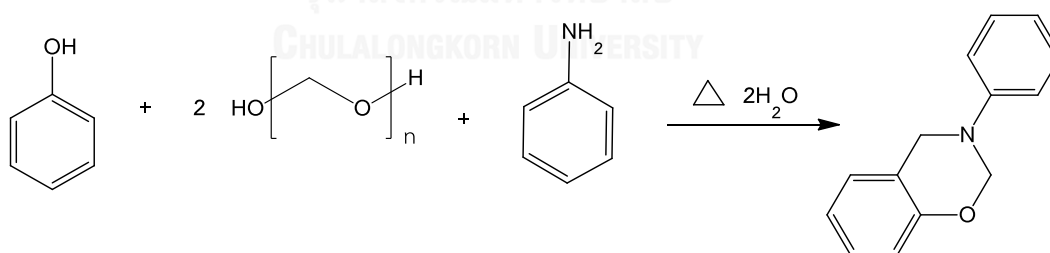
Figure 4.1 Mono-functional benzoxazine monomer synthesis (Ph-a) [40].
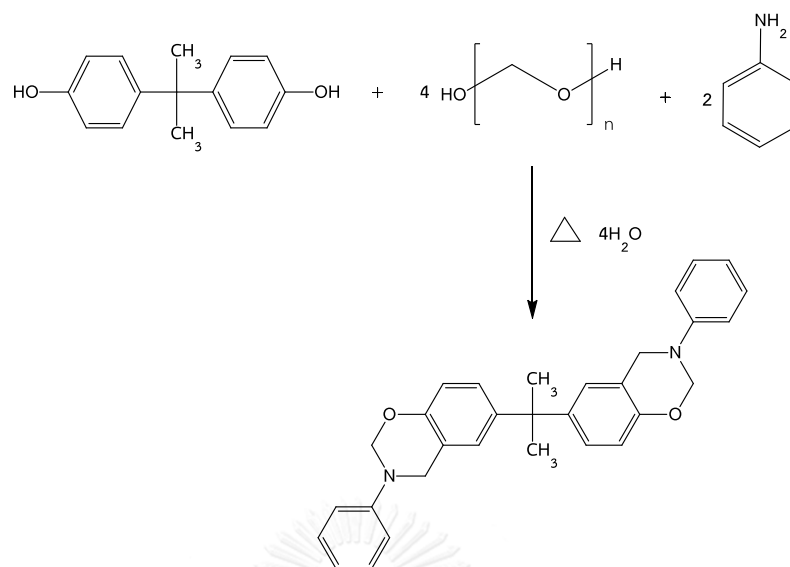
Figure 4.2 Bi-functional benzoxazine monomer synthesis (BA-a) [55].
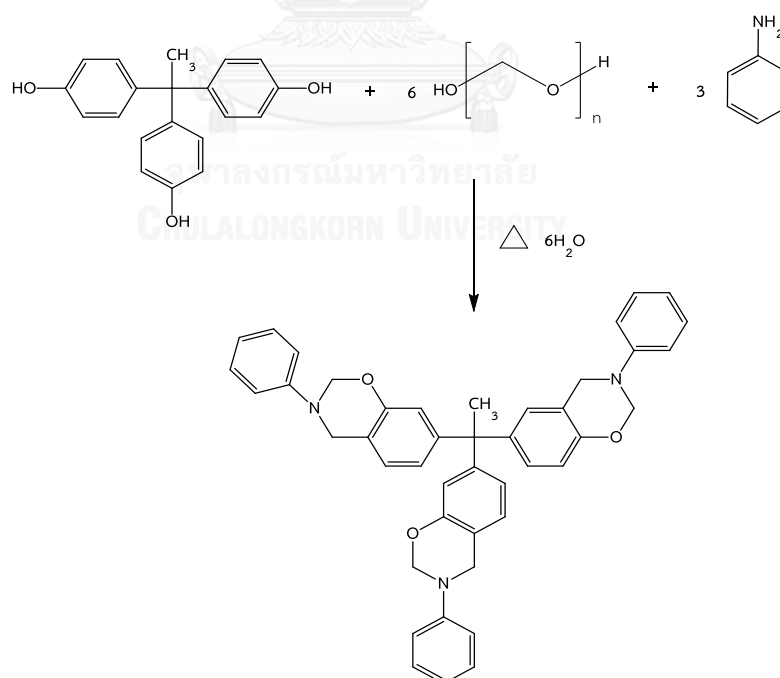
Figure 4.3 Tri-functional benzoxazine monomer synthesis (Tris P-a) [41].

4.2.3 Synthesis of Tri-functional Benzoxazine Resin (Tris P-a)

1,1,1 Tris (4hydroxyphenyl) ethane, paraformaldehyde and aniline at a ratio of 1:6:3 by molar were mixed and stirred at 95-100 °C for 30 minutes. Then heat up to 130 °C for 30 minutes. The monnomer was obtained as pale yellow solid. The chemical structures of Tris P-a monomer is shown in Figure 4.3.

4.3 Preparation of Benzoxazine Resins Modified Asphalt

About 300 g of base asphalt was heated to fluid condition at $80 \pm 5\,^{\circ}C$ and stirred using a low shear laboratory type mixer stirring at 500 rpm. All benzoxazine modifiers at ratio 0, 3, 6, and 9% by weight were then added slowly into the base asphalt and continuously stirred for 1 h. Then all samples were immediately cured at $190 \pm 5\,^{\circ}C$ for 1 hr in an oven to crosslink the benzoxazine.

4.4 Characterization Methods

4.4.1 Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared (FTIR) spectra of benzoxazine monomers and benzoxazine modified asphalt were verified at room temperature using a Spectrum GX FTIR spectrometer. All spectra were recorded with 64 scans in the range of 4000-400 cm^{-1} and at a resolution of 4 cm^{-1}. For the measurement in the transmission mode, a silicon substrate with 350 μm thickness was used and the thin asphalt binder sample was spread on the silicon substrate.

4.4.2 Thermogravimetric Analysis (TGA)

Thermal stability of benzoxazine-modified asphalt was measured by a thermogravimetric analyzer model TGA/SDTA 851^e from Mettler-Toledo (Thailand). The sample prepared about 10 mg. The test was heated from 25 to 850°C at a heating rate of 20°C/min under nitrogen gas. The degradation temperature at 5% weight loss and char residue of each sample measured at 800°C were recorded for each sample

4.4.3 Differential Scanning Calorimetry (DSC)

The curing characteristic of the benzoxazine modifiers and benzoxazine-modified asphalts was measured by Temperature Modulated Differential Scanning Calorimetry (TMDSC) for the DSC1 from Mettler-Toledo (Thailand). Amount of the sample ranging from 10-15 mg was placed on the aluminum pan. The experiment was used a heating rate of 10°C/min from 30 to 300°C for benzoxazine modifiers under nitrogen purging. The nitrogen gas used constant flow rate at 50 ml/min. The percentage of benzoxazine resin conversion and glass transition temperature were observed from the DSC thermograms.

4.4.4 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical properties of the benzoxazine-modified asphalts were examined by dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH Instrument. The experiment was performed under the tree-point bending

mode and dimension of specimens was 50 mm × 10 mm × 2.5 mm (W × L × T). The test was performed under the constant frequency of 1 Hz. The testing temperature was varied from -70 to 40 °C on heating rate 1°C/min under nitrogen atmosphere. The storage modulus (G′) and loss modulus (G″) were obtained. The glass transition temperature (T_g) was determined as the maximum point on the loss modulus curve in the DMA thermogram.

4.4.5 Dynamic shear rheometer

Rheological properties of benzoxazine-modified asphalt were measured with HAAKE RheoStress 600 dynamic shear rheometer in a parallel plate with 1 mm. gap and 25 mm. diameter. A dynamic shear properties temperature sweep test was examined under the strain controlled mode at a constant frequency of 10 rad/s.

4.4.6 Morphology by Confocal laser scanning microscope

The morphology of the benzoxazine modified asphalt was observed by confocal laser scanning microscope (model Olympus OLS3000) under micrometric eyepiece with objective lens (50× magnifications).

4.4.7 Penetration Measurement

Penetration value was a conventional test for pavement application. Penetration Test (ASTM D 5): measures the consistency of asphalt binder by measuring the depth to which a standard needle will penetrate into a sample under a specified load at a specified temperature within a specific period of time (5 sec). Normally, the load is 100g and the temperature is 25°C.

4.4.8. Softening Point Measurement

Softening point, ring and ball method (ASTM D36) was the temperature that the asphalt becomes softens which affects the road pavement surface in bleeding. The samples are prepared in the specimen in the ring and assembly the specimen rings, ball-centering guides and thermometer in position and fill the bath so that distilled water depth is 105 ± 3 mm. Balls are placed in each ball-centering guide and heated the bath by control uniform rate 5°C/min in a water bath until the binder deforms to let the ball to move down a distance of 25.4 mm. Data is recorded the temperature when the ball touches the bottom plate.

4.4.9 Ductility Measurement

The ductility of a bituminous material is measured (ASTM D113) by the distance to which it will elongate before breaking when two ends of a briquet specimen of the material, of the form described in Section 4, are pulled apart at a specified speed and at a specified temperature. Unless otherwise specified, the test

shall be made at a temperature of 13 °C and with a speed of 5 cm/min ±5.0 %. At other temperatures the speed should be specified.

4.4.10 Tenacity and toughness

Toughness means energy used to make test piece broken completely under the force. Tenacity means work provided from maximum force to tear the sample. From ASTM D 5801, the test is made by sinking half circle head of test equipment into the sample and stretch with constant velocity of 500 ± 5 mm. per minute until the sample torn separately from each other, record value of force and elongation.

4.4.11 Viscosity

Viscosity test is conducted (ASTM D 4220) by using Brookfield rotational Model DV-II + Pro viscometer at 135 and 165 °C. Only one kind of spindle 21 is used to measure the viscosity which is appropriate for asphalt binder.

CHAPTER V

RESULTS AND DISCUSSION

5.1   Benzoxazine Modifiers Characterization

5.1.1   FTIR spectra of benzoxazine monomers of varied functionalities

The FTIR absorption peaks of benzoxazine monomers, Ph-a, BA-a and TrisP-a, are shown in Figures 5.1. The important characteristic absorptions peak of all monomers observed at about 947 cm^{-1} was corresponded to C-H out-of-plane deformation of the 1,2,4-tri-substituted benzene ring and the sharp peak of 1495-1497 cm^{-1} attributes to the tri-substituted benzene ring mode in the oxazine ring structure, respectively. Also, the asymmetric stretching vibration of C-O-C group of oxazine ring was found to be located at 1230 cm^{-1}, 1248 cm^{-1} and 1030 cm^{-1} respectively. In addition, the C-H stretching region can be found around 3100-2700 cm^{-1}. The asymmetric and symmetric stretching vibration of C-N-C located at 1120-1159 cm^{-1} and around 824 cm^{-1} confirmed the formation of benzoxazine ring structure. The peak at 3400 cm^{-1} (assigned to OH stretching) was observed. It could be due to ring-opening benzoxazine monomer structure [43, 49].
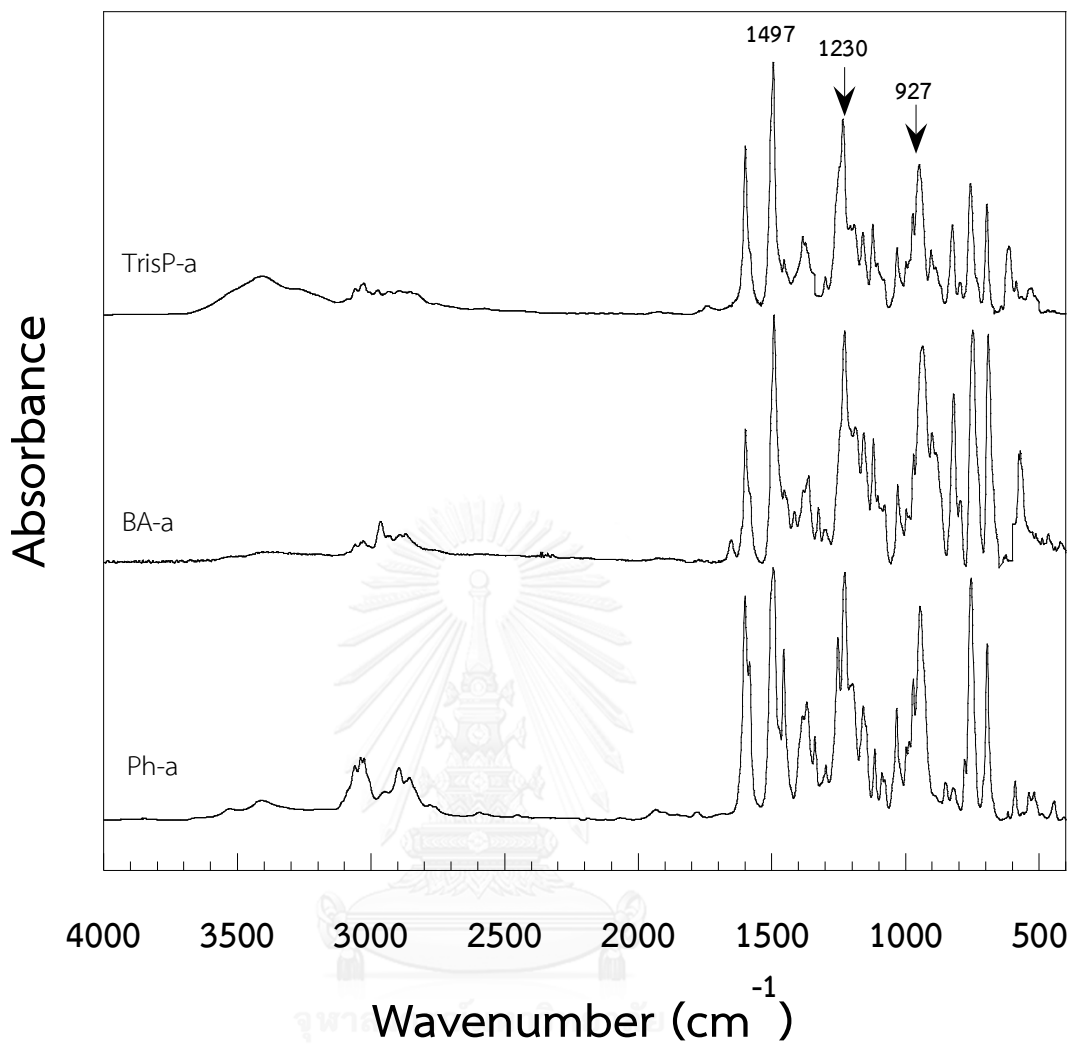
Figure 5.1 FTIR spectra of benzoxazine monomers of varied functionalities prepared by solventless synthesis.

