วัสดุแอสฟัลต์ที่ดัดแปรด้วยเบนซอกซาซีน

นางสาวอัญชลี อ่วมพันธ์เจริญ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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BENZOXAZINE-MODIFIED ASPHALTS

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อัญชลี อ่วมพันธ์เจริญ : วัสดุแอสฟัลต์ที่ดัดแปรด้วยเบนซอกซาซีน (BENZOXAZINE-MODIFIED ASPHALTS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. ศราวุธ ริมดุสิต, 57 หน้า.

พอลิเมอร์นิยมใช้ในการเพิ่มอายุการใช้งานและปรับปรุงคุณสมบัติเชิงกลและทางความร้อนของยางมะตอยโดยเฉพาะอย่างยิ่งสำหรับงานการทาง วัตถุประสงค์ของงานวิจัยนี้เพื่อเพิ่มคุณสมบัติเชิงกลและทางความร้อนของยางมะตอยสำหรับงานการทางโดยใช้เบนซอกซาซีนเรซินเป็นสารดัดแปร ในงานวิจัยนี้ใช้ยางมะตอยเกรด 60/70 โดยเติมเบนซอกซาซีนเรซินในอัตราส่วน 1, 3, 5, 7 และ 9 เปอร์เซ็นต์โดยน้ำหนัก ผสมโดยใช้เครื่องกวนที่อุณหภูมิ 80 องศาเซลเซียส เป็นเวลา 1 ชั่วโมง ที่ความเร็วรอบ 500 รอบต่อนาที จากนั้นบ่มด้วยตู้อบที่อุณหภูมิ 190 องศาเซลเซียส เป็นเวลา 1 ชั่วโมง และศึกษาผลของการปรับปรุงคุณสมบัติยางมะตอยด้วยเบนซอกซาซีนเรซิน พบว่ามอดุลัสการสะสม มีค่าสูงขึ้นเมื่อปริมาณเบนซอกซาซีนเพิ่มขึ้นและอุณหภูมิการเปลี่ยนสถานะคล้ายแก้ว (Tg) ของยางมะตอยดัดแปรมีค่าสูงขึ้นเท่ากับ 4.4 องศาเซลเซียสจากยางมะตอยปกติที่ -14.3 องศาเซลเซียส อุณหภูมิการสลายตัวของยางมะตอยดัดแปรด้วยเบนซอกซาซีนเพิ่มขึ้นเป็น 380 องศาเซลเซียสจาก 354 องศาเซลเซียส ของยางมะตอยปกติ คุณสมบัติทางการไหลทั้งมอดุลัสการสะสม, มอดุลัสการสูญเสีย และความหนืดที่อุณหภูมิ 60 องศาเซลเซียส เพิ่มขึ้นเมื่อปริมาณเบนซอกซาซีนเพิ่มขึ้น อุณหภูมิสูงสุดของค่าความต้านทานการเกิดร่อง (Rutting parameter) เพิ่มขึ้นจาก 65 องศาเซลเซียส ไปเป็น 84 องศาเซลเซียส ค่าความถ่วงจำเพาะเพิ่มขึ้นจาก 1.034 เป็น 1.053 และการศึกษาการกระจายตัวของการผสมของเบนซอกซาซีนกับยางมะตอยพบว่าเบนซอกซาซีนกระจายตัวเป็นเม็ดเล็กๆ อยู่ในยางมะตอย จุดอ่อนตัว (Softening point) เพิ่มขึ้นในขณะที่ค่าความต้านทานการเจาะทะลุ (Penetration) ลดลง เมื่อปริมาณเบนซอกซาซีนเพิ่มขึ้น จากการศึกษาการดัดแปรยางมะตอยด้วยเบนซอกซาซีนสามารถลดการเสียรูปของผิวถนนในการเกิดร่องล้อ (Rutting), การเยิ้ม (Bleeding) และรอยแตก (Cracking) ได้

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....
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ANCHALEE OUMPANCHAROEN: BENZOXAZINE MODIFIED ASPHALTS. THESIS ADVISOR: ASST. PROF. SARAWUT RIMDUSIT, Ph.D., 57 PP.

The use of polymers for modification of asphalt is an attempt to prolong the service life and improve the performance of asphalt particularly for road pavement applications. This research aims to study mechanical and thermal properties of asphalt modification by bisphenol A based benzoxazine resin. The 60/70 penetration grade asphalts were modified by varying the amount of benzoxazine resin at 1wt%, 3wt%, 5wt%, 7wt% and 9wt%. The suitable mixing condition was achieved by mechanical mixing for 1 hr at 80°C and a mixing speed of 500 rpm with a stirrer followed by curing for 1 hr at 190°C. The storage modulus increased when benzoxazine contents increased and the glass transition temperature (Tg) of benzoxazine-modified asphalt increased to 4.4°C from -14.3°C of the unmodified asphalt. The degradation temperature of benzoxazine-modified asphalt increased to 380°C from 354°C of unmodified asphalt. Rheological properties as storage shear modulus, loss shear modulus and viscosity at 60°C increased when benzoxazine contents increased. The maximum temperature of rutting parameter ($G^*/\sin\delta$) increased from 65°C to 84°C and specific gravity increased from 1.034 to 1.053 when benzoxazine contents increased. Morphology of benzoxazine resin and asphalts blend revealed that benzoxazine fraction to disperse as small particles in the asphalts. Softening point of the benzoxazine-modified asphalt increased with increasing the benzoxazine resin contents while the penetration depth decreased when the benzoxazine ratio increased. Appreciable decrease in formation of rutting, bleeding and cracking are thus expected to be achieved by the use of the benzoxazine-modified asphalts.

Department : Chemical Engineering	Student's Signature ....
Field of Study : Chemical Engineering	Advisor's Signature ....
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CONTENTS

PAGE

PAGE

PAGE

LIST OF FIGURES

FIGURE **PAGE**

FIGURE **PAGE**

LIST OF TABLES

TABLE **PAGE**

CHAPTER I

INTRODUCTION

1.1 General Introduction

Asphalts are widely used for road pavement application. Asphalts have viscoelastic properties and performance as a pavement material. Asphalts are from crude oil distillation processes and are a colloidal system in which the asphaltenes are dispersed into an oily matrix of the maltenes. [1] Asphalts pavement road are viscoelastic behavior, so they are flexible and flowable at high temperature, brittle at low temperature and able to permanent deformation at high loading. [2] Most of highway networks in Thailand made from asphalt. Because of hot climate and high traffic loading, the asphalt road becomes rutting, cracking and striping deformation [3], so they have short service life than usual and it is costly in terms of maintenance. [4] Polymers have been widely used to modify and improve properties of asphalt for rutting resistance, fatigue resistance, cracking resistance and stripping resistance by increaseing in elasticity and stiffness of asphalts. [5] Generally, Plastomer or elastomer polymers such as styrene-butadiene styrene copolymer are widely used to modify asphalt for road pavement application. However, plastomer or elastomer polymers modified asphalt cannot develop the thermoplastic behavior of asphalt that means modified asphalt by elastomer are flowable at high temperature. The solution to improve this problem is modified by epoxy resin that kind of polymer is in thermosetting group. Epoxy modified asphalt is prepared by mixing an epoxy, asphalt and curing agent with complex step to preparation. This study uses a benzoxazine resin base bisphenol A to modify asphalt. Benzoxazine resin has easy synthesis, no need of curing agent for ring opening, no volatile by product, low viscosity, high thermal stability and low price.

The objective of the study is to investigate effects of additional benzoxazine resin on the properties of the modified asphalt for potential pavement applications.

Benzoxazine-modified asphalt was characterized the morphology, thermal, mechanical properties and conventional test for road pavement by varying contents of benzoxazine resin.

1.2 Objectives

1. To develop polymer-modified asphalt using benzoxazine resin as a modifier.
2. To investigate effects of benzoxazine resin on rheological properties, physical properties, mechanical properties and thermal properties of polymer modified asphalt.
3. To evaluate major characteristics for pavement application i.e. penetration resistance and softening point.

1.3 Scope of the study

1. Prepare polymer modified asphalt using benzoxazine resin as a modifier with 0%, 1%, 3%, 5%, 7%, 9% by weight.
2. Determine the effect of benzoxazine modified asphalts on rheological properties, physical properties, mechanical properties and thermal properties of polymer modified asphalt.
3. Examine the major characteristics for pavement application using polymer modified asphalt as a binder.

1.4 Procedure of the study

1. Sample preparation

   1.1 Synthesis of Benzoxazine resin

   Mix bisphenol A, Paraformaldehyde and aniline on 1:4:2 by mole in aluminum foil. It's stirred for 40 min keeping the temperature on 110-120°C. Mixture was yellow liquid and few bubbles keeping at room temperature and milling.

   1.2 Modified asphalts

   Asphalts grade 60/70 was mixed with benzoxazine resin and heated to $80\pm5^{o}C$ by stirrer 500 rpm and mixed for 1 hr at ratio 1%, 3%, 5%, 7% and 9% by weight.

2. Analysis of properties of the obtained benzoxazine-modified asphalts
   - Rheological properties : Rheometer
   - Thermal properties : DSC, TGA
   - Thermomechanical properties : DMA
   - Physical properties
     - Morphology : Optical microscope
     - Specific gravity : Specific gravity measurement
   - Penetration
   - Softening point

3. Analyze and conclude the experimental results.
4. Preparation of the final report.

CHAPTER II

THEORY

2.1 Asphalts

Asphalts are the petroleum refinery bottoms product. Asphalts are a complex chemical mixture of molecules that are dominantly hydrocarbons with a small amount of structurally analogous heterocyclic species and functional groups constraining sulphur, nitrogen and oxygen atoms. [6] Bitumen also contains trace quantities of metals such as vanadium, nickel, iron, magnesium and calcium, which occur in the form of inorganic salts and oxides or in porphyrine structure. The most bitumen contains:

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

2.1.1 Asphalts Constitution

Chomatographic techniques have been most widely used to define bitumen constitution. The chomatographic method precitate asphaltenes using n-heptane followed by chromatographic separation of the remaining material, using this technique, bitumens can be separate into four groups : asphaltenes, resins, aromatics and saturates. Figure 2.1 shows a schematic representation of chromatographic method.

2.1.1.1 Asphaltenes

Asphaltenes are black or brown amorphous solid containing and insoluble in n-heptane. Main composition is carbon and hydrogen, some nitrogen, sulphur and oxygen. Asphaltenes are highly polar and complex aromatic material of high molecular weight. Figure 2.2 shows chemical structure of asphaltene.

-Molecular weight : 1,000-100,000

-Particle size : 5-30 nm.

-Ratio of hydrogen/carbon 1:1

The amount of asphaltene has more effect on the rheological properties of asphalt. increaseing the asphaltene content produces a harder, more viscous bitumen with a lower penetration, higher softening point and higher viscosity. Asphaltenes constitute 5 to 25% of asphalt.

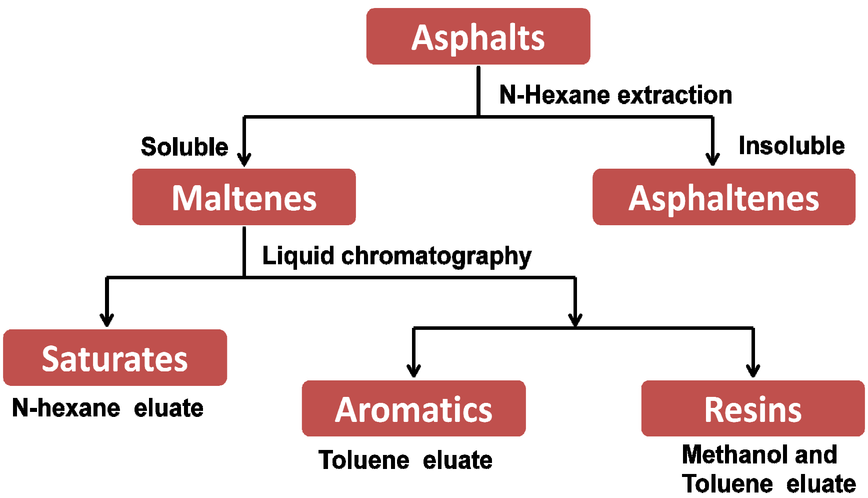


Figure 2.1 Schematic representation of the analysis for chemical composition of asphalt. [7]

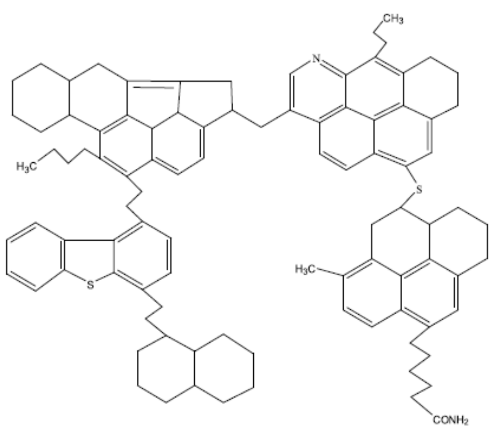


Figure 2.2 chemical structure of asphaltenes[7].

2.1.1.2 Resins

They are soluble in n-heptane. Resins are dark brown color, solid or semi-solid and, being polar in nature, they are strongly adhesive. Resins are dispersing agent or peptisers for the asphaltenes. Figure 2.3 shows chemical structure of resins.

-Molecular weight : 500-50,000

-Particle size : 1-5 nm.

-Ratio of hydrogen/carbon 1:3, 1:4

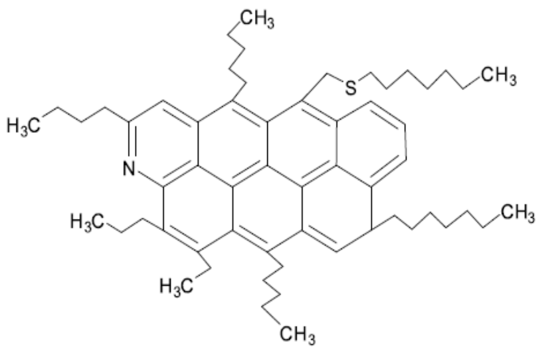


Fig.2.3 chemical structure of resins. [7]

2.1.1.3 Aromatics

Aromatics are dark brown viscouse liquids and they are non polar.Aromatics have the lowest molecular weight aromatic compounds in the asphalt and represent the major proportion of the dispersion medium for peptised asphaltenes. They constitute 40 to 65% of the total bitumen nd are dark brown vicous liquids. Figure 2.4 Shows chemical structure of aromatic. Molecular weight of aromatics is in the range of 300 to 2,000.

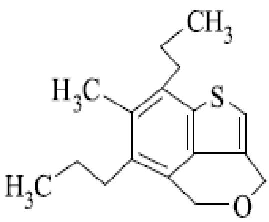


Figure2.4 chemical structure of aromatics. [7]

2.1.1.4 Saturates

Saturates are non polar viscous oils and they are straw or white color. Saturates consist of straight and branch chain aliphatic hydrocarbons. This fraction forms 5-20% of bitumen. Figure 2.5 shows chemical structure of saturates. Molecular weight of saturates is in the range of 300 to 2,000.

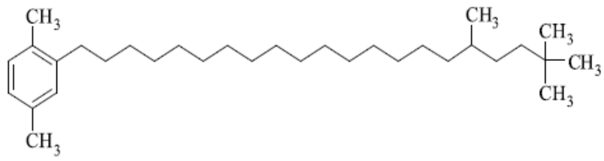


Figure2.5 chemical structure of saturates. [7]

2.1.1.5 Metallic Constituents of Asphalt

The elements occur principally in the heavier or involatiole components of the oils, some as inorganic contaminants, transition metal complexes. The metals present in most fuel oils are sodium, vanadium, iron, nickel and chromium with most of the sodium present as sodium chloride.

Asphalt is colloidal system consisting of high molecular weight asphaltene micells dispersed in lower molecular weight oily medium(maltene).in Figure 2.6

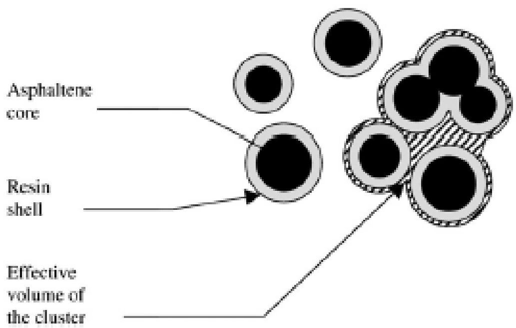


Figure 2.6 A simplified view of the colloidal structure of asphalt.[8]

2.1.2 Advantage of Asphalt

Asphalt have a good properties for pavement applicastion show as below;

- Good adhesiopn
- Water proofing
- Thermoplastic characteristic
- Good acid and base resistance

2.2 Specification of Aphalts

Four type of asphalts are combination of penetration, softening point and viscosity.

2.2.1 Penetration Grade

Penetration grade asphalts have standard grade 5 grades that is 60/70, 80/100, 120/150 and 200/300 for suitable application and weather of each area. The 60/70 penetration grades have widely use in Thailand because of proper for hot and humid region and for cold weather counties use penetration grade 120/150. The Highway Department of Thailand use standdard Specification No. DH-SP. 401/2531 (Table2.1).These are specified the penetration and softening point tests.

Majority of penetration grade asphalts produced are used in road construction.

Table 2.1 Specification of asphalt cement. [9]

Properties		Penetration Grade						Test Method
		60-70		70-80		80-100		
		Min.	Max.	Min.	Max.	Min.	Max.	
Penetration at 25 C (77 F), 100 g, 5 s	0.1 mm	60	70	70	80	80	100	ทล.-ท. 403/2518
Flash point (Cleveland open cup)	degree C (F)	232 (450)	- -	232 (450)	- -	232 (450)	- -	ทล.-ท. 406/2519
Ductility at 25 C (77 F), 5 cm per min	cm	100	-	100	-	100	-	ทล.-ท. 405/2519
Solubility in Trichloroethylene	percent	99.0	-	99.0	-	99.0	-	ทล.-ท. 409/2520
Thin-film oven test, 3.2 mm., 163 C (325 F), 5 hour								AASHTO T 179
Loss on heating	percent	-	0.8	-	0.9	-	1.0	
Penetration of residue	percent of original	54	-	52	-	50	-	
Ductility of residue at 25 C (77 F), 5 cm per min	cm	50	-	62	-	75	-	
Loss on heating, 163 C (325 F), 5 hour	percent	-	0.8	-	0.9	-	1.0	ทล.-ท. 404/2518

2.2.2 Oxidised Asphalts

Oxidised asphalts are used almost in roofing, flooring, mastics, pipe coatings and paints. They are designated by softening point and penetration test, e.g. 85/40 is an oxidised grade asphalt with a softening point of 85±5°C and penetration of 40±5 dmm. The softening points of oxidised grades of bitumen are much higher than those of corresponding penetration grade asphalt.

2.2.3 Hard Asphalts

Hard asphalt grade produces from distillated penetration grade unger atmosphere pressure and high temperature for harder asphalt. Hard asphalts always used for industrial application, e.g. coal briquetting, paints, etc. They are also specified by reference to both softening point and penetration tests but are designated by a softening point range only, e.g. H80/90.