5.1.2   Curing profiles of benzoxazine monomers of varied functionalities

Figure 5.2 shows the DSC thermograms of the three benzoxazine monomers. The observed thermal transition of BA-a and TrisP-a were assigned to the T_gs of these monomers i.e. about 35°C for BA-a monomer and about 75°C for TrisP-a monomer. No transition temperature was found in the thermogram of P-a confirming the solid nature of the first two monomers and the liquid nature of the last. All three monomers exhibit exothermic peaks which are assigned to the polymerization or curing processes of each monomer [41]. In addition, the DSC thermograms of Ph-a and BA-a monomers showed a relatively sharp exothermic peak with maximum at 220 and 230 °C, respectively, corresponding to the ring-opening polymerization reaction of these monomers. While TrisP-a showed a relatively broad exothermic peak with maximum at 244°C. The characteristics of peak exotherms above suggest P-a and Ba-a monomers are purer than TrisP-a monomers under the solventless synthesis condition used. It is expected that TrisP-a might contain some oligomers besides monomers. The area under the peak indicated the enthalpies of the ring opening polymerization of each monomer. Also, the curing enthalpy values of Ph-a, BA-a and TrisP-a are 332, 346 and 393 J/g respectively.
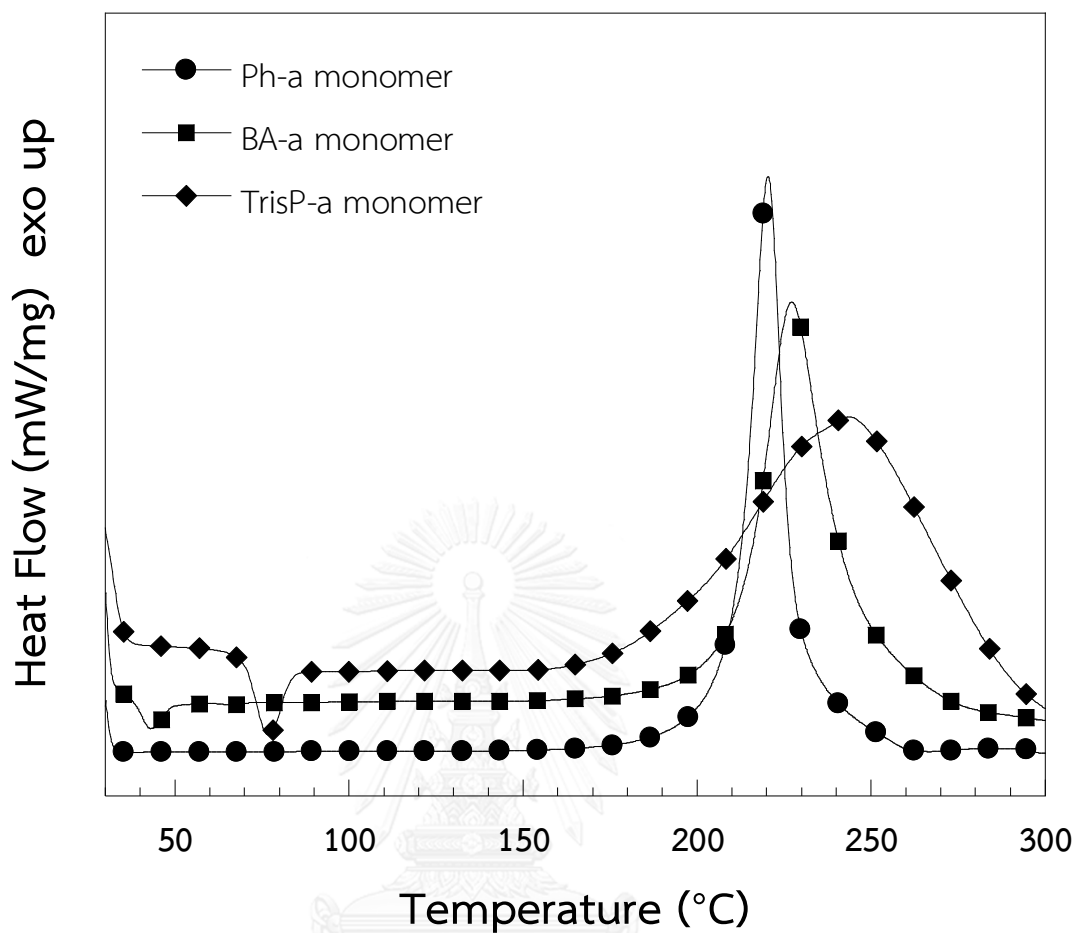
Figure 5.2 DSC thermograms of benzoxazine monomers of varied functionalities: (●)

Ph-a benzoxazine, (■) BA-a benzoxazine and (◆) TrisP-a benzoxazine.

5.1.3   Thermal stability of polybenzoxazines of varied functionalities

The thermal stability of the fully cured polybenzoxazines was investigated by TGA as shown in Figure 5.3. From the figure, TGA curves reveal a steady increase in thermal stability with an increase in a number of oxazine functionalities in the monomers i.e. the degradation temperature at 5% weight loss ($T_{d5\%}$s) of Ph-a, BA-a, and TrisP-a are 292, 325 and 340°C, respectively.

In addition, the residual weights at 800 °C of Ph-a, BA-a and TrisP-a were measured to be 37, 29 and 41%, respectively. From the results, no direct correlation between number of functionality and char forming ability in benzoxazine resins. That is the amount of char is not only dependent on the crosslink density but also the chemical structure of the reactants used for the monomer preparation.
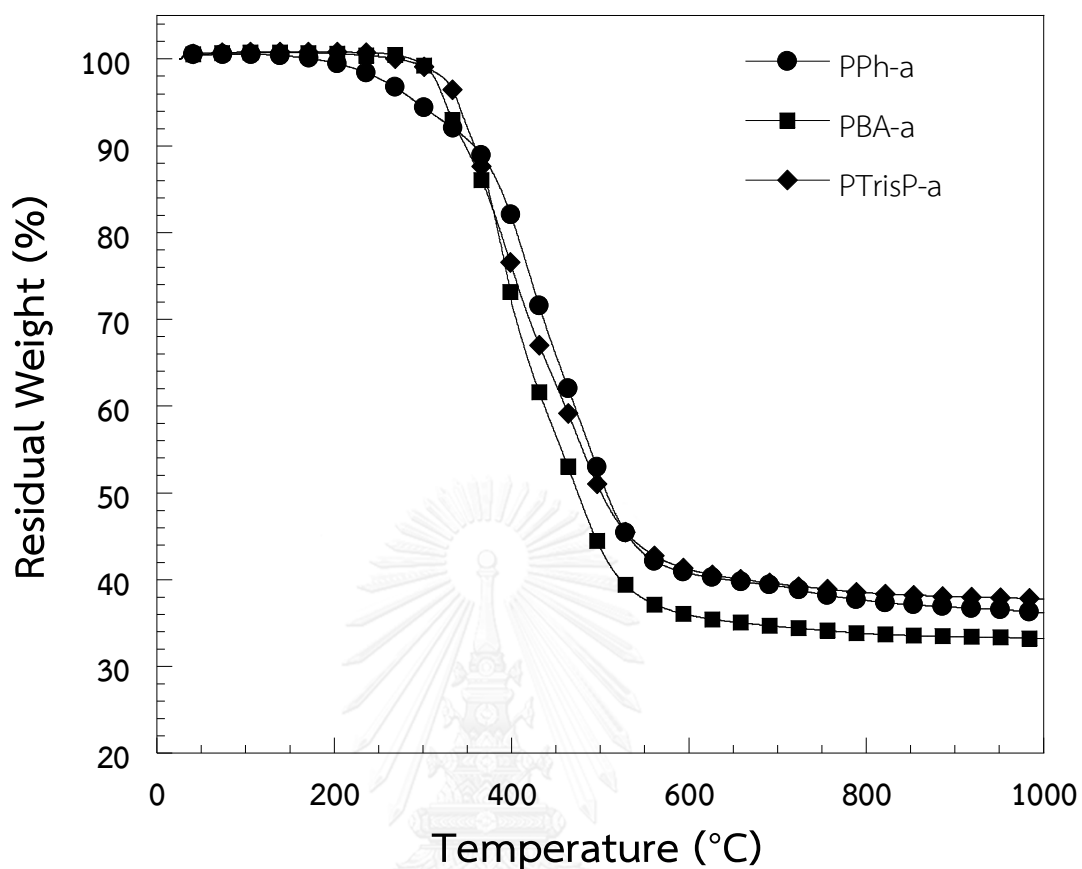
Figure 5.3 TGA thermograms of polybenzoxazines of varied functionalities: (●) Ph-a benzoxazine, (■) BA-a benzoxazine and (◆) TrisP-a benzoxazine.

5.1.4   Viscoelastic properties of polybenzoxazines of varied functionalities

Viscoelastic properties of the three polybenzoxazines were investigated by a DMA machine. Figure 5.4 shows temperature dependence comparison of storage modulus of Ph-a, BA-a and TrisP-a polymers. The effects of benzoxazine functionality on the crosslink density, ρ_x, of their polymer network can be calculated from a value of equilibrium storage shear modulus in the rubbery region, which equals to

E´/ 3 following Equation 5.1 based on statistical theory of rubber elasticity by Nielsen [48].

The crosslink density is one of the most important factors in determining thermal stability of thermosetting polymer. The crosslink density values of Ph-a, BA-a and TrisP-a calculated from Equation 5.1 are 1169, 2126 and 3347 mol/m^3 respectively. The values expectedly increased with an increase in oxazine functionality of the monomers. The storage modulus at room temperature (25°C) of Ph-a, BA-a and TrisP-a polybenzoxazine were determined to be 3.93, 5.02 and 5.78 GPa, respectively. The storage modulus is consistent with an increase in crosslink density of each polymer. Figure 5.5 exhibited glass transition temperature (T_g) determined from the maximum peak of loss modulus (E″). The T_gs of the fully cured polybenzoxazines of Ph-a, BA-a and TrisP-a were found to be 148, 170 and 244 °C, respectively. The results also indicated that increasing oxazine functionality in monomers provided a significant enhancement in both the storage modulus (E′) and T_gs of the obtained polybenzoxazines.

$$\log \left(\frac{E'_e}{3} \right) = 7.0 + 293 \left(\rho_x \right) \tag{5.1}$$

Where: E'_e is an equilibrium storage modulus in rubbery plateau [$dyne/cm^2$]

ρ_x is crosslink density [mol/cm^3] which is the mole number of network chains per unit volume of the polymers.
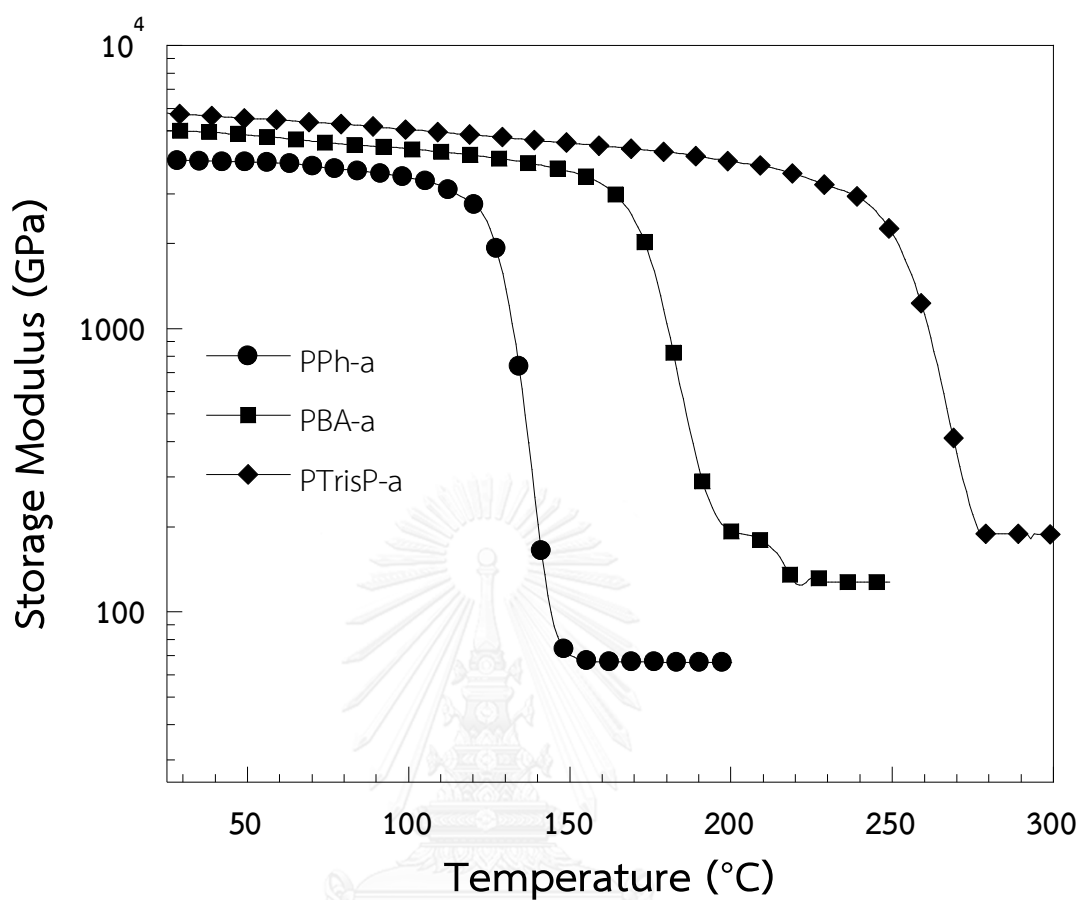
Figure 5.4 DMA thermograms of storage modulus of polybenzoxazines of varied