2.2.4 Cutback Asphalts

Cutback asphalts are produced by blending e 70/100 pen or 160/220 pen asphalt with kerosene to comply with a viscosity specification. The majority of cutback asphalt is used in surface dressing.

2.3 Asphalt for Road Pavement

2.3.1 Road Structure

Road structure shows in Figure 2.7

- Surface Cource
- Prime Coat
- Base Course
- Sub-base Course
- Sub-grade Course
- Shoulder

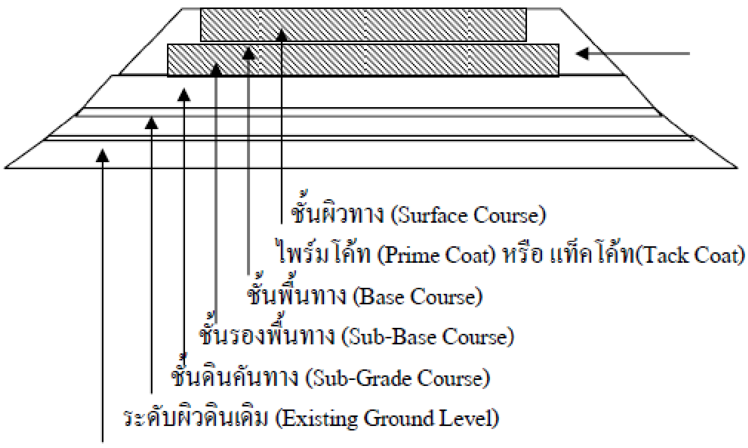


Figure 2.7 Road structure by asphalt cement. [10]

Asphaltic concrete (Hot-mix Asphalt) method is used with road pavement. The aggregate is mixed with asphalt cement. Before mixed, the aggregate heated at 163±8°C and asphalt heated at 159±8°C and after mixed asphalt concrete temperature around 121-168°C.

2.3.2 Permanent Deformation of Road Pavement

As the asphalt is responsible for the visco-elastic behaviour characteristic of asphalts. Asphalt is expose with wide temperature range and heavy truck traffic. It tends to permanent deformation as

2.3.2.1 Rutting

Surface depression in the wheel path Pavement uplift (shearing) may occur along the sides of the rut in Figure 2.8. Subgrade rutting occurs when the subgrade exhibits wheel path depressions due to loading. In this case, the pavement settles into the subgrade ruts causing surface depressions in the wheel path.

Figure 2.8 Rutting permanent deformation. [6]

2.3.2.2 Cracking

Cracking deformation occurs from road surface has low elasticity. Road surface contained repeat traffic loading and fatigue failure. After repeated loading, the longitudinal cracks connect forming many-sided sharp-angled pieces that develop into a pattern resembling the back of an alligator or crocodile. Figure 2.9 show the cracking deformation of road pavement.

Figure 2.9 Cracking permanent deformation. [6]

2.3.2.3 Bleeding

Bleeding in Figure 2.10 occurs when asphalt binder fills the aggregate voids during hot weather and then expands onto the pavement surface. Since bleeding is not reversible during cold weather, asphalt binder will accumulate on the pavement surface over time.

Figure 2.10 Bleeding permanent deformation. [6]

2.3.2.4 Potholes

Potholes are small, bowl-shaped depressions in the pavement surface in Figure 2.11 that penetrate all the way through the surface layer down to the base course. They generally have sharp edges and vertical sides near the top of the hole. As alligator cracking becomes severe, the interconnected cracks create small chunks of pavement, which can be dislodged as vehicles drive over them. The remaining hole after the pavement chunk is dislodged is called a pothole.

Figure 2.11 Potholes permanent deformation. [6]

Permanent deformation makes to study modified asphalt for improve mechanical and thermal properties and increase the service ageing of road pavement.

2.4 The Modification of Asphalts

Polymers are used as additives to improve ther performance of asphalts pavement. Polymers are improve permanent deformation, thermal cracking, Fatigue, moisture damage and ageing. Polymer additive used to modify bitumen that maay be classified into four main group :

- **Rubbers** : natural rubber, polybutadiene, polyisoprene.
- **Thermoplastic polymers** : ethylenss vinyl acetate(EVA), polyethylene(PE), polypropylene(PP), polyvinyl chloride(PVC), polystyrene(PS).
- **Thermosets** : epoxy resin, polyurethane resin, acrylic resin, phenilic resin.
- **Block copolymers** : styrene-butadiene-styrene(SBS), styrene-butadiene-rubber(SBR), styrene-ethylene-butadiene-styrene(SEBS), ehylens-propylene-diene terpolymer(EPDM).

For the polymer modifier to be effective and for its use to be both practicable and economic, it must :

- Resist degradation at atphalt mixing temperatures
- Blend with asphalt
- Improve resistance to flow at high road temperatures without makung the asphalt too viscous at mixing and laying temperatures or too stiff or brittle at low road temperatures
- Be cost effective

The modifier, when blended with asphalts, should:

- Maintain its premium properties during storage, application and in service
- Be capable of being processed by conventional equipment

- Be physically and chemically stable during storage, application and in service
- Achieve a coating or spraying viscosity at normal application temperatures

Benefits of polymer modified asphalt as[11];

- Improve consistency
- Reduce temperature susceptibility
- Improved stiffnees and cohesion
- Improved flexibility, resilience and toughness
- Improved resistance to in-service ageing

This research is a study of modified asphalts by thermosetting polymer.

2.5 Modified asphalts by thermosetting binder

Themosetting polymers are produced by blending two liquid component, one containing a resin and the other a hardener, that react chemically to form a strong three-dimensional structure. In relatively low concentration, 2 to 5%, it reduce the high-temperature viscosity and the deformation when cold.

2.5.1 Benzoxazine resin

Due to good mechanical property, dimensional stability, chemical resistivity, flame resistance property, phenolic or epoxy resins have myriad applications in diverse fields starting from commodity materials to high technology aerospace industries.[12] Benzoxazine resin has low viscosity, no by-product during curing process and open ring by heating that not use curing agent for easy mixing process.Benzoxazine is a single benzene ring fused to another six-membered heterocycle containing one oxygen atom and a nitrogen atom. Reaction of polybenzoxaxine polymerization and ring opening in Figure 2.12 and Figure 2.13 shows benzoxazine powder and molding.

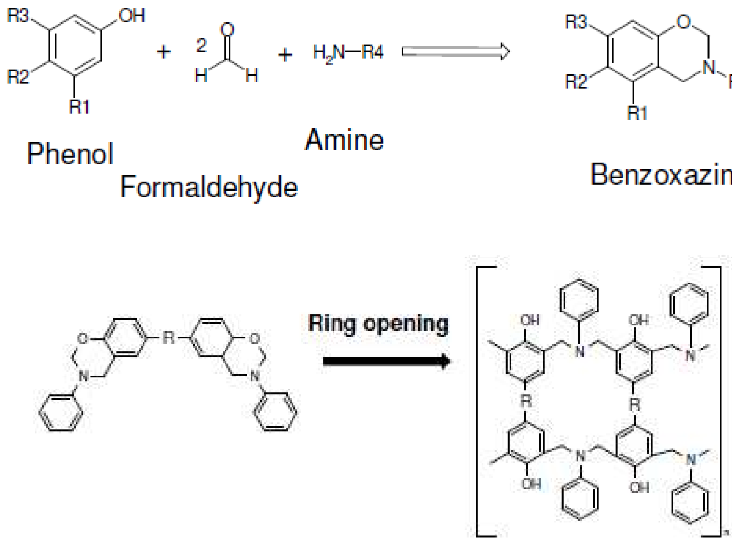


Figure 2.12 Reaction of benzoxazine and ring opening reaction of polybenzoxazine. [12]

Figure 2.13 Benzoxaxine resin powders and molding. [12]

CHAPTER III

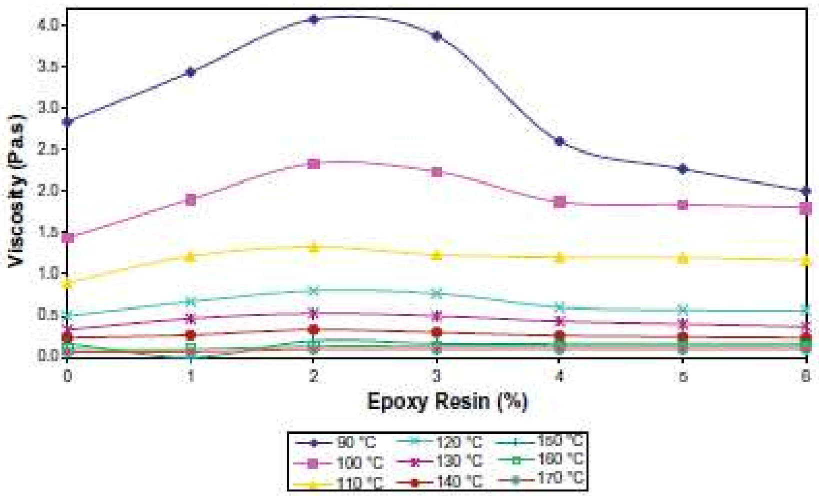
LITERATURE REVIEWS

Cubuk, et. al. studied the modification of bitumen with epoxy resin. Asphalt were modified by varying the amount of epoxy resin at 1wt% to 6wt%. The effects of the epoxy modifier were viscosity, softening point, transition glass temperature and stability increased and heat sensitivity, surface energy, penetration and striping decreased when bitumen was modified by 2wt% epoxy resin. For improving of thermal and mechanical property of modified bitumen was recommended for the use in hot climate, humid regions, in road with heavy traffic load, prevent rutting, bleeding, cracking, striping and aging. (Cubuk, et. al., 2009)

Figure 3.1 showed viscosities of bitumen and epoxy modified bitumen, the result showed newtonian properties of bitumen. Penetration and softening point test were applied to the original bitumen and 2% epoxy modified bitumen.