functionalities: (●) Ph-a benzoxazine, (■) BA-a benzoxazine and (◆) TrisP-a
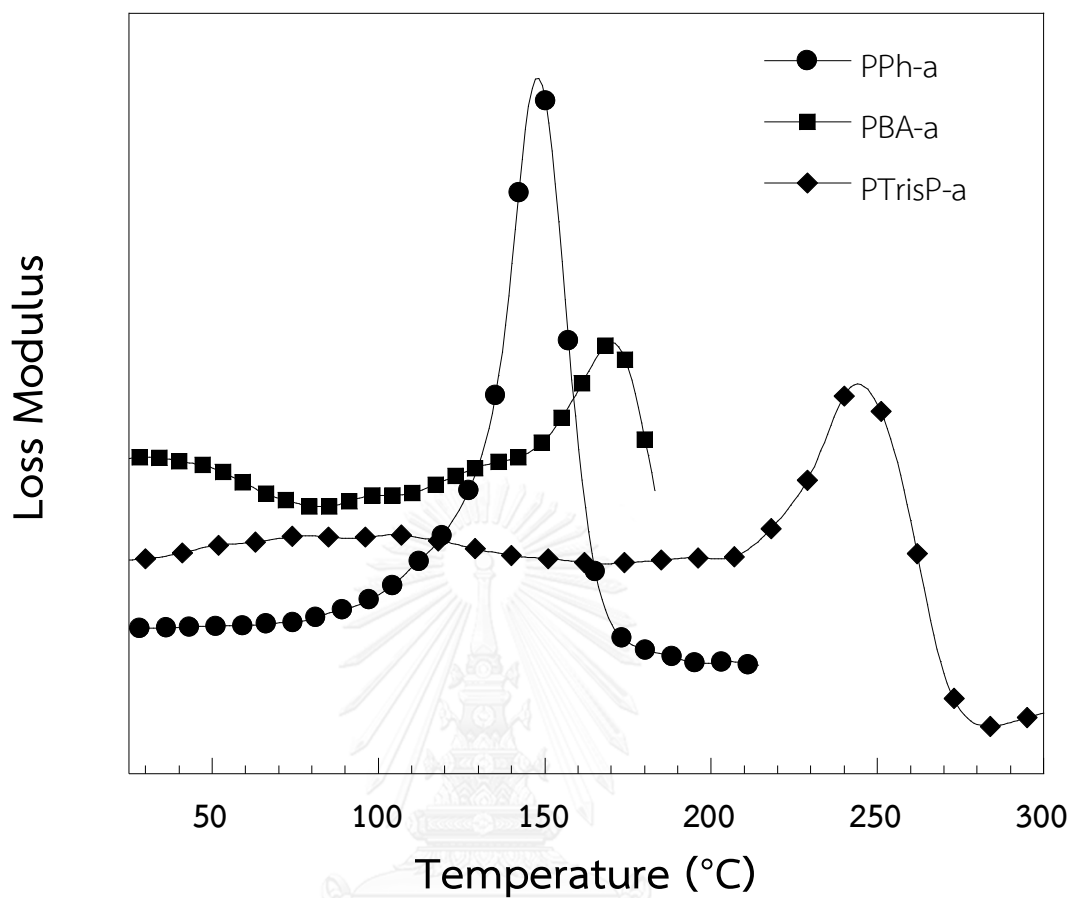
benzoxazine.

Figure 5.5 Overlay plot of DMA thermograms of loss modulus of polybenzoxazines of

varied functionalities: (●) Ph-a benzoxazine, (■) BA-a benzoxazine and (◆) TrisP-a

benzoxazine

5.2 Benzoxazine Resins Modified Asphalts Characterization

    5.2.1   Softening point of benzoxazine resins modified asphalts

Softening point temperature is an important performance for asphalt materials. It is critical temperature that the asphalt becomes softened at constant loading which affects bleeding behavior of the asphalt binder. A high softening point which is an indicator of the stiffening effect of polymer modified asphalt. It is favorable since asphalt with higher softening point will not flow during service, lower the temperature sensitivity and reduction of bleeding, stripping, also may be less susceptible to rutting deformation [14-19].

    Figure 5.6, the test shows that the softening points of asphalt after addition of Ph-a, BA-a and TrisP-a significantly increase with increasing the benzoxazine resins. From this figure, the softening point of the neat or unmodified asphalt was found to be 46°C and the value increased to 69.7°C, 73.2°C and 77.7°C, with the presence of 3, 6 and 9% by weight of the Ph-a benzoxazine resin, respectively.

    The softening point of BA-a modified asphalt significantly increased from the neat asphalt of 46 $^{\circ}$C to 72.5, 77.5 and 81.1 $^{\circ}$C with increasing the benzoxazine resins contents from 3, 6 and 9 by weight. For the modified asphalt by TrisP-a benzoxazine resin at 3, 6 and 9% by weight provided increasing in their softening point i.e. 75.2, 79.7 and 86 $^{\circ}$C, respectively. Also, considering that the same content of benzoxazine

resins found the softening point increase with increasing functionality of benzoxazine resins. In addition the softening point of the TrisP-a modified asphalt was found to increase 29.2 °C whereas epoxy modified asphalt can increase by 19.4 °C by comparing at the same content of 3% by weight of modifier [42]. Furthermore, compared between asphalt modified with SBS modified asphalt found that the softening point of the TrisP-a modified asphalt was found to increase 33.7 °C whereas SBS modified asphalt can increase by 20 °C at the same content of 6% weight of modifier [51].

It can be concluded that the benzoxazine reins could enhance the softening point of benzoxazine modified asphalt, which is required to reduce permanent deformation such as rutting, stripping and bleeding.

Figure 5.6 Softening point temperature of benzoxazine resins modified asphalt at various benzoxazine contents: (●) Ph-a benzoxazine modified asphalt, (■) BA-a benzoxazine modified asphalt and, (◆) TrisP-a benzoxazine modified asphalt.

5.2.2   Penetration value of benzoxazine resins modified asphalts

Penetration is an important parameter to investigate stiffness, temperature susceptibility and rutting resistance of the asphalt [47]. Figure 5.7 shows penetration value of benzoxazine resins modified asphalt at different functionality of benzoxazine resins and contents ranging from 0 to 9 % by weight at 25°C. The penetration value of the neat asphalt was 68 dmm. The addition of benzoxazine resins contents resulted in a reduction of penetration. It can be seen that the penetration value of the Ph-a benzoxazine modified asphalt of 3, 6 and 9 % by weight of modifier was 67.3, 65.3 and 59.6 dmm, respectively.

For the BA-a benzoxazine modified asphalt found that the penetration value reduce from 68 dmm of neat asphalt to 65.6, 62.0 and 56.3 dmm respectively of the BA-a benzoxazine of 3, 6 and 9 % by weight of modifier. In parts of the TrisP-a benzoxazine modified asphalt was found that the penetration drop to 64.3, 60.3 and 51.6 dmm, respectively of 3, 6 and 9% by weight of modifier. In comparison to the three modifiers, at the same content of benzoxazine resins the penetration value was found to decrease with increasing functionality of benzoxazine resins. It can be noticed that an addition of benzoxazine resins in asphalt matrix provided a decrease in penetration value compared to neat asphalt. Blending between polymer and asphalt commonly leads to increase in consistency of the modified asphalts [46].

This indicates an increase in the hard consistency of asphalt which might be due to diffusion of maltenes penetrated into benzoxazine. In addition, they swell and disperse thoroughly in the asphalt phase. Also, the interaction between polymer and polar molecules of asphaltene makes the molecules of asphaltene larger with a higher molecular weight [12, 14]. However, benzoxazine resins modified asphalt at 6% by weight of all benzoxazine resins provided balance the penetration value to be in the range of 60-70 dmm which pass the requirement specifications of Highways Department of Thailand (DH-SP. 408/2536). From these results, benzoxazine resins could improve hardness of benzoxazine modified asphalt, indicating high resistance to permanent deformation in the road pavement.
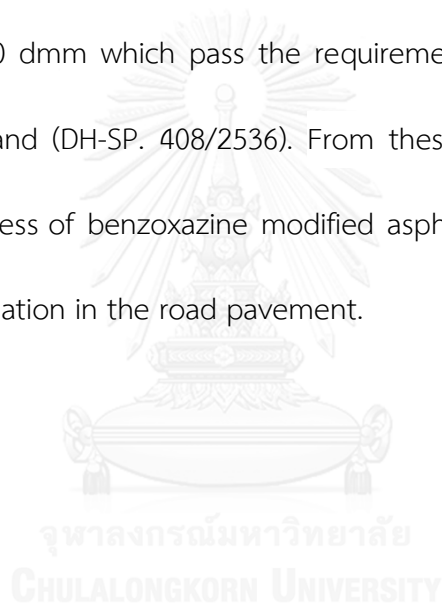
Figure 5.7 Penetration values of benzoxazine resins modified asphalt at various benzoxazine contents: (●) Ph-a benzoxazine modified asphalt, (■) BA-a benzoxazine modified asphalt and, (◆) TrisP-a benzoxazine modified asphalt.

5.2.3   Penetrability index of benzoxazine resins modified asphalts

Thermal susceptibility of modified asphalt can be evaluated by using penetrability index which defined as the change in the consistency parameter as a function of temperature and the value can be calculated from equation 5.2. The temperature susceptibility of benzoxazine resins modified asphalt samples was calculated in terms of penetrability index (PI) using the values obtained from penetration and softening point temperature. A classical approach related to PI calculation is reported in the Shell Bitumen Handbook as shown in the following equation [2].

$$PI = \frac{1952 - 20 \cdot SP - 500 \cdot \log(Pen_{25})}{50 \cdot \log(Pen_{25}) - 120 - SP} \tag{5.2}$$

Where: Pen_{25} is the penetration of the modified asphalt at 25 ^{O}C.

SP is the softening point temperature of the modified asphalts.

The value of PI ranges from -3 highly temperature susceptible asphalt to + 7 for low temperature susceptible asphalt [2]. As seen in Figure 5.8, the initial PI value of the base asphalt is -1.27; this value increased with increasing functionality and contents of benzoxazine resins. The PI value of 3, 6 and 9 % by weight of Ph-a benzoxazine modified asphalt was 3.62, 4.09 and 4.49, respectively.

For BA-a benzoxazine modified asphalt; penetrability index was 3.99, 4.58 and 4.88 of 3, 6 and 9 % by weight of modifier. In addition, the PI value of TrisP-a benzoxazine was 4.35, 4.80 and 5.18 of 3, 6 and 9 % by weight of modifier, respectively. It can be concluded that higher value of PI exhibited less temperature susceptibility and more rubbery elastic behavior, which resist to low temperature cracking as well as permanent deformation [50].
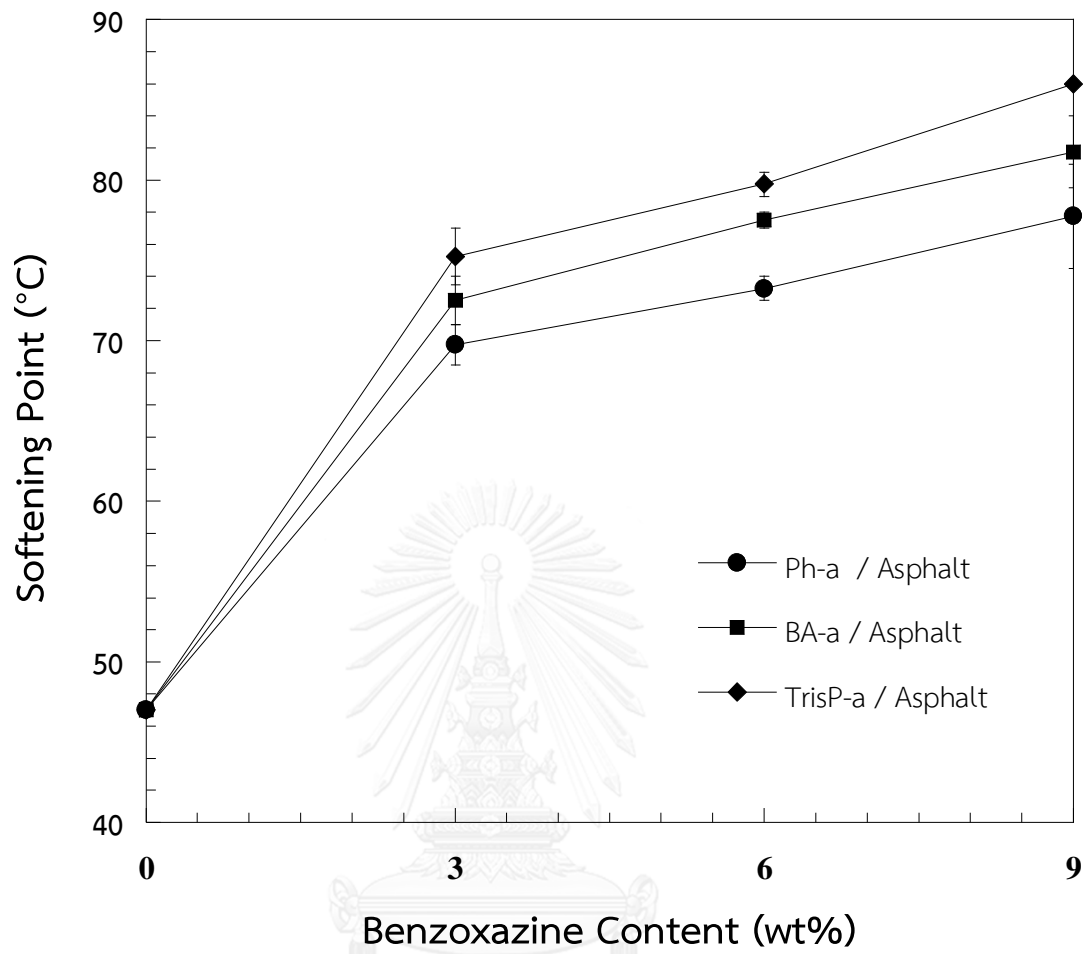
Figure 5.8 Penetrability index of benzoxazine resins modified asphalt at various benzoxazine contents: (●) Ph-a benzoxazine modified asphalt, (■) BA-a benzoxazine modified asphalt and, (◆) TrisP-a benzoxazine modified asphalt.

5.2.4   Rotational viscosity of benzoxazine resins modified asphalts

The viscosity of asphalt binders at high temperature is considered to be an important property to decide working temperature because it represents binder's ability to be pumped through an asphalt plant, thoroughly coat aggregate in asphalt concrete mix, and be placed and compacted to form a new pavement surface [56]. Figure 5.9 and 5.10 exhibit viscosity of benzoxazine resin modified asphalt with different benzoxazine functionality at varied contents by 0, 3, 6 and 9% by weight at 135℃ and 165℃. From the plot, at 135℃, it represents binder's ability to be pumped through an asphalt plant, the viscosity of the asphalt was found to increase exponentially when benzoxazine content increased.

The viscosity of Ph-a benzoxazine modified asphalt increased from 225 mPa.s of the unmodified asphalt to 344, 553 and 744 mPa.s at benzoxazine resin contains of 3, 6 and 9% by weight in the asphalt matrix. The viscosity of BA-a benzoxazine modified asphalt was 406, 650 and 861 mPa.s of 3, 6 and 9 % by weight of Ph-a benzoxazie, respectively. In addition, the viscosity of TrisP-modified asphalt significantly increased from the neat asphalt of 225 mPa.s to 410, 725 and 880 mPa.s with increasing the benzoxazine resins contents from 3, 6 and 9 by weight. Likewise, the viscosity at 165℃ that the temperature for the mix between asphalt and aggregate.

It was found that the viscosity of benzoxazine modified asphalt increased with increasing content and functionality of benzoxazine resins as shown in Table 5.1-5.3. In practice, the increase in viscosity can reduce softening and bleeding problems of asphalt material. It can also lower rate of stripping phenomenon and increases asphalt stability for road pavement application.

Figure 5.9 Viscosity at 135 $^{\circ}$C of benzoxazine resins modified asphalt at various benzoxazine contents: (●) Ph-a benzoxazine modified asphalt, (■) BA-a benzoxazine modified asphalt and, (◆) TrisP-a benzoxazine modified asphalt.
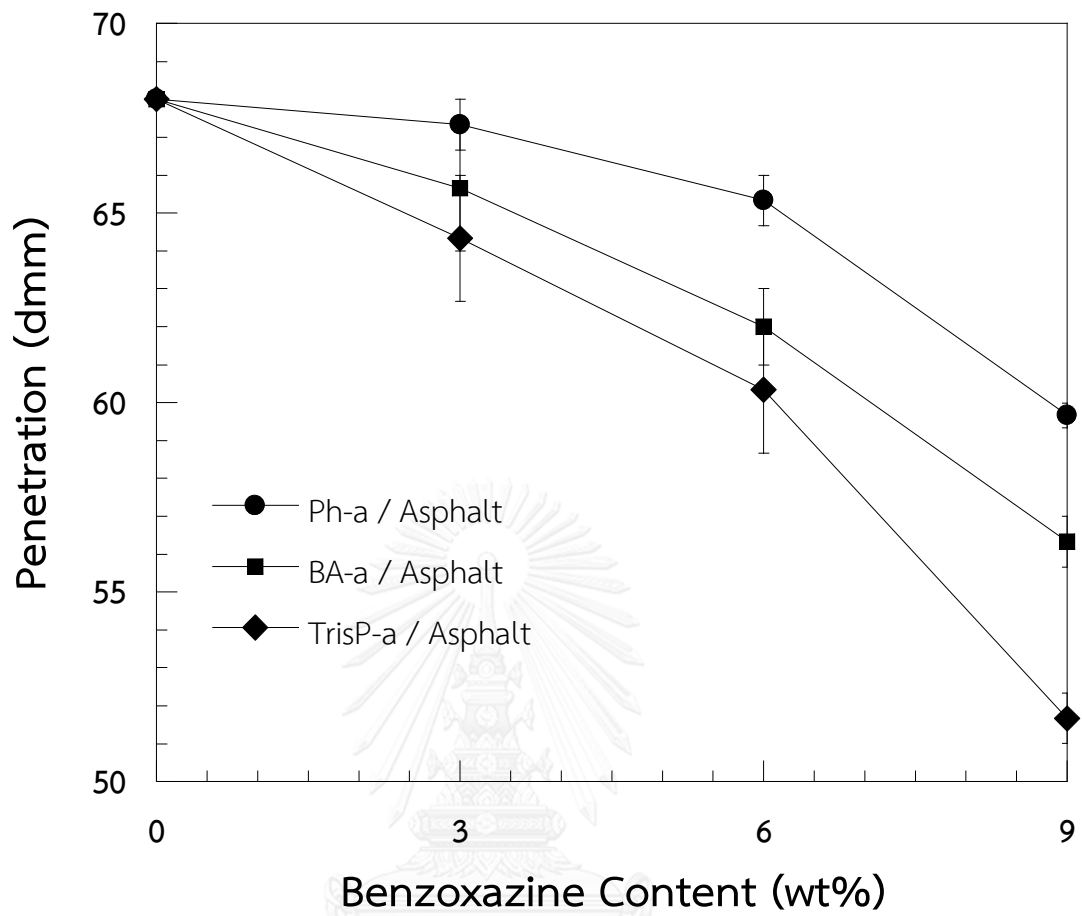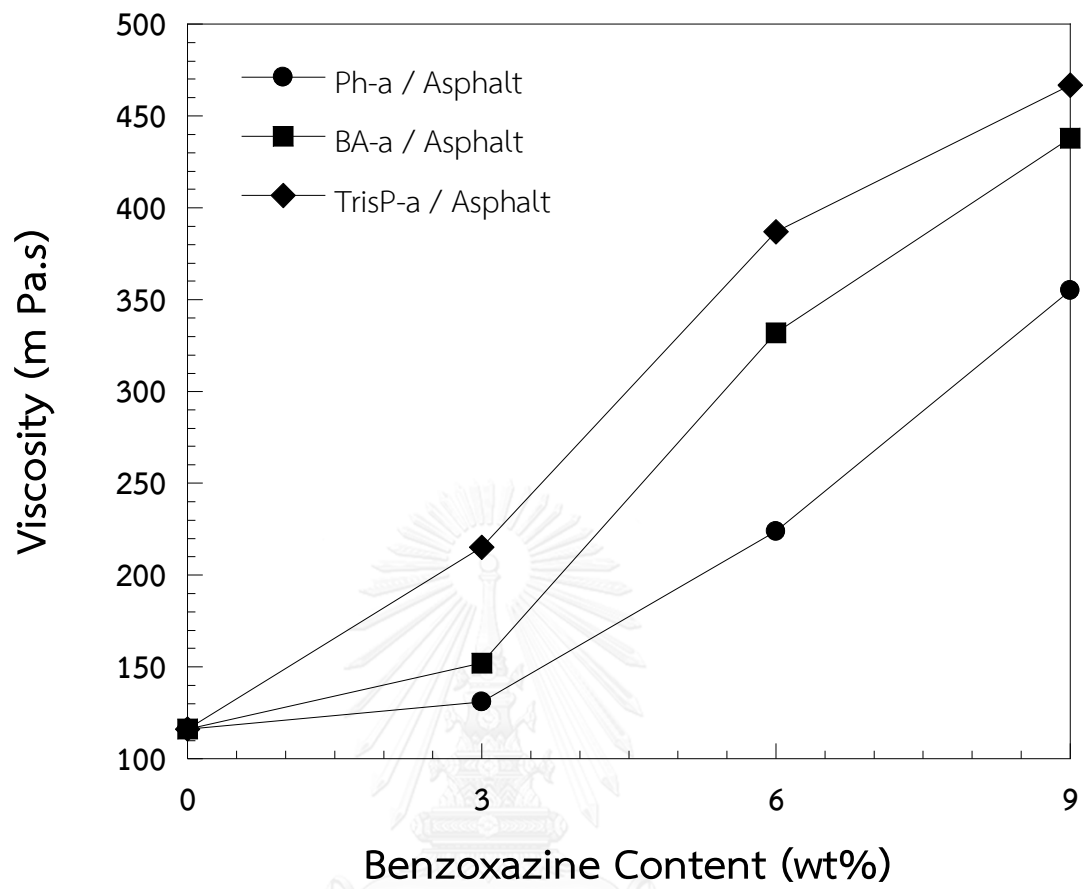
Figure 5.10 Viscosity at 165 $^{\circ}$C of benzoxazine resins modified asphalt at various benzoxazine contents: (●) Ph-a benzoxazine modified asphalt, (■) BA-a benzoxazine modified asphalt and, (◆) TrisP-a benzoxazine modified asphalt.

Table 5.1 Viscosity of Ph-a benzoxazine resins modified asphalt at various benzoxazine contents

Ph-a Content	Viscosity (m Pa.s) at 135 $^\circ$C	Viscosity (m Pa.s) at 165 $^\circ$C
0	225	116
3	344	131
6	553	244
9	744	355

Table 5.2 Viscosity of BA-a benzoxazine resins modified asphalt at various benzoxazine contents

BA-a Content	Viscosity (m Pa.s) at 135 $^\circ$C	Viscosity (m Pa.s) at 165 $^\circ$C
0	225	116
3	406	152
6	650	332
9	861	438

Table 5.3 Viscosity of TrisP-a benzoxazine resins modified asphalt at various benzoxazine contents

BA-a Content	Viscosity (m Pa.s) at 135 $^{\circ}$C	Viscosity (m Pa.s) at 165 $^{\circ}$C
0	225	116
3	410	215
6	725	387
9	880	467

5.2.5 Ductility of benzoxazine resins modified asphalts

The ductility test gives adhesive property of bitumen and its ability to stretch. In flexible pavement design, it is necessary that binder should form a thin ductile film around aggregates so that physical interlocking of the aggregates is improved. Binder material having insufficient ductility gets cracked when subjected to repeat traffic loads and it provides pervious pavement surface [58]. From Figure 5.11, the ductility value of benzoxazine resins modified asphalt was clearly higher than that of the neat asphalt. The reason is that the network structure formed in benzoxazine resins modified asphalt and the reaction may happen between benzoxazine resin and reactive functional group in asphaltene of neat asphalt to form chemical bond, which generates network structure between benzoxazine resins and asphalt.

The ductility of Ph-a benzoxazine modified asphalt could elongate from 65 cm of neat asphalt to 92 cm of 3% by weight of modifier. Also, it could elongate as much as over 100 cm when 6% by weight of modifier was added. After that, the ductility at 9% by weight of Ph-a benzoxazine reduce to 87.3 cm. Similarly, the ductility of BA-a benzoxazine modified asphalt at content of 3, 6 and 9% by weight of modifier was 94.3, 96.6 and 84.6 cm, respectively. For the ductility of TrisP-a benzoxazine modified asphalt at content of 3, 6 and 9% by weight of modifier was 98.0, 97.0 and 82.3 cm, respectively. Therefore the ductility of modified asphalt was evident; especially benzoxazine resins modified asphalt at 6 % by weight of all benzoxazine resins provided optimum the ductility to be over 55 cm, which pass the requirement specifications of Highways Department of Thailand (DH-SP. 408/2536).