- Penetration decreased from 62 to 54 dmm.
- Softening point increased from 49.2^{o}C to 52.2^{o}C.
- Transition glass temperature increased from -22.5^{o}C to -13.85^{o}C.

As a result of the study, epoxy modified asphalts can improve the rheological and performance properties of asphalt. Epoxy modified asphalt significantly decreased in the rutting, bleeding, stripping and cracking deformation in road pavement application.



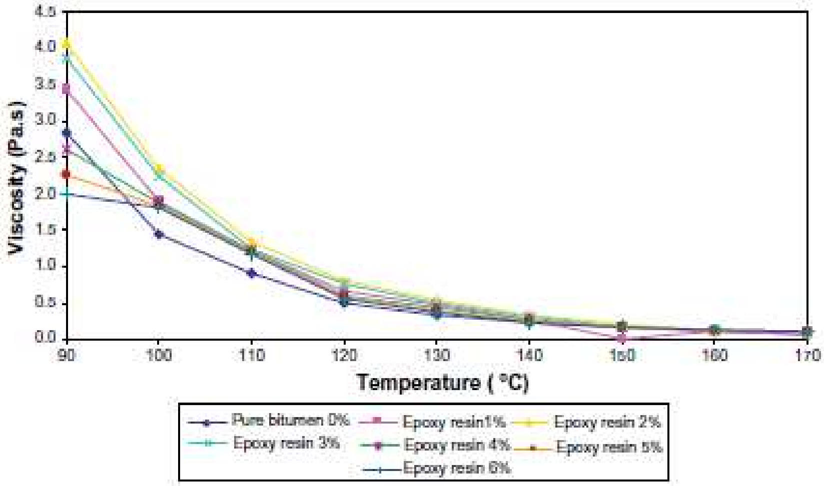


Figure 3.1 Variation of bitumen viscosity as function of epoxy concentration.[13]

Kang, et al. studied to improve poor compatibility of the modified asphalt by using epoxy resin, maleic anhydride and adipic acid. Figure 3.2 showed the glass transition temperature increased when curing agent increased. Table 3.1 showed mechanical properties of epoxy modified asphalt by various curing agent contents. The result revealed tensile strength, rupture elongation and young's modulus were increased with curing agent contents increased. Figure 3.3 showed colloid of modified asphalt by epoxy resin by optical microscrope. Epoxy modifier can imcprove mechanical and thermal properties of asphalt. The mechanism of reaction is showed in Figure 3.4. (Kang, et al., 2009)

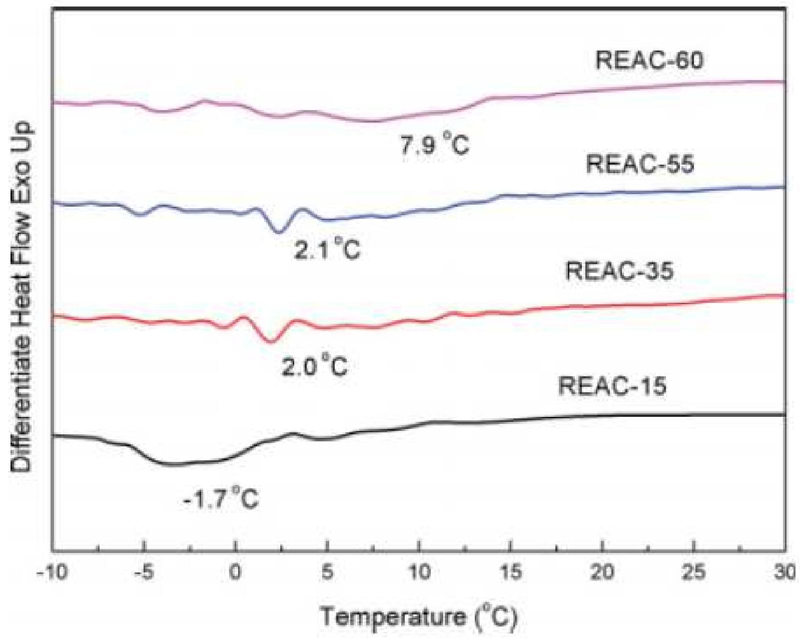


Figure 3.2 Differential of DSC curve of glass transition temperature with various curing agent content.[14]

Table 3.1 : Mechanical properties of modified asphalts by epoxy resin and addition curing agent. [14]

	REAC-60	REAC-55	REAC-35	REAC-15	REAC-0
Cure condition	4 h at 120°C	4 h at 120°C	4 h at 120°C	4 h at 120°C	8 h at 120°C
Tensile strength(MPa)	6.13±0.5	9.87±0.8	7.67±0.4	2.85±0.2	1.92±0.1
Rupture elongation(%)	156.2±6.3	226.1±7.1	259.4±8.0	286.0±9.2	243.4±7.5
Young's Modulus(MPa)	81.9±1.3	85.8±1.3	75.7±0.9	36.5±0.5	34.5±0.5

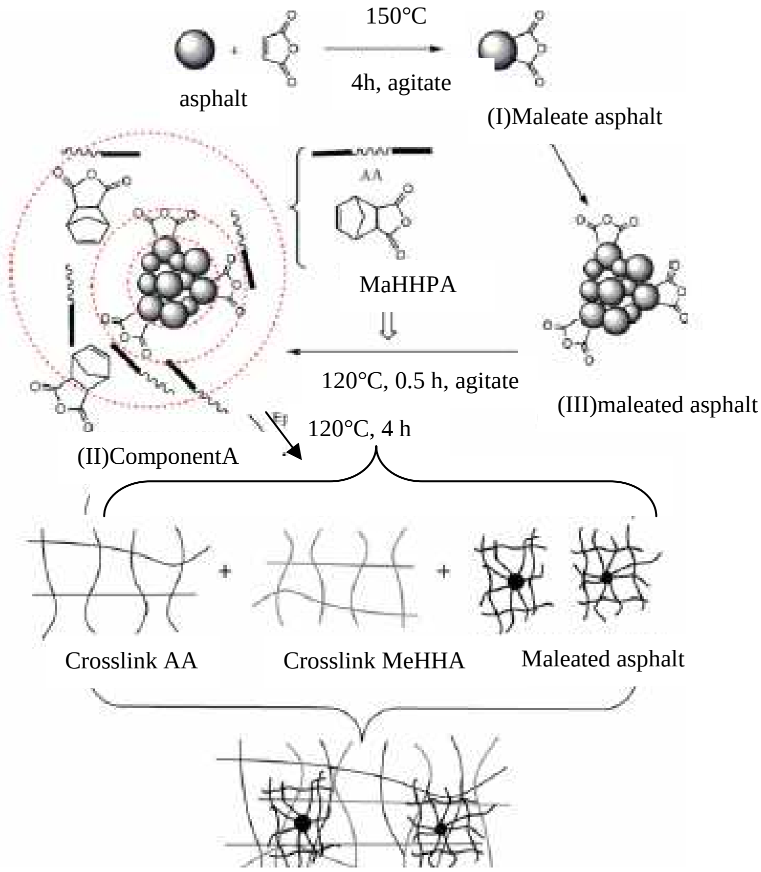


Figure 3.3 Schematic of the formation process of Epoxy modified asphalt by adipic acid and meleic anhydride is curing agent. [14]

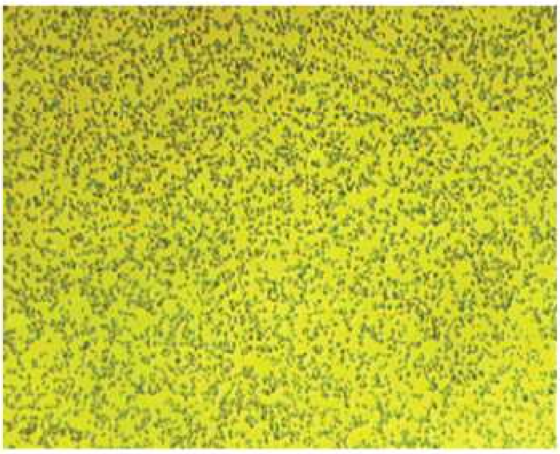


Figure 3.4 Microstructure of modified asphalt by epoxy resin. [14]

Gallagher, et al. 1997 developed an asphalt by thermoset as modifier. Asphalts were modified by epoxy resin in an amount within range of 4 to 30 percent by weight of the asphalt and epoxy combination. The epoxy-functionalized polymer reacts with reactive sites in the asphalt to form a stable, the modified asphalt with thermoset characteristics, i.e., lack of flow or melting upon an increase in temperature [15]. In addition, the materials provide improvements in cold flow, solvent resistance and toughness compared to conventional asphalt material. The epoxy-functionalized polymer was suitable reactive sites in the form of epoxy side groups which can react to the functional groups on the asphalt to form covalent bonds characteristic of thermosetting product. (Gallagher, et al. ,1997)

Martìnez-Boza, et al. studied the rheology of a polymer-modified asphalt(SBS). Figure 3.5 exhibits the storage and loss modulus between neat asphalt and SBS modified ashalt. The result indicated that SBS modified asphalt showed a viscoelastic behavior. Storage and loss modulus increased when SBS content increased. The SBS modified asphalt was more elastic than original asphalt. (Martìnez-Boza, et al., 2000)