As a result, the compatibility between benzoxazine resin and asphalt is reinforced. So the performance of the benzoxazine resins modified asphalt in low temperature, ability to adhesion to aggregate as well as permanent deformation are developed greatly.
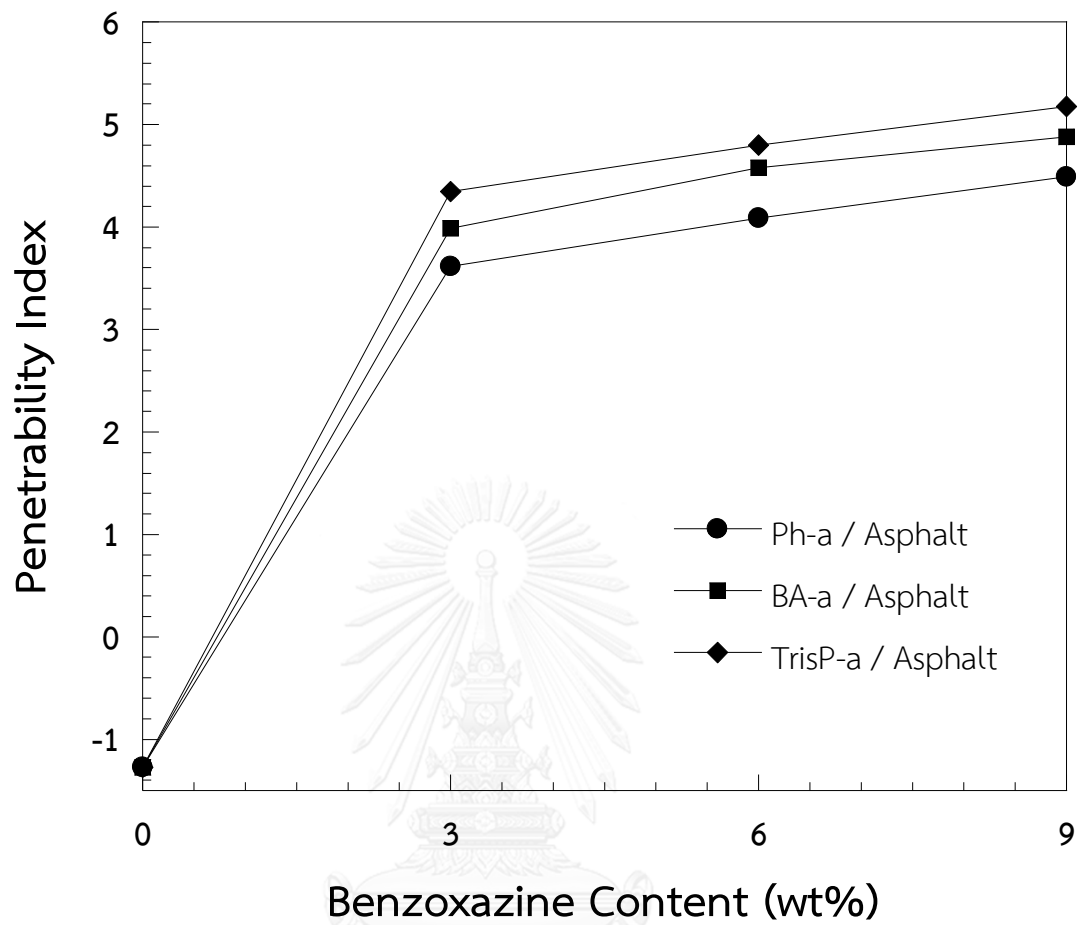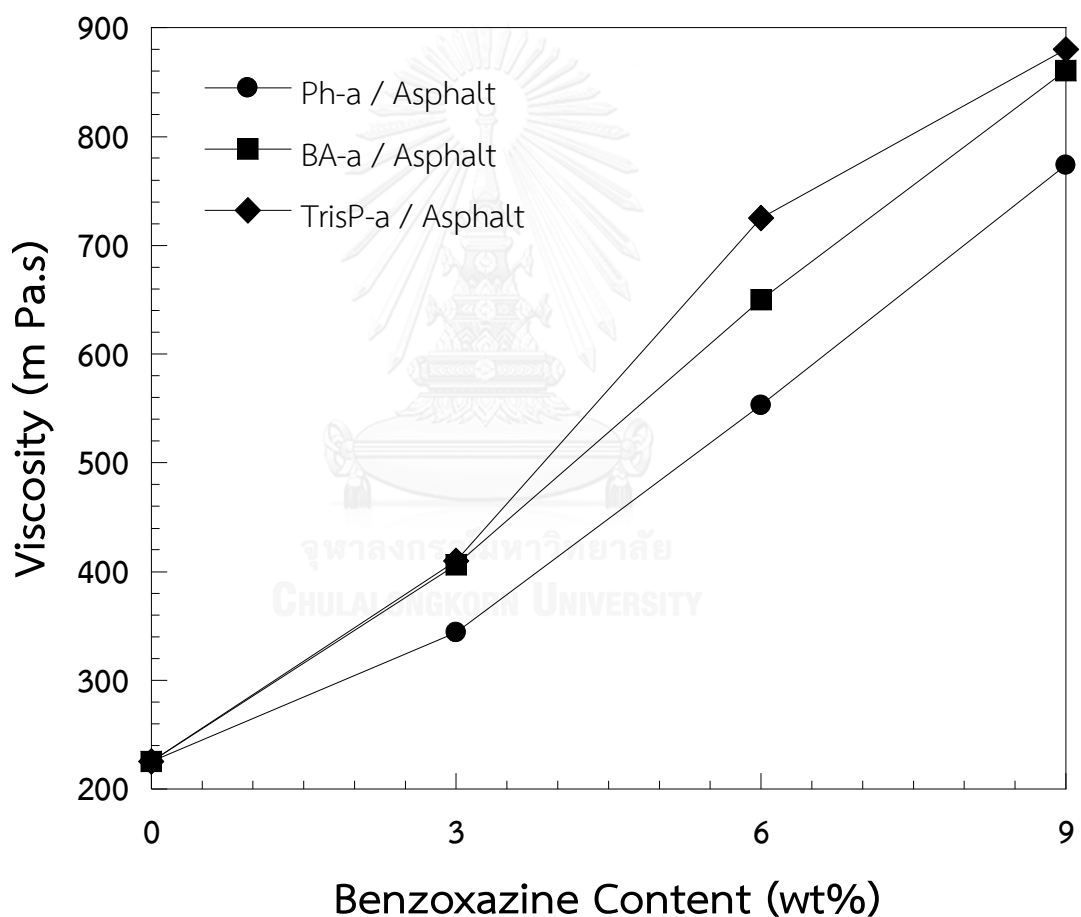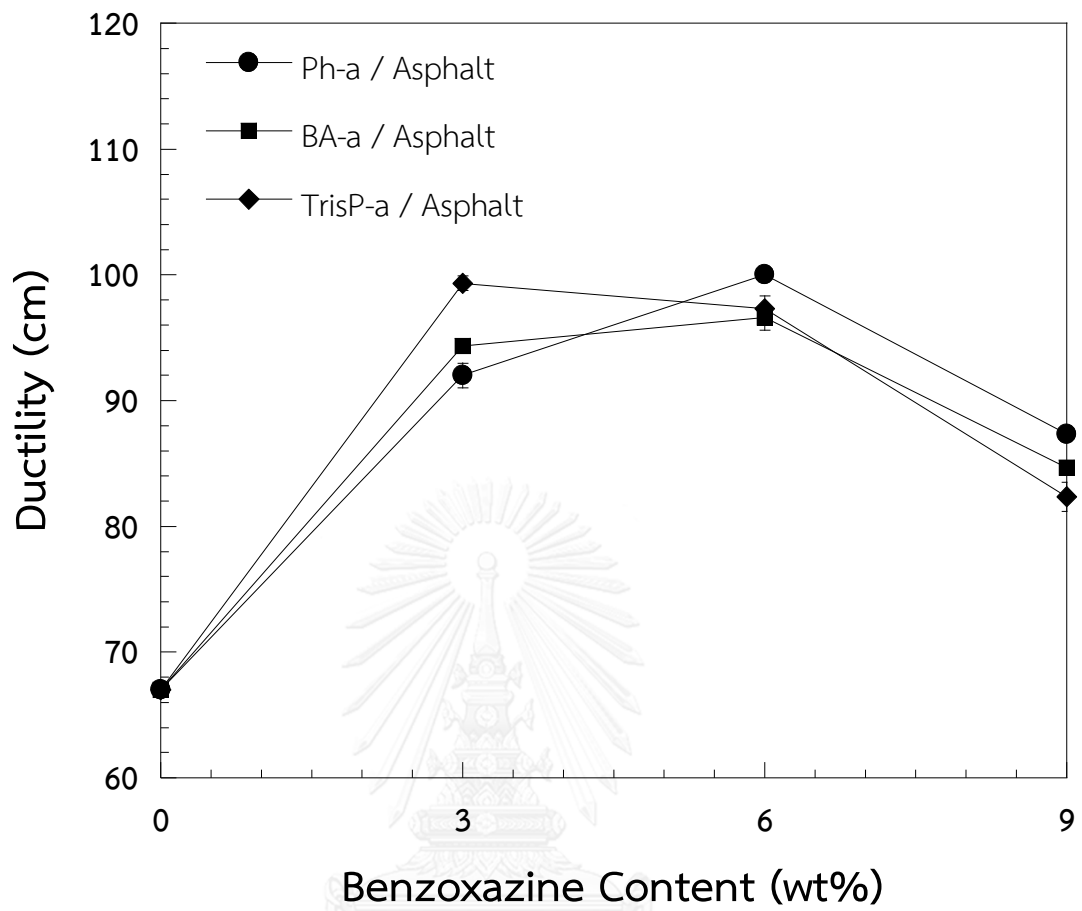
Figure 5.11 Ductility of benzoxazine resins modified asphalt at various benzoxazine contents: (●) Ph-a benzoxazine modified asphalt, (■) BA-a benzoxazine modified asphalt and, (◆) TrisP-a benzoxazine modified asphalt.

5.2.6   Toughness and Tenacity of benzoxazine resins modified asphalts

Toughness and tenacity as two important parameters have been adopted to measure the adhesion ability of benzoxazine resins modified asphalt to stone matrix in many professional standards. The toughness shows the holding power to aggregate, the tenacity indicates the ability of resisting deformation under different loads and the tenacity is a main consisting element of the toughness [52].

Figures 5.12 and 5.13 show the toughness and tenacity of benzoxazine resins modified asphalt was clearly higher than neat asphalt; the values were reported in Tables 5.4-5.6. It can be seen that the toughness and the tenacity of the benzoxazine resins modified asphalt were improved to some extent through crosslink network and increased with increasing benzoxazine functionality. With increasing benzoxazine contents, the toughness and the tenacity increased correspondingly.

When 6% by weight of all benzoxazine resins were added, the toughness and the tenacity were increased maximum value. But, benzoxazine resins at 9 % by weight were added in asphalt matrix, the toughness and the tenacity were decreased. From the results, increasing crosslinking density could lead to high rigidity in modified asphalt. This is consistent with the ductility of polymer additives on more than 6% by weight. The ductility, toughness, and tenacity should be considered together because they contribute to improve aggregate retention and improve low

temperature susceptibility. From considering about the main properties of benzoxazine resins modified asphalt including the softening point, the penetration value, the ductility, the toughness and the tenacity, it could be seen that 6% by weight of all benzoxazine resins used was the best one.

In addition the toughness and tenacity of the TrisP-a modified asphalt was found to 92 kg.cm and 16 kg.cm whereas PPA/SBR modified asphalt can increase by 66 kg.cm and 12 kg.cm, respectively by comparing at the same content of 6% by weight of modifier [58].
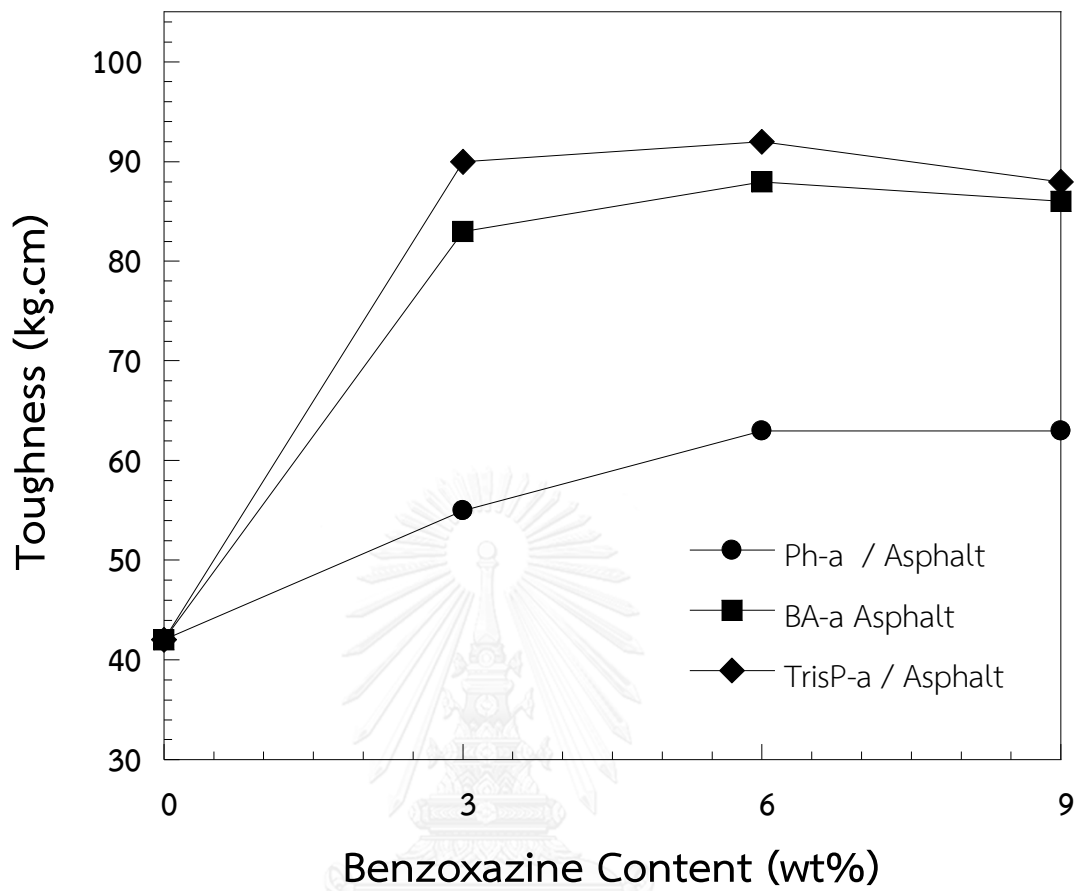
Figure 5.12 Toughness of benzoxazine resins modified asphalt at various benzoxazine contents(●) Ph-a benzoxazine modified asphalt, (■) BA-a benzoxazine modified asphalt and, (◆) TrisP-a benzoxazine modified asphalt.

Figure 5.13 Tenacity of benzoxazine resins modified asphalt at various benzoxazine contents: (●) Ph-a benzoxazine modified asphalt, (■) BA-a benzoxazine modified asphalt and, (◆) TrisP-a benzoxazine modified asphalt

Table 5.4 Toughness and tenacity of Ph-a benzoxazine resins modified asphalt at various benzoxazine contents

Ph-a Content	Toughness (kg.cm)	Tenacity (kg.cm)
0	42	3
3	55	6
6	63	8
9	63	8

Table 5. 5 Toughness and tenacity of BA-a benzoxazine resins modified asphalt at various benzoxazine contents

BA-a Content	Toughness (kg.cm)	Tenacity (kg.cm)
0	42	3
3	83	12
6	88	12
9	86	10

Table 5.6 Toughness and tenacity of TrisP-a benzoxazine resins modified asphalt at various benzoxazine contents

TrisP-a Content	Toughness (kg.cm)	Tenacity (kg.cm)
0	42	3
3	90	15
6	92	16
9	88	13
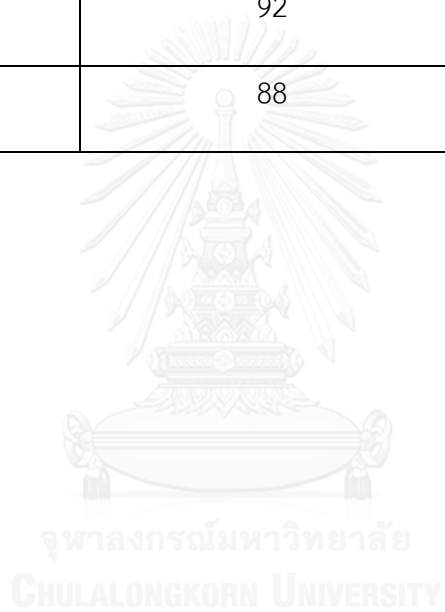
5.2.7   Rutting parameter of benzoxazine resins modified asphalt

Rutting parameter ($G^*/\sin\delta$) is a rheological parameter to analyze the properties of asphalt binders used in road pavement application which recommended by the Strategic Highway Research Program (SHRP) of the United State. Complex modulus (G^*) and phase angle (δ) are important rheological parameters for asphalt pavement application. Complex modulus (G^*) refers to stiffness and phase angle (δ) refers to material behavior. [24] When phase angle (δ) approaches zero degree, the material has elastic behavior. While phase angle (δ) approaches 90 degree, the material has viscous behavior. The rutting parameter is the temperature plotted between the elastic and the viscous response of asphalt for road pavement. The test is performed at 10 rad/s to simulate traffic load at 75 to 90 km/h. The testing temperature is 76 $^{\circ}$C. The strain and torque were measured and inputted into a computer for calculating complex modulus and phase angle.

Figure 5.14 and Table 5.7 show rutting parameter of benzoxazine modified asphalts at different benzoxazine resin contents from 0 to 9% by weight. When increasing the quantity and functionality of benzoxazine resin, the rutting parameter was increased and higher than the base. In particular, the performance temperature of asphalt modified with amount of benzoxazine (6% by weight) changes dramatically. When the modifiers more than 6% by weight (9% by weight), the rutting

resistance slightly increased. This suggests that the benzoxazine resins modified asphalts can provide performance and found that at 6% by weight of all benzoxazine resins modified asphalt sufficient for improving asphalt when considered together with other properties such as softening point, penetration value, ductility, toughness and tenacity.

Table 5.7 Rutting parameter of TrisP-a benzoxazine resins modified asphalt at various benzoxazine contents

| Content	$G^*/\sin \delta$ (kPa)		
	Ph-a benzoxazine	BA-a benzoxazine	TrisP-a benzoxazine
0	1.3		
3	1.6	2.3	2.4
6	1.8	2.4	2.6
9	2.0	2.3	2.6
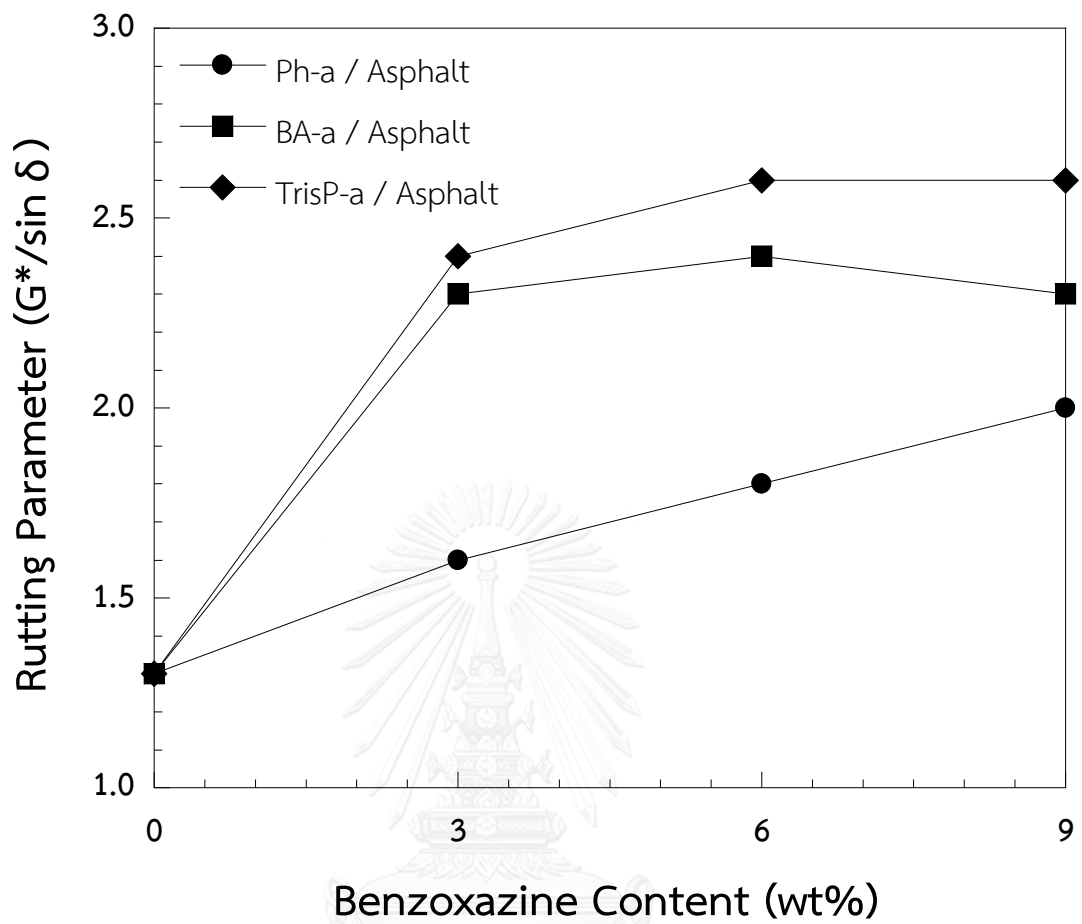
Figure 5.14 Rutting parameter of benzoxazine resins modified asphalt at various

benzoxazine contents: (●) Ph-a benzoxazine modified asphalt, (■) BA-a

benzoxazine modified asphalt and, (◆) TrisP-a benzoxazine modified asphalt.
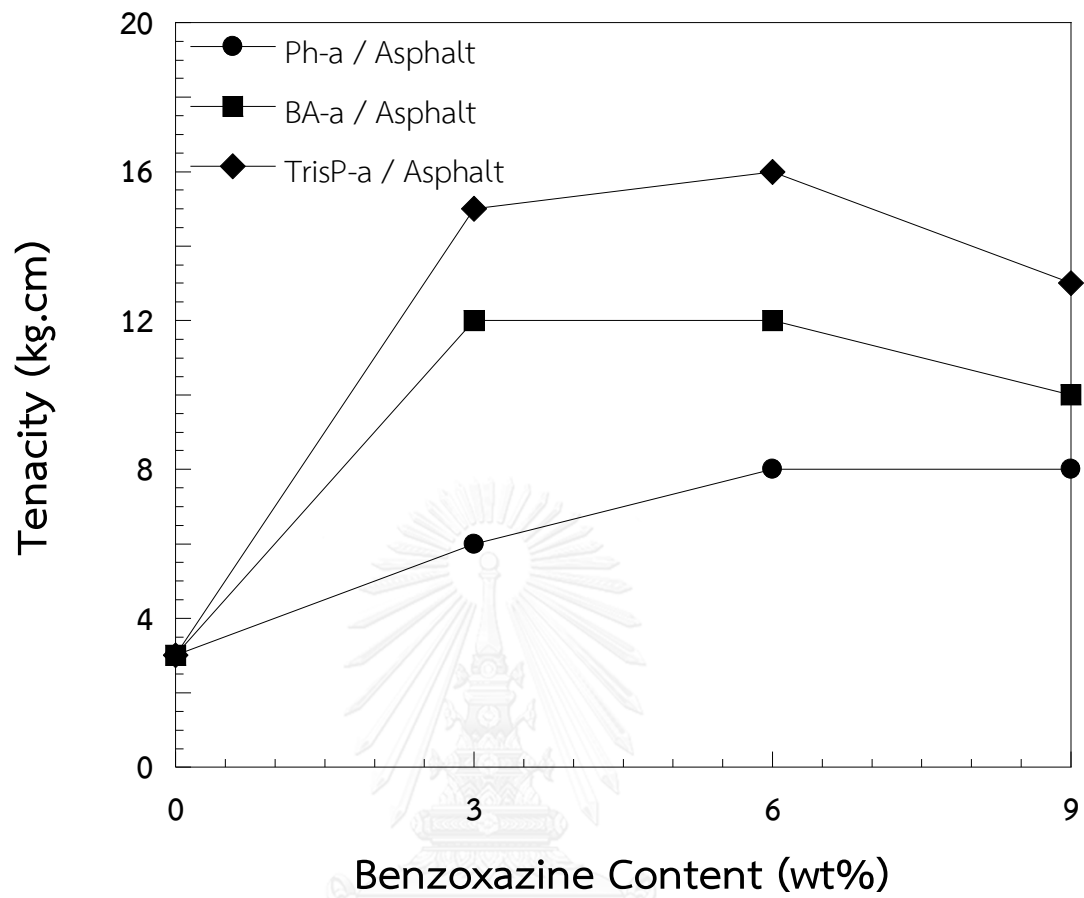
5.2.8   Morphology of benzoxazine resins modified asphalts

Confocal laser scanning microscope (CLSM) is an imaging tool to analysis the morphology of thermosetting heterogeneous asphalt blends [60]. The phase morphology has a great effect on the road performance of polymer asphalt blends [47]. The technique used to measure interface width, distribution and size of polymer particles dispersed in asphalt matrix. The microscopy of benzoxazine modified asphalt samples were compared to the neat asphalt with 50× magnifications.

The CLSM images of the neat asphalt and 6% by weight of benzoxazine resins modified asphalt are shown in Figure 5.15, the morphology of benzoxazine resins modified asphalt change during a number of functionalities of benzoxazine resin. For the neat asphalt, the image shows light domains with corresponding to a dispersion of the asphalt components within asphalt microstructure.

Furthermore, the Figure 5.15 reveals the benzoxazine mass fraction was found to coalescence disperse of small particles, this phenomenon is favored when the crosslink networks of the matrix is formed. From this figure, the light domains of the components of the asphalt were observed to increase with increasing the number of functional groups of benzoxazine resin. The appearance of the two domains suggested that phase separation characteristic of the mixture, this characteristic of phase separation can be found with other systems such as epoxy, EVA, SBS or PE modified asphalts [44, 45, 52, 56]. In this case, the formation of benzoxazine crosslink

networks effects on the enhancement of thermal stability and mechanical properties

of the asphalt mixture.
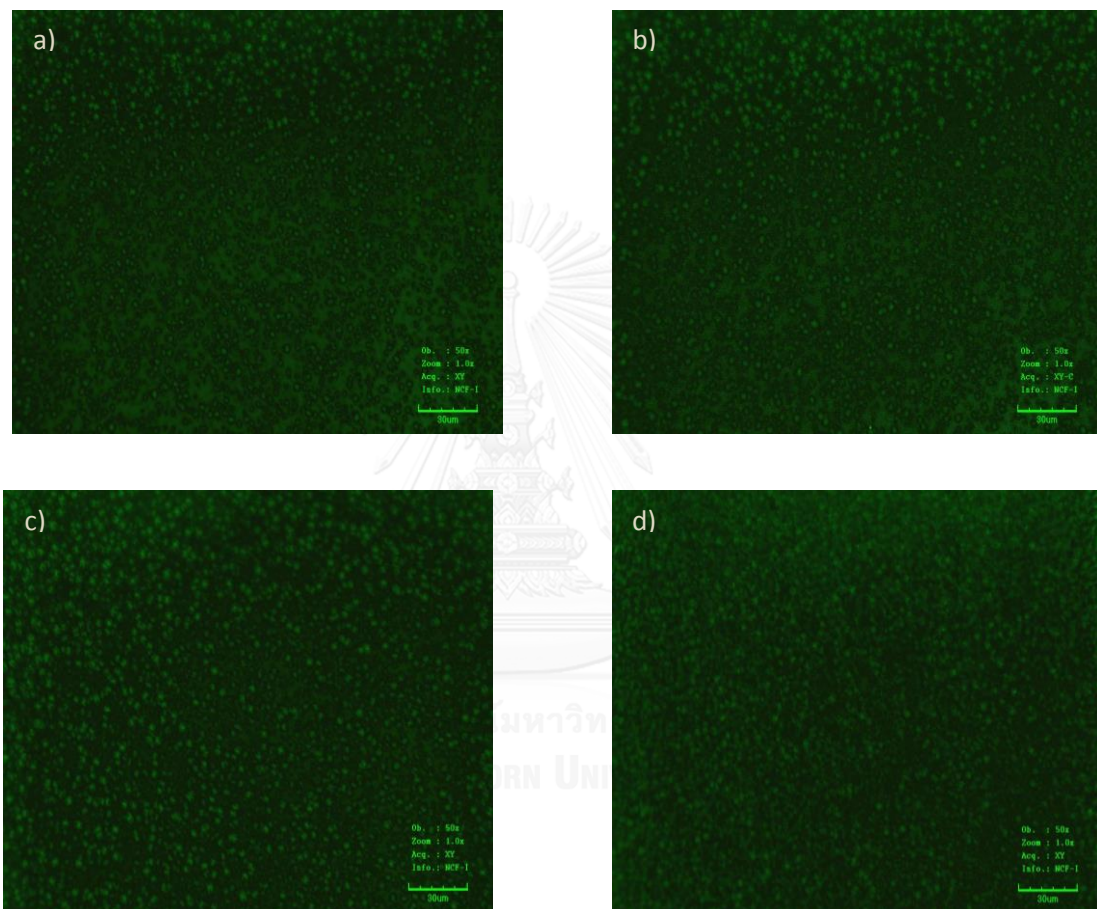
Figure 5.15 Confocal laser scanning microscope of benzoxazine-modified asphalt: (a)

neat asphalt,(b) 6wt% Ph-a benzoxazine modified asphalt, (c) 6 wt% BA-a

benzoxazine modified asphalt, (d) 6wt %TrisP-a benzoxazine modified asphalt with

50× magnifications.