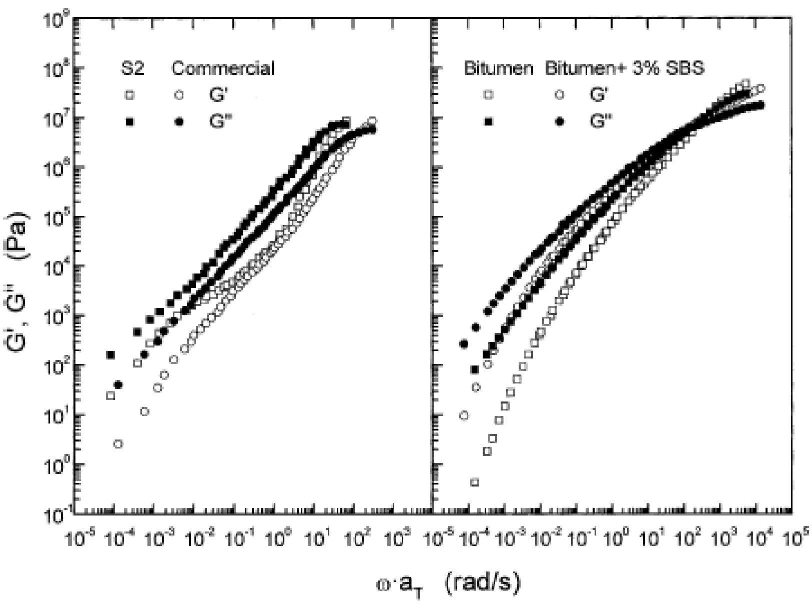


Figure 3.5 The storage and loss modulus between neat asphalt and SBS modified ashalt.[16]

Peiliang, et al. studied the effect of epoxy resin content on rheological properties of epoxy-modified asphalt binders. The epoxy-modified asphalt showed excellent heat resistance and low temperature cracking resistance.The result showed the improvement in viscoelastic performance of asphalt binder that it indicated by the rutting parameter (G*/sinδ). The Strategic Highway Research Program (SHRP) tests used the rheological measurement to determine rutting parameter for analysing properties of asphalt for road pavements. Figure 3.6 showed rutting parameter (G*/sinδ) with temperature. The rutting parameter (G*/sinδ) at 1 kPa was simulated on a car speed at 90 km/hr. [15] The result revealed that the maximum temperature of original asphalt was 75°C whereas epoxy-modified asphalt containing 20 wt%, the rutting was 96°C. This indicated that the epoxy-modified asphalt performances were better than the original asphalt. (Peiliang, et al., 2010)

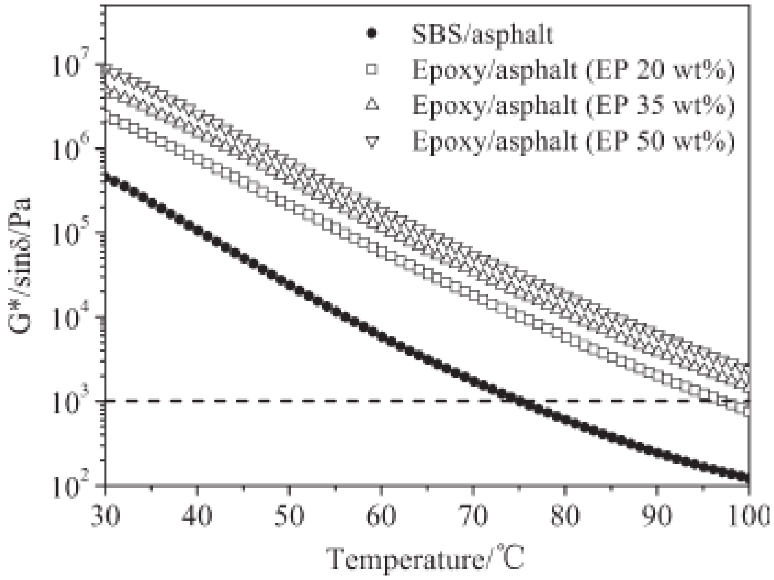


Figure 3.6 Maximum temperature and G*/sinδ at 10 rad/sec of asphalt and epoxy-modified asphalt.[17]

Ghosh, et.al. revealed the new high performance thermosetting in terms of systhesis and properties. Polybenzoxazine was a newly developed for addition in phenolic polymerization.

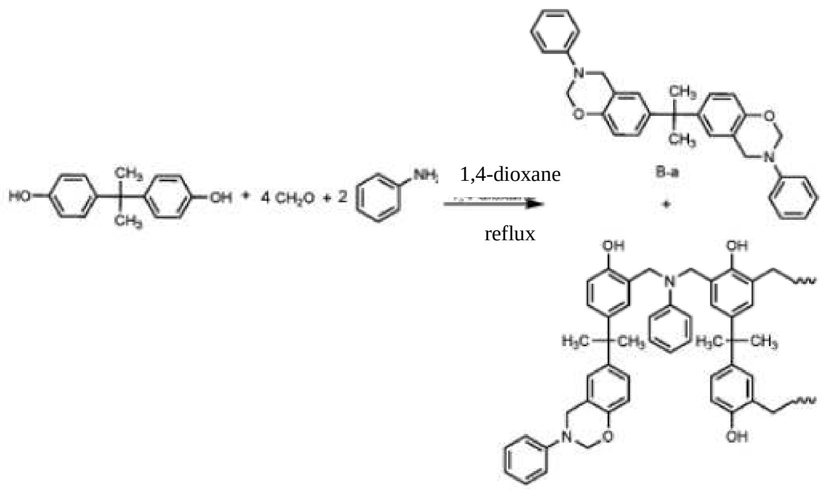


Figure 3.7 Synthesis of bisphenol-A and aniline based benzoxazine (B-a) monomer.[18]

The advanctage of polybenzoxazine was close to zero volumetric change, high char yield, low water absorption, no strong acid catalysts required during curing process and no toxic product during curing process.(Ghosh, et.al., 2007)

Ishida studied that copolymerization reaction occured via the opening of the epoxide ring by the phenolic hydroxyl functionalities presented in the polybenzoxazine precursor. The incorporation of epoxy into the polybenzoxazine network structure results in copolymer that had both higher crosslink density and Tg than the polybenzoxazine homopolymer. Figure 3.8 showed glass transition temperature of of the benzoxazine-epoxy copolymers as a function of composition. (Ishida, 1996)

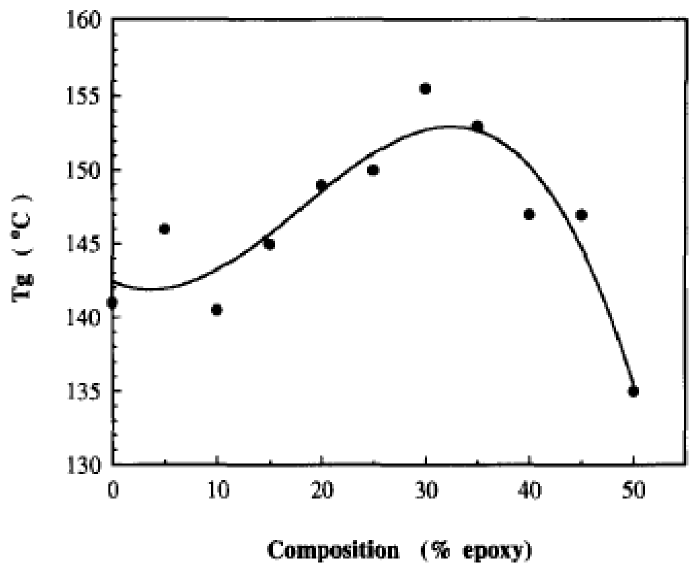


Fig.3.8 Glass transition temperature (Tg) of the benzoxazine-epoxy copolymers with a varying composition (%epoxy).[19]

Rao, et.al. studied that the benzoxazine–epoxy copolymers were prepared without the use of any external curing agent, but by the copolymerization of benzoxazine precursor with epoxy and chain-extended epoxies in Figure 3.9. Table 3.2 showed DMTA results of cured epoxy–benzoxazine copolymers. Figure 3.10 showed DSC thermogram of epoxy–benzoxazine copolymers. The incorporation of epoxy into the polybenzoxazine network structure in a copolymer that had both higher crosslink density and glass transition temperature (Tg) than its homopolymer. DSC thermogram of the copolymer showed a single exothermic peak at 248°C, whereas a marginal increase in storage modulus (E’) was observed with chain extension. (Rao, et.al., 2005)

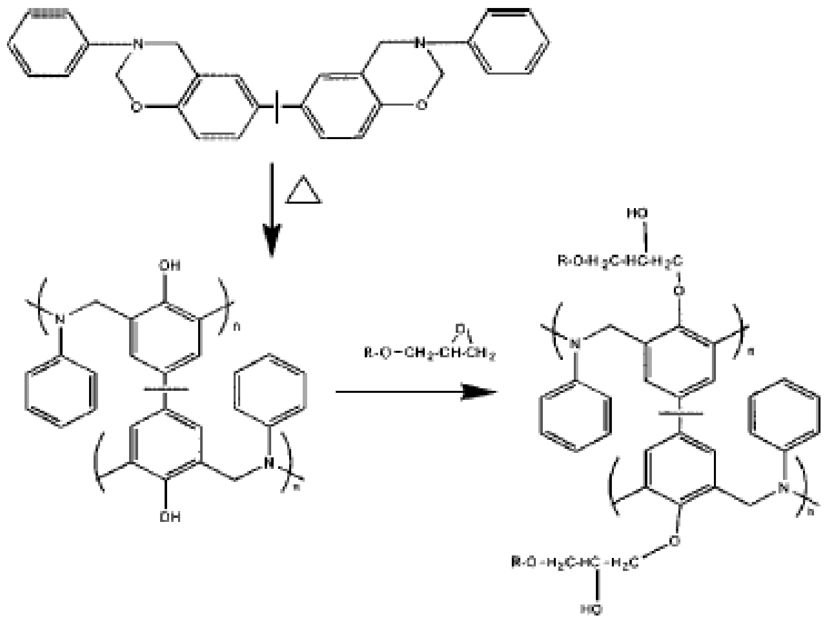


Fig.3.9 Reaction of benzoxazine with epoxy.[20]