However, regular particle, good dispersion of polymer particles was observed in asphalt matrix with 6% benzoxazine modifier. To achieve polymer modified asphalt with good road performance, small and regular particles and good dispersion fineness are required [53].

5.2.9   Chemical interaction between benzoxazine resin and asphalt of 6 % by weight of benzoxazine resins modified asphalt

FTIR spectroscopy is a simply analytical technique that has been wildly applied to study chemical and structure change in different samples. The FTIR spectra of the neat asphalt and modified asphalts are show in Figure 5.16.

The spectrum of the neat asphalt was given in Figure 5.16. The peak of carbonyl group in carboxylic acid can be found in the range 1670-1700 cm^{-1}; the peak of C-O stretching can be observed at 1310 cm^{-1}. The evidence of the hydroxyl group is shown from raised and broad area in the range of 2500-3300 cm^{-1} [57]. The strong peaks within 2853.3 – 2964.5 cm^{-1} region were typical C-H stretching vibration, two peaks in aliphatic chains. The peak at 1604.3 cm^{-1} was attributed to C=C stretching vibrations in aromatic. The C-H symmetric deforming in CH_3 vibrations of aliphatic branched was observed at 1455.9 cm^{-1} and 1376.7 cm^{-1} respectively. The small peck at 1031.3 cm^{-1} was ascribed to S=O stretching vibration. The peaks within 739.3 -910 cm^{-1} region were typical C-H vibrations of benzene ring [14, 54, 57, 58].

Comparing spectrum of in Figure 5.10, the peaks absorbance of the neat asphalt and benzoxazine resins modified asphalt show difference, new peaks absorbance appear and peaks absorbance disappear. Therefore, verified reactions occured between the neat asphalt and benzoxazine modifier.

From the observation of the FTIR spectra in Figure 5.16, there are new peak absorbance in 1739.5 cm^{-1}, the peak absorbance of C=O stretching vibration and one peck absorbance of C-O stretching vibration in 1231.3 cm^{-1}, two peak for ester carbonyl in benzoxazine resins modified asphalt. In addition, the hydroxyl group is shown from broad area in the range of 2500-3300 cm^{-1} of neat asphalt in Figure 5.16 a) disappears. Therefore, these polymers can be functionalized to produce a modifier that can chemically react with the asphalt matrix.

This result suggests the interaction between benzoxazine resin and polar molecules of asphaltene makes the molecules of asphaltene larger with a higher molecular weight; the asphalt structure was changed from sol to gel type. It can cause better performance of asphalt which can be observed from the improved properties of asphalt such as high softening point temperature, good ductility, high toughness and tenacity etc.
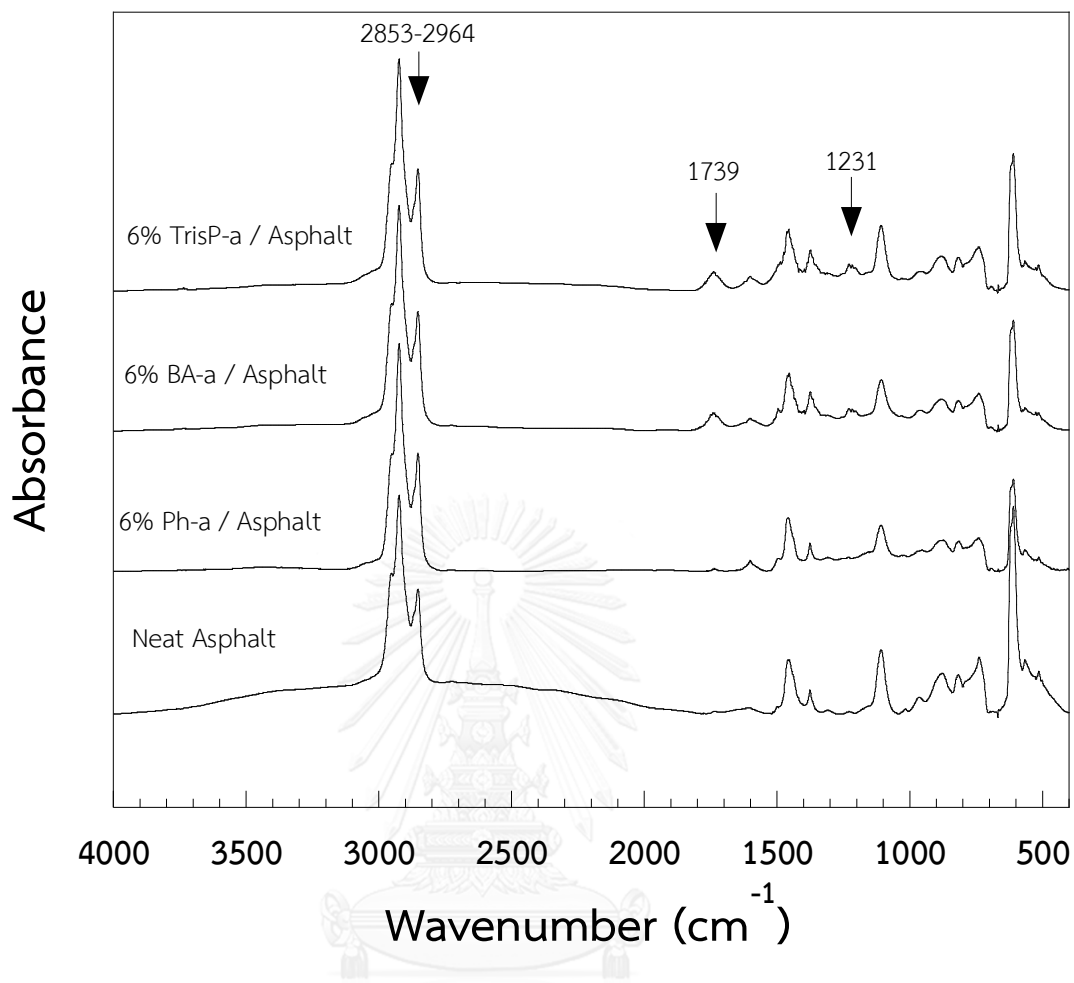
Figure 5.16 FTIR spectra of neat asphalt and benzoxazine resins modified asphalt

5.2.9 Thermal stability of 6 % by weight of benzoxazine resins modified asphalt

TGA is a method employed to measure the weight loss of a polymeric material during the temperature rise. The characteristics associated with thermal stability including degradation temperature and residual weight for each sample can be obtained from it TGA profile. The temperature at 5% by weight loss occurs is

commonly considered as degradation temperature and char residual at 800 $^{\circ}$C in nitrogen atmosphere were reported as a function of benzoxazine functionality.

Figure 5.17 exhibits thermogravimetry curve for 6% by weight of benzoxazine resins modified asphalt with different functionality. The results show that the degradation temperature and char residue at 800°C increased with the addition of the benzoxazine resin to the asphalt matrix. The degradation temperature at 5% weight loss of the neat asphalt was 362 °C while the degradation temperature at 5% weight loss of the benzoxazine resins modified asphalt increased to 369, 379 and 396 °C at benzoxazine resin content of 6 % by weight of Ph-a, BA-a and TrisP-a benzoxazine modified asphalt, respectively. In addition, the char residue at 800°C of the neat asphalt was measured to be 13.8 % whereas the char residue at 800°C of Ph-a, BA-a and TrisP-a benzoxazine modified asphalt slightly differ from neat asphalt to be 14.0, 14.2 and 14.3 %, respectively.

The results showed that the thermal stability significantly increases with increasing functionality of benzoxazine resins, suggesting TrisP-a benzoxazine modified asphalt as the highest thermal stability. It occurs due to the presence of benzoxazine resin in benzoxazine asphalt matrix increase the network cross-link of modified asphalt attributed to a greater thermal stability of the polybenzoxazine modifier

Figure 5.17 TGA thermograms of 6 %wt benzoxazine resins modified asphalt: (▲) neat asphalt, (●) Ph-a benzoxazine modified asphalt, (■) BA-a benzoxazine modified asphalt and, (◆) TrisP-a benzoxazine modified asphalt

5.2.10   Dynamic mechanical analysis of 6 % by weight of benzoxazine resins modified asphalt

Dynamic mechanical analysis (DMA) is measured of the storage and loss modulus of modified asphalt under an oscillating load against temperature. By raising the temperature through the region of glass transition, the storage modulus decreases, whereas the loss modulus shows a maximum peak. The glass transition temperature can be detected at the midpoint of the transition in the storage modulus or at the peak position in the loss modulus curves. The storage modulus (E') refers to the stiffness and resistance to deformation of the samples. Loss modulus (E'') indicates the amount of mechanical energy dissipated by a material. Relaxation process assigned to main chain fluctuations [21, 29, 53].

Figure 5.18 shows storage modulus of benzoxazine resins modified asphalt at different functionalities of benzoxazine resins at 6 % by weight and at various temperatures ranging from -70°C to 40°C was greater than that of the neat asphalt. The storage modulus at - 30 °C increase with increasing in benzoxazine functionality from 1.37 GPa of neat asphalt to 1.74, 2.00 and 2.59 GPa of Ph-a, BA-a, and TrisP-a benzoxazine modified asphalt, respectively. Therefore, it was indicated that benzoxazine resins modified asphalts were stiffer than the unmodified asphalt, which is continuous network structure.

The results showed that the storage modulus significantly increases with increasing functionality of benzoxazine resins, suggesting TrisP-a benzoxazine modified asphalt as the highest rigid.

Figure 5.19 exhibits loss modulus of benzoxazine resins modified asphalt at different functionalities of benzoxazine resins at 6 % by weight and at various temperatures ranging from -70°C to 40°C. The maximum peak of the loss modulus is generally used to indicate the glass transition temperature of each sample. From the Figure, the loss modulus curve reveal a glass transition temperature (Tg) of the unmodified asphalt to be -14.3°C whereas the glass transition temperature (Tg) of the benzoxazine resins modified asphalts were found to be higher than that of the unmodified asphalt and were observed to systematically increase with the amount of the benzoxazine modifier. The glass transition temperatures (Tg) of the benzoxazine resins modified asphalt were determined to be -3.2°C, 2.6°C and 4.7 °C at 6% by weight of Ph-a, BA-a and TrisP-a benzoxazine resins , respectively. It is due to an introduction of benzoxazine rigid phases in polymer modified asphalt.