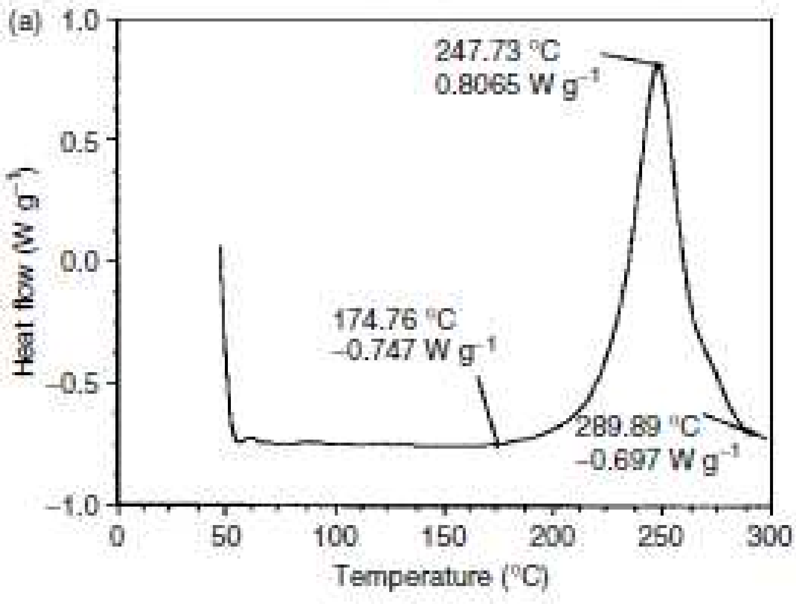


Fig.3.10 DSC thermogram of E-ba at a heating rate of 10 ◦C/min in nitrogen. [20]

Table 3.2 DMTA results of cured epoxy–benzoxazine copolymers. [20]

Sample	Storage modulus E’(Pa)	Tan δ			
		Position(°C)	Peak height	Width at halt height(°C)	EEW
E-ba	1.7×10^9	188	0.52	46	192
EB-ba	2.0×10^9	184	0.59	30	438
ETB-ba	2.1×10^9	171	0.84	34	606

EEW – epoxy equivalent weight

CHAPTER IV

EXPERIMENTAL

4.1 Materials Preparation

The 60/70 penetration grade asphalt used was obtained from IRPC Co., Ltd. Table 4.1 shows the properties of asphalt 60/70. Benzoxazine resin (BA-a) is based on bisphenol-A, aniline, and formaldehyde. Bisphenol-A (polycarbonate grade) was supplied from Thai Polycarbonate Co., Ltd. (TPCC). Aniline (AR grade) and Paraformaldehyde (AR grade) were purchased from Panreac Quimica SA Company and Merck Company, respectively.

Table 4.1 Specification of asphalt penetration grade 60/70.

Property	**Data**
Penetration, 25°C	71
Softening point (°C)	47
Ductility (cm.)	100
Viscosity, 135°C (Pa s)	0.5

4.1.1 Benzoxazine Resin Preparation

The benzoxazine resin used is based on bisphenol-A, aniline and formaldehyde in the molar ratio of 1:4:2. Benzoxazine resin was synthesized by using method in the U.S. Patent 5,543,516 (Ishida, 1996). The benzoxazine monomer is clear-yellowish powder at room temperature.

4.2 Preparation of Blends

Asphalt was heated at 80±5°C. Then benzoxazine resin was added to the hot asphalt at varying ratios of 1wt%, 3wt%, 5wt%, 7wt% and 9wt% and stirred mechanically at 500 rpm for 1 hr. This asphalt samples were cured at 190±5°C in an air-circulated oven for 1 hr. to crosslink the benzoxazine.

4.3 Characterization Methods

4.3.1 Differential Scanning Calorimetry (DSC)

The curing characteristic of the benzoxazine-modified asphalts were measurement by a differential scanning calorimeter (DSC) model 2910 from TA Instrument. Amount of the sample ranging from 25-28 mg was placed on the aluminum pan. The experiment was used a heating rate of 10°C/min. from 30°C to 300°C under nitrogen purging. The nitrogen gas used constant flow rate at 50 ml/min. The percentage of benzoxazine resin conversion was calculated from the DSC thermograms.

4.3.2 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 variesd from -70°C to 40°C at heating rate 1°C/min under nitrogen atmosphere. The storage modulus (E’) and loss modulus (E”) were obtained. The glass transition temperature (Tg) was determined as the maximum point on the loss modulus curve in the DMA thermogram.

4.3.3 Thermogravimetric Analysis (TGA)

A 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 6 mg. The test was heated from 50°C 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.

4.3.4 Rheological Analysis

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. Test temperature varied from 30°C to 100°C with 2°C/min and recorded viscosity at 60°C. Frequency sweeps at 0.1 rad/s to 100 rad/s were tested at 60°C.

4.3.5. Morphology by Optical Microscope

Morphology of benzoxazine modified asphalt was examined by optical microscope using a Nikon ECLIPSE E600 POL. This method reveals the dispersed benzoxazine-rich phase as bright, while the continuous asphalt-rich phase as dark.

4.3.6. Penetration Measurement

Penetration value was a conventional test for pavement application. Penetration test (ASTM D5) was measured from depth of standard needle of Penetrometer sank into asphalt samples under pressed weight of 100 grams at 25°C for 5 minutes.

4.3.7. 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. Data is recorded the temperature when the ball touches the bottom plate.

4.3.8. Specific Gravity measurement

The specific gravity was determined by water displacement method. Samples were prepared at 5-20 grams. Each sample was weighed in air and in water at 25 ± 0.2°C. An average value from at least four samples was calculated.

CHAPTER V

RESULTS AND DISCUSSION

5. Benzoxazine-Modified Asphalts Characterization

5.1 Investigation of Benzoxazine-Modified Asphalt Curing Condition

The exothermic peak in DSC thermograms reveals the cure characteristic and suggests appropriate thermal curing condition of benzoxazine resin. Figure 5.1 shows the exothermic peak containing 9 wt% of benzoxazine modified asphalt at different curing temperature ranging from 80°C to 190°C for 1 hour at each temperature. The DSC thermograms revealed the area under the curing peaks to decrease with increasing curing temperature. The above uncured benzoxazine modified asphalt possessed a heat of reaction obtained from the area under the exothermic peak which was 7.17 J/g and decreased to 5.55 J/g, 4.09 J/g, 3.30 J/g and 0.437 J/g after curing at 150°C, 165°C, 180°C and 190°C for 1 hour, respectively. The degree of conversion determined by Equation (5.1) was calculated to be 22.6%, 42.9% and 53.9% after curing at 150°C, 165°C and 180°C for 1 hour each. After curing at 190°C for 1 hr, the degree of conversion of benzoxazine modified asphalt was about 93.8%.which is sufficiently high for thermoset modified asphalt and provides enough strength for Marshall test e.g. epoxy systems [21] As a consequence, the curing temperature at 190°C for 1 hour was used to cure every sample of benzoxazine-modified asphalt.

$$\%Conversion = \left(1 - \frac{H_{rxn}}{H_o}\right) \times 100$$

Where: H_{rxn} is the heat of reaction of the partially cured specimens.

H_0 is the heat of reaction of the uncured resin

5.2 Dynamic Mechanical Analysis (DMA) of Benzoxazine-Modified Asphalts.

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. [22]

Figure 5.2 shows storage modulus of benzoxazine-modified asphalt at different benzoxazine resin contents from 0 to 9% by weight and at various temperatures ranging from -70°C to 40°C. The results clearly suggested that the storage modulus (E') of benzoxazine-modified asphalt was higher than that of the unmodified asphalt and the storage modulus (E') of benzoxazine-modified asphalt was increased with increasing benzoxazine resin contents. The result, therefore, indicated that benzoxazine-modified asphalts were stiffer than the unmodified asphalt. This asphalt property is desirable in pavement application etc.

Figure 5.3 exhibits loss modulus (E") curve of benzoxazine-modified asphalt at different benzoxazine contents from 0 to 9% by weight and at various temperatures from -70°C to 40°C. The peak of the loss modulus is generally used to indicate the glass transition temperature of each sample. From the plots, the loss modulus curve shows a glass transition temperature (T_g) of the unmodified asphalt to be -14.3°C whereas the glass transition temperature (T_g) of the benzoxazine-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 (T_g) of the benzoxazine-modified asphalt were determined to be -5.23°C, -4.4°C, -3.04°C, 2.6°C and 4.4°C at 1, 3, 5, 7 and 9% by weight of the benzoxazine resin, respectively. The results also suggest that the benzoxazine-modified asphalt can improve thermal stability of asphalt which is essential in pavement application in the tropical climate region.

5.3 Thermal Degradation of Benzoxazine-Modified Asphalts

Thermogravimetric analysis (TGA) is a method to measure the weight loss of polymeric materials during a temperature rise. The characteristics of TGA thermogram related with thermal stability including degradation temperature and char residue. In this study, both characteristics of each benzoxazine-modified asphalt were investigated. In this study, the temperature at 5% weight loss occurs as the thermal degradation temperature of each sample and char residue at 800°C in nitrogen atmosphere were reported as a function of benzoxazine contents. Figure 5.4 shows TGA thermograms of benzoxazine-modified asphalt at different benzoxazine contents ranging from 0 to 9% by weight. The results reveal 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 unmodified asphalt was 354.3°C while the degradation temperature at 5% weight loss of the benzoxazine modified asphalt increased to 359, 365, 367, 375 and 380°C at the benzoxazine contents of 1, 3, 5, 7 and 9% by weight, respectively. Furthermore, the char residue at 800°C of the unmodified asphalt was measured to be 16.41% whereas the char residue at 800°C of the benzoxazine modified asphalt were 16.5, 17.0, 17.5, 17.6 and 17.9% at benzoxazine contents of 1, 3, 5, 7 and 9% by weight. The results indicated that the thermal stability of the asphalt can be improved by an addition of benzoxazine modifier. The observed thermal stability enhancement is attributed to a greater thermal stability of the polybenzoxazine modifier.

5.4 Rheological Properties of Benzoxazine-Modified Asphalts

Asphalts are viscoelastic material. That is asphalts behave partly like an elastic solid (deformation due to loading is recoverable or it is able to recover to its original shape after removing a load) and partly similar to a viscous liquid (deformation due to loading is non-recoverable or it cannot recover to its original shape after removing a load). The rheological analysis is capable to quantify both elastic and viscous properties of asphalt. This makes it well suitable for characterizing asphalts in the service pavement temperature range. The service temperature of road pavement surface in Thailand is about 50 to 60°C [23], as a result the rheological behavior of asphalts at 60°C was investigated in this work.

5.4.1 Viscosity

Viscosity is an important parameter to consider processing, aging and servicing condition of asphalt. Figure 5.5 exhibits viscosity of benzoxazine-modified asphalt with different benzoxazine content from 0 to 9% by weight at 60°C. From the plot, the viscosity of the asphalt was found to increase exponentially when benzoxazine content increased. The viscosity increased from 248 Pa.s of the unmodified asphalt 276.6, 333.8, 495.4, 754.7 and 845 Pa.s at benzoxazine contains of 1, 3, 5, 7 and 9% by weight in the asphalt. In practice, the increase in viscosity can reduce softening and bleeding problems of asphalt material, can also lower rate of stripping phenomenon, thus increase asphalt stability for road pavement application.

5.4.2 Storage and Loss Modulus as a Function of Frequency at 60°C of Benzoxazine-Modified Asphalts

Figures 5.6 and 5.7 show storage modulus and loss modulus of the benzoxazine-modified asphalt with different benzoxazine resin contents at 60°C and at various angular frequencies from 0.1 rad/s to 100 rad/s. The results reveal that the storage modulus and loss modulus of the benzoxazine-modified asphalt at 60°C is greater than that of the unmodified asphalt and those values increased when benzoxazine contents increased. The modified asphalts by benzoxazine resin as a modifier can increase both storage and loss modulus over the entire range of test frequency used above. This means the benzoxazine modified asphalts at 60°C tended to be more elastic than the unmodified asphalt. This is probably the polymer modifier may disperses into the maltenic medium of the asphalt, thus enhancing mechanical properties of the mixtures. Consequently, the benzoxazine-modified asphalt has better deformation resistance at service temperature of 60°C than the unmodified asphalt.

5.4.3 Rutting Parameter of Benzoxazine Modified Asphalts

Rutting parameter (G*/sinδ) 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. Asphalt aging implies an increasing complex modulus (G*) and a decreasing phase angle (δ) providing more resistance to the deformation. The rutting parameter establishes a maximum working temperature, which is defined as a minimum rutting parameter value (G*/sinδ) at 1 kPa for road pavement asphalt.

Figure 5.8 shows rutting parameter of benzoxazine-modified asphalts at different benzoxazine resin contents from 0 to 9% by weight and at various temperatures. According to the SHRP test, the temperature of G*/sinδ at 1 kPa marks the maximum temperature for a good viscoelastic performance of the asphalt for road pavement application. Our result shows the maximum temperature of the unmodified asphalt to be about 65°C whereas those of the benzoxazine modified asphalt were found to be greater with values of 68, 74, 75, 78 and 84°C at the benzoxazine contents of 1, 3, 5, 7 and 9% by weight, respectively. This suggests that the benzoxazine-modified asphalts can provide asphalt with improved performance for road pavement with high rutting resistance.

5.5 Morphology of Benzoxazine-Modified Asphalts by Optical Microscope

The compatibility between the benzoxazine modifier and asphalt is critical to the properties of the resulting asphalt mixture and can be partly observed from its morphology. The morphology of benzoxazine modified asphalt was usually investigated by characterizing the dispersion and fineness of the polymer modifier phase in the asphalt matrix. [25]

Figure 5.9 shows phase morphology of the unmodified asphalt and its mixture with the benzoxazine modifier at different benzoxazine contents. The light color phase in the picture represents the benzoxazine resin domain, whereas the dark phase represents the asphalt domain. From the figure, the benzoxazine fraction was found to disperse as small particles in the asphalt and the light color domains were observed to increase in both size and number when the benzoxazine resin content in the asphalt increased. Although the appearance of the two domains suggested phase separation characteristic of the mixture, we observed relatively small domains with uniform distribution of benzoxazine modifier even after exposing to relatively high temperature of 190°C of the benzoxazine curing condition. This kind of phase separation behavior was also observed in various polymer modified asphalt systems such as epoxy, SBS or PS modified asphalts. [26, 27]

5.6 Penetration Measurement of Benzoxazine-Modified Asphalts

Penetration value at 25°C is a specified property of asphalt for road pavement application of Department of Highway of the US. Penetration test can be to investigate stiffness, temperature susceptibility and rutting resistance of the asphalt. Figure 5.10 shows penetration value of benzoxazine-modified asphalts at different benzoxazine contents ranging from 0 to 9 wt% at 25°C. The benzoxazine-modified asphalts have penetration value lower than that of the unmodified asphalt and the penetration values systematically decreased when the benzoxazine contents increased. In this work, the tested asphalt is AC60/70 grade which means its penetration value is 70 dmm. The modified asphalt by benzoxazine resin at 1, 3, 5, 7 and 9% by weight provided lowering in their penetration value i.e. 45.75, 37.25, 32, 26 and 22 dmm, respectively. This suggested the improve load-bearing characteristic of resulting modified asphalt and is consistent with an observed enhancement in their modulus in the previous section.

5.7 Penetration Index

Penetration index (PI) is a parameter that measures temperature susceptibility of asphalt and can be calculated by Equation (5.2). In practice, the penetration index value can be classified into 3 levels [28],

- PI value lower than -1 referred to high sensitivity of temperature change.
- PI value over than +1 referred to low sensitivity of temperature.
- PI value between -1 and +1 refers to normal sensitivity of temperature.

Positive penetration index value indicates that such material has low temperature susceptibility.

$$PI = \frac{20U - 300V}{U + 30V} \qquad (5.2)$$

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

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

Where: T_{RB} is softening point value (°C)

T_P is temperature of penetration test (°C)

P_T is penetration value at T_P

Figure 5.11 depicts penetration index of benzoxazine-modified asphalts at different benzoxazine resin contents ranging from 0 to 9% by weight. The penetration index values were found to be more positive when the amount of the benzoxazine resin increased. Penetration index value of the unmodified asphalt was calculated to be -1.42 suggesting high temperature sensitivity of the pure asphalt. The penetration index value were increased to be -1.37, -0.88, -0.81, -0.14 and 0.15 at the benzoxazine contents of 1, 3, 5, 7 and 9% by weight, respectively. Therefore, it is evident that the temperature susceptibility of asphalt can be suppressed by the presence of benzoxazine modifier and the 9% by weight of the benzoxazine resin is high enough to give a positive value of the penetration index.

5.8 Softening Point of Benzoxazine-Modified Asphalts

Softening point temperature is the key parameter and standard requirement of asphalt for road pavement application. Softening point is critical temperature that the asphalt becomes softened at constant loading which affects bleeding behavior of the asphalt binder. A high softening point ensures that they will not flow during service and the higher the softening point, the lower the temperature sensitivity and the bleeding phenomenon. Figure 5.12 illustrates softening points of benzoxazine-modified asphalts at different benzoxazine contents ranging from 0 to 9% by weight. From this figure, the softening point of the unmodified asphalt was found to be 46°C and the value increased to 50°C, 54°C, 55°C, 61°C and 65°C, with the presence of 1, 3, 5, 7 and 9% by weight of the benzoxazine resin, respectively. In addition the softening point of the benzoxazine-modified asphalt was found to increase 7°C whereas epoxy modified asphalt can increase by 3°C at comparing at the same content of 2% by weight of modifier. [29] Therefore, benzoxazine resin seems to provide a better improvement on the softening point of the asphalt compared to epoxy resin.