The results showed that the glass transition temperature increases with increasing functionality of benzoxazine resin, suggesting 6% by weight of TrisP-a benzoxazine modified asphalt as the highest mechanical and thermal stability, which is essential in pavement application in the tropical climate region.
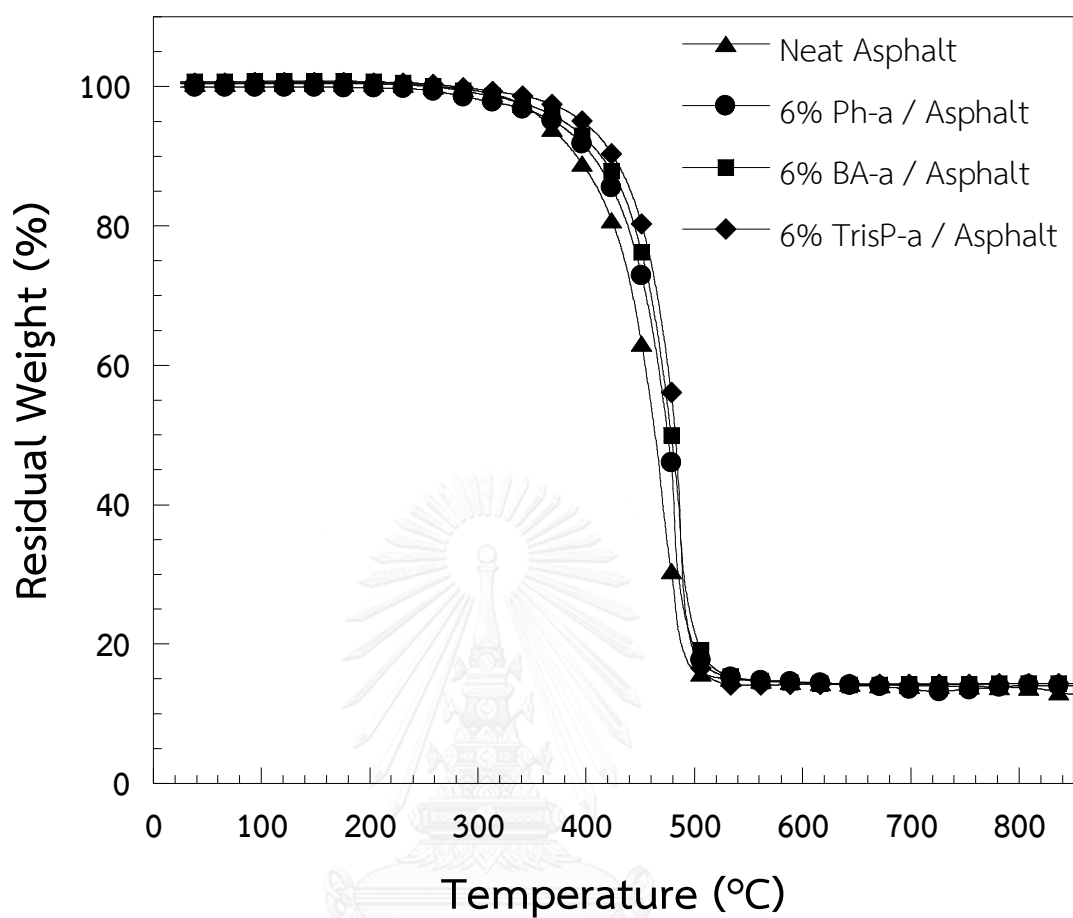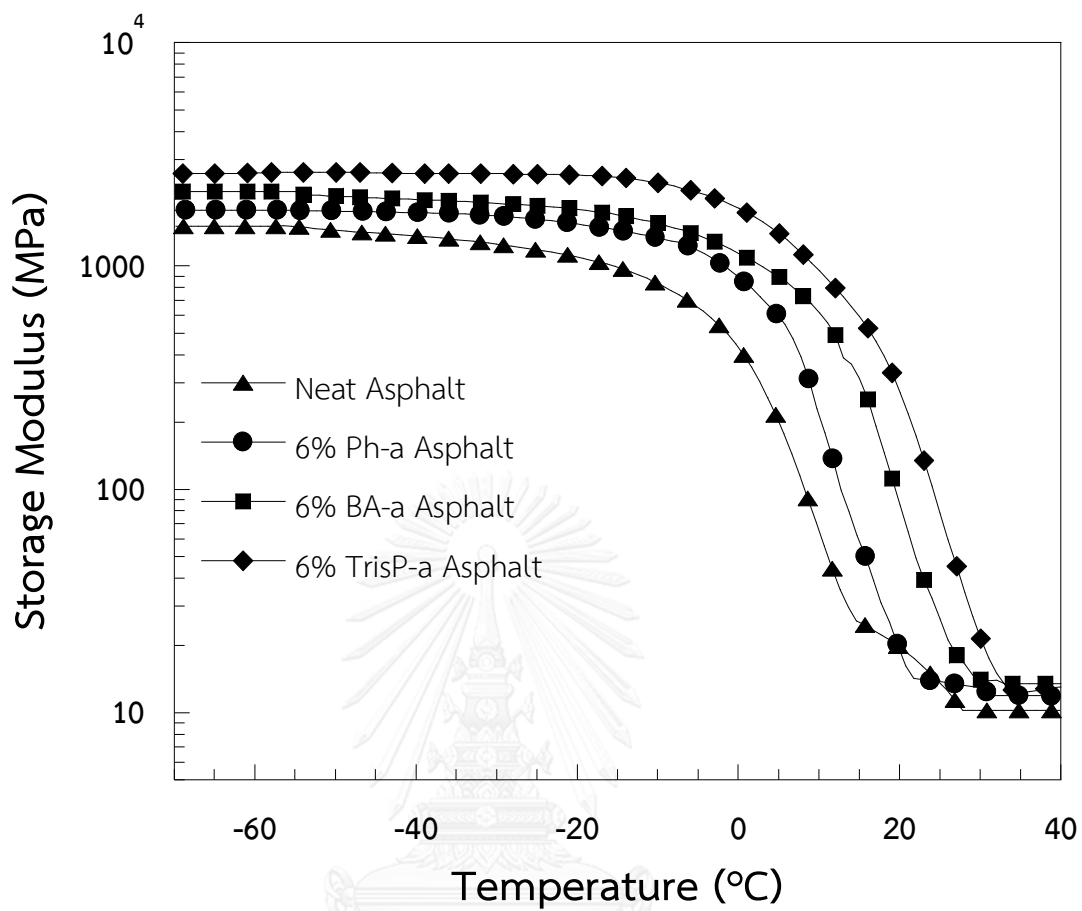
Figure 5.18 DMA thermograms of 6 %wt benzoxazine resins modified asphalt: (▲) neat asphalt, (●) Ph-a benzoxazine modified asphalt, (■) BA-a benzoxazine modified asphalt and, (◆) TrisP-a benzoxazine modified asphalt
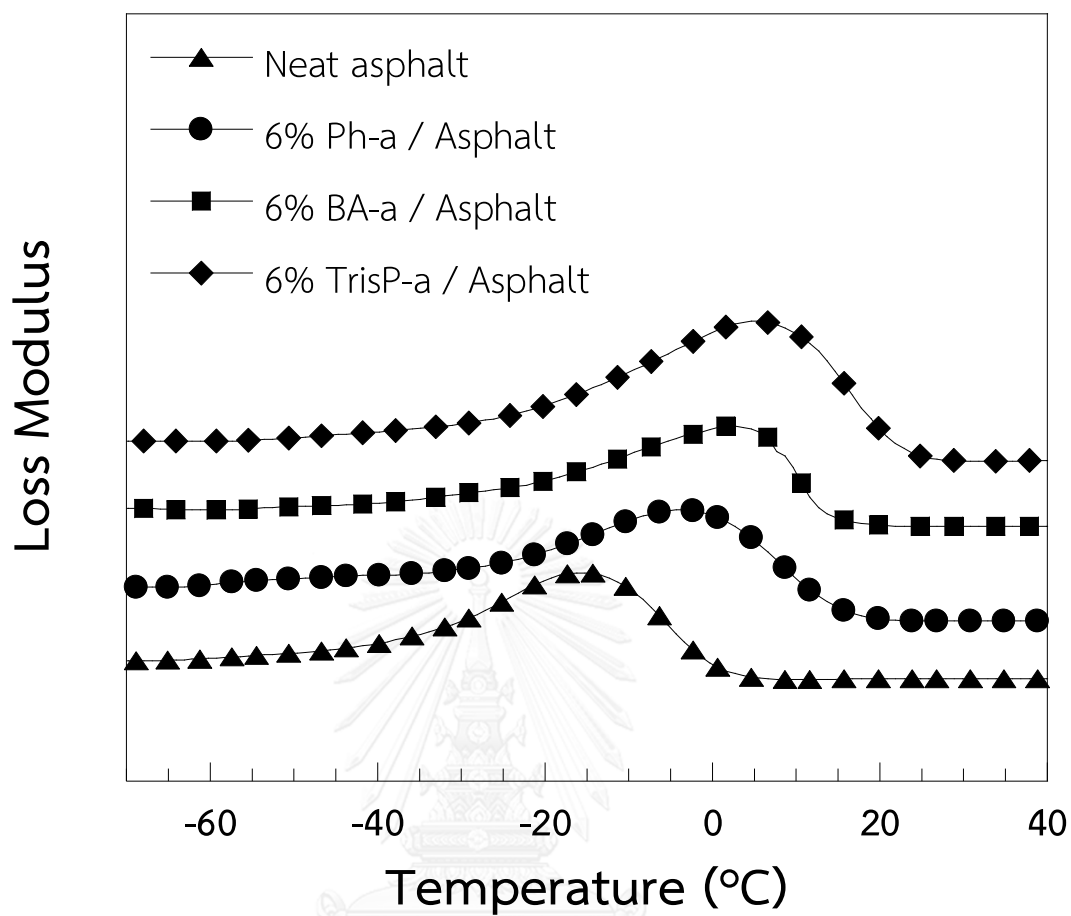
Figure 5.19 Overlay plot of DMA thermograms of 6 %wt benzoxazine resins modified asphalt: (▲) neat asphalt, (●) Ph-a benzoxazine modified asphalt, (■) BA-a benzoxazine modified asphalt and, (◆) TrisP-a benzoxazine modified asphalt

CHAPTER VI

CONCLUSIONS

Asphalts modified with varied benzoxazine functionality at different proportion can develop conventional test, chemical, thermal and mechanical properties of asphalt. Ph-a, BA-a and TrisP-a modification cause increases in softening point and decreases in penetration. Since, the decreased penetration and increased softening point temperature and penetrability index indicate increased stiffness (hardness) of the PMAs, the results revel that the asphalt mixtures prepared with the Ph-a, BA-a and TrisP-a may be less sensitive to permanent deformation. Along with the parameters related to penetration and softening point test; increased viscosities and indices also indicate the stiffening effect of Ph-a, BA-a and TrisP-a modification.

However, based on viscosity test results, a clear distinction between investigated polymers can be made. The increase in viscosity is not favourable since high viscosity makes mixing and compaction of the mixture more difficult. Ductility, toughness and tenacity of 6 % by weight of all benzoxazine resins show remarkable increased, which can promote the adhesion. Also, from the results, at 6 % by weight of all benzoxazine resins used, asphalts showed balanced properties such as softening point, penetration value ductility, toughness and tenacity that suitable for road application according to the requirement specifications of Highways Department

of Thailand. The optical microscopy shows that at 6 % by weight the PMAs showed that benzoxazine fraction to disperse as small particle and dispersion fineness of polymer particles in asphalt. In terms of FT-IR spectroscopy, it is found that the regeneration of main bands of benzoxazine resins modified asphalt are identical and the significant variation is the peak intensity, represent the chemical bonding that occurs between benzoxazine and asphalt matrix.

The result of rutting parameter of the Strategic Highway Research Program (SHRP) showed the maximum value increased with increasing benzoxazine functionality. That is increased resistance to permanent deformation or rutting at high temperatures, better flexibility at low temperatures and also enhanced thermal and fatigue cracking resistance. The thermomechanical and thermal properties of benzoxazine resins modified asphalts were higher than unmodified asphalt and those increased when benzoxazine functionality increased. The degradation temperature (at 5% weight loss) and char residue (at 800°C) of benzoxazine resins modified asphalt increase to 396 $^{\circ}$C from 362 $^{\circ}$C of neat asphalt with increasing functionality of benzoxazine resin. The viscoelastic properties, thermomechanical properties (i.e. storage modulus and loss modulus) can improve storage moduli and loss modulus of polymer modified asphalt. The glass transition temperature (Tg) of benzoxazine resins modified asphalt increased to 4.7 $^{\circ}$C from -14.3 of neat asphalt.

Although TrisP-a modified asphalt revealed the highest properties , some properties of BA-a modified asphalt such as toughness, tenacity and rutting resistance are nearby from TrisP-a modified asphalt. Therefore, we can use the BA-a benzoxazine which sufficient to modified the properties of asphalt and this resin is lower costs than TrisP-a benzoxazine resin.

Consequently, benzoxazine resins modified asphalts decreased in formation of highly heavy traffic loads in rutting, bleeding, cracking deformation and enhanced the ductility as well as toughness and tenacity of asphalt mixtures, which may be able to promote the adhesion between modified asphalt and aggregate.

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APPENDIX

APPENDIX A

Appendix A Specification for Polymer Modified Asphalt Cement

Appendix A- 1 Specification for Polymer Modified Asphalt Cement for Asphalt

Concrete (Asphalt Concrete or Hot-mix Asphalt) Specification

No.DH-SP. 408/2536

Item No.	Properties	Unit	Min	Max	Test Method
1.	Penetration at 25 °C, 100 gm., 5 sec.	0.1 mm.	60	70	DH-T 403
2.	Softening Point, Ring and Ball	°C	70	-	ASTM D36
3.	Penetration Index	-	+3	-	NLT-181 *
4.	Ductility at 13 °C, 5 cm/min	cm.	55	-	DH-T 405
5.	Torsional Recovery at 25 °C	%	70	-	NLT-329 *
6.	Float Test at 60 °C	sec.	3000	-	ASTM D139
7.	Toughness/Tenacity Test, 25 °C				ESM NE-31 **
	Toughness	Kg.cm	200	-	
	Tenacity	Kg.cm	100	-	
8.	Brookfield Viscosity, Shear Rate 18.6 s-1, Spindle 21				
	At 135 °C	cP	1100	-	
	At 165 °C	cP	300	-	
9.	Storage Stability at 165 °C, 120 hrs. Difference in Softening Point	°C	-	5	NLT-328 *
10.	Density at 25 °C	gm/cc	1.00	1.05	ASTM D70
11.	Flash Point, Cleveland Open Cup	°C	220	-	ASTM D92
12.	Solubility in Trichloroethylene	% wt	99.0	-	DH-T 409

Test on Residue from Thin Film Oven Test					
13.	Weight Loss	% wt.	-	0.5	ASTM D1754
14.	Retained Penetration at 25 °C	%	70	-	DH-T 403
15.	Variation in Softening Point	°C	4	6	ASTM D36
16.	Ductility at 13 °C, 5 cm/min	cm.	40	-	DH-T 405
17.	Torsional Recovery at 25 °C	%	60	-	NLT-329 *

Note   * Refer to the National Laboratory of Transportation Madrid, Spain

** Refer to Elpidio Sanchez Marcos, Spain

VITA

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