5.9 Specific Gravity Determination of Benzoxazine-Modified Asphalts

Table 5.2 exhibits specific gravity of benzoxazine-modified asphalt at different benzoxazine resin contents ranging from 0 to 9% by weight. The specific gravity values were calculated from Equation 5.3 below. It was observed that specific gravity of benzoxazine-modified asphalts steadily increased with increasing the amount of the benzoxazine resin. The density specification for polymer modified asphalt of Highways department in Thailand was recommended to be in the range of 1.00 to 1.05. [30] Our results revealed that the specific gravity of benzoxazine-modified asphalt was found to be within this standard requirement.

$$\text{Specific gravity at } 25°\text{C} = \frac{A}{A + B} \qquad (5.3)$$

where A = weight of the sample in air (mg)

B = weight of the specimen in liquid (water) at 25 ± 0.2^{o}C (mg)

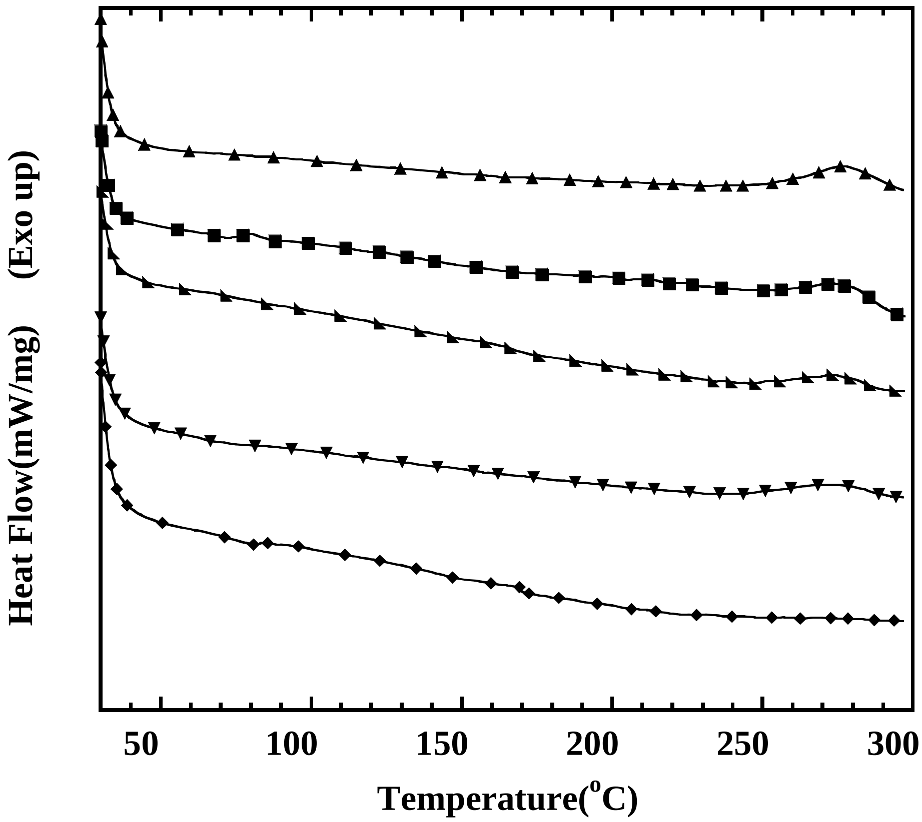


Figure 5.1 DSC thermograms of benzoxazine-modified asphalt at different curing temperature: (♦) 9wt% benzoxazine-modified asphalt at 80°C, (▼) 9wt% benzoxazine-modified asphalt at 150°C, (◣) 9wt% benzoxazine-modified asphalt at 165°C, (■) 9wt% benzoxazine-modified asphalt at 180°C, (▲) 9wt% benzoxazine-modified asphalt at 190°C.

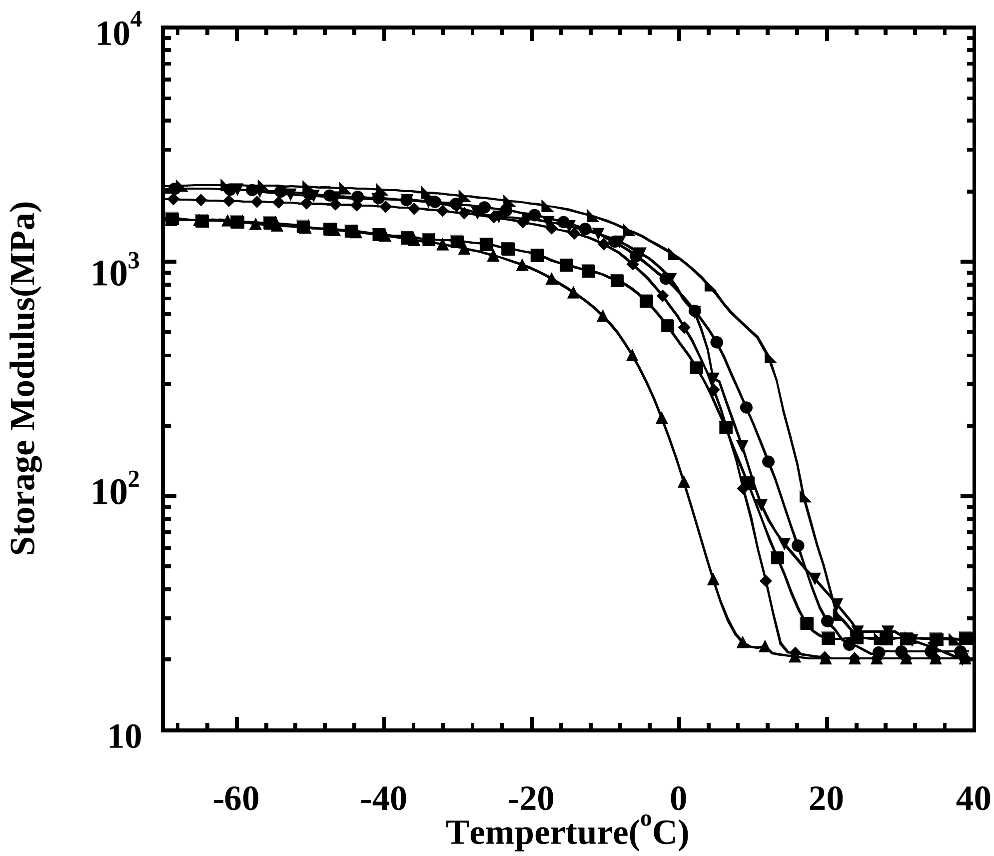


Figure 5.2 DMA thermograms of storage modulus of benzoxazine-modified asphalt: (▲) neat asphalt, (■) 1wt%, (♦) 3wt%, (▼) 5wt%, (●) 7wt%, (◣) 9wt%.

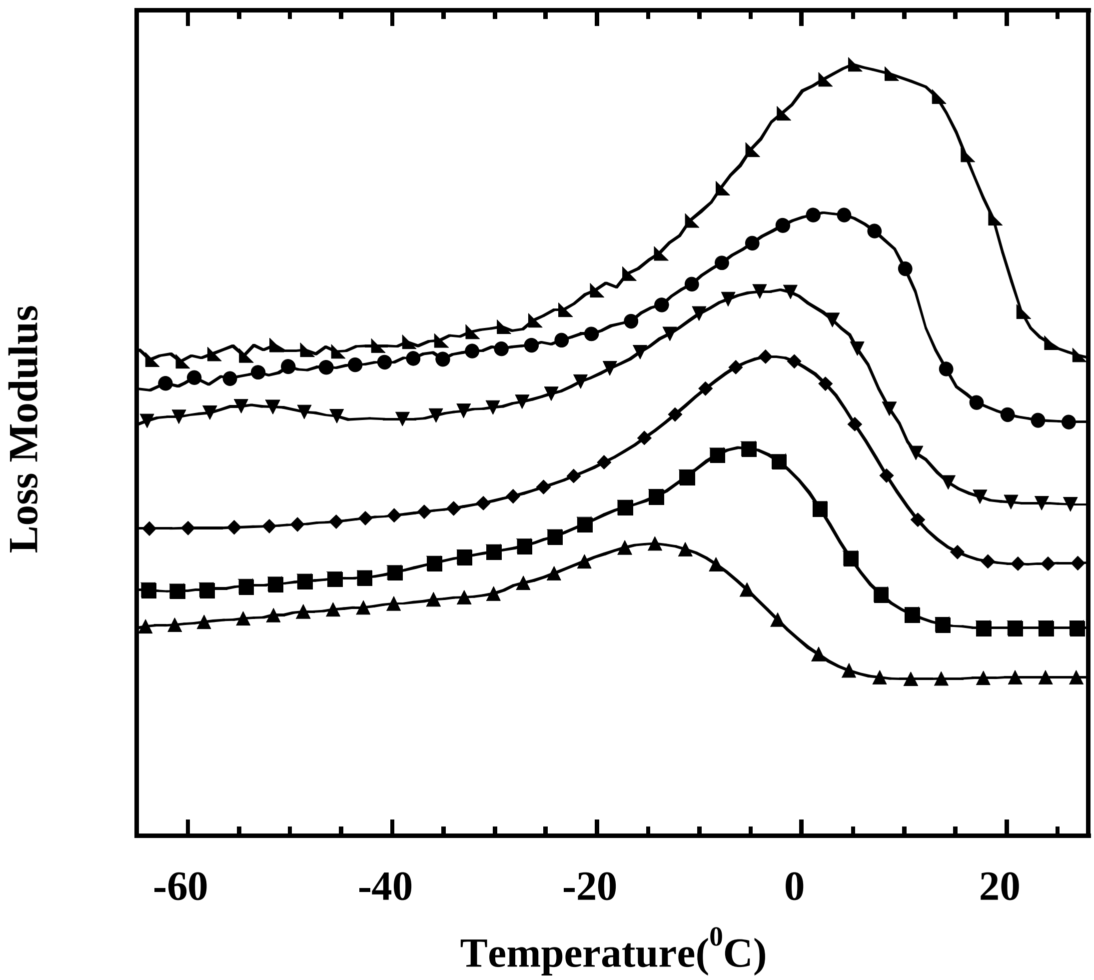


Figure 5.3 Overlay plot of DMA thermograms of loss modulus of benzoxazine-modified asphalt: (▲) neat asphalt, (■) 1wt%, (♦) 3wt%, (▼) 5wt%, (●) 7wt%, (◣) 9wt%.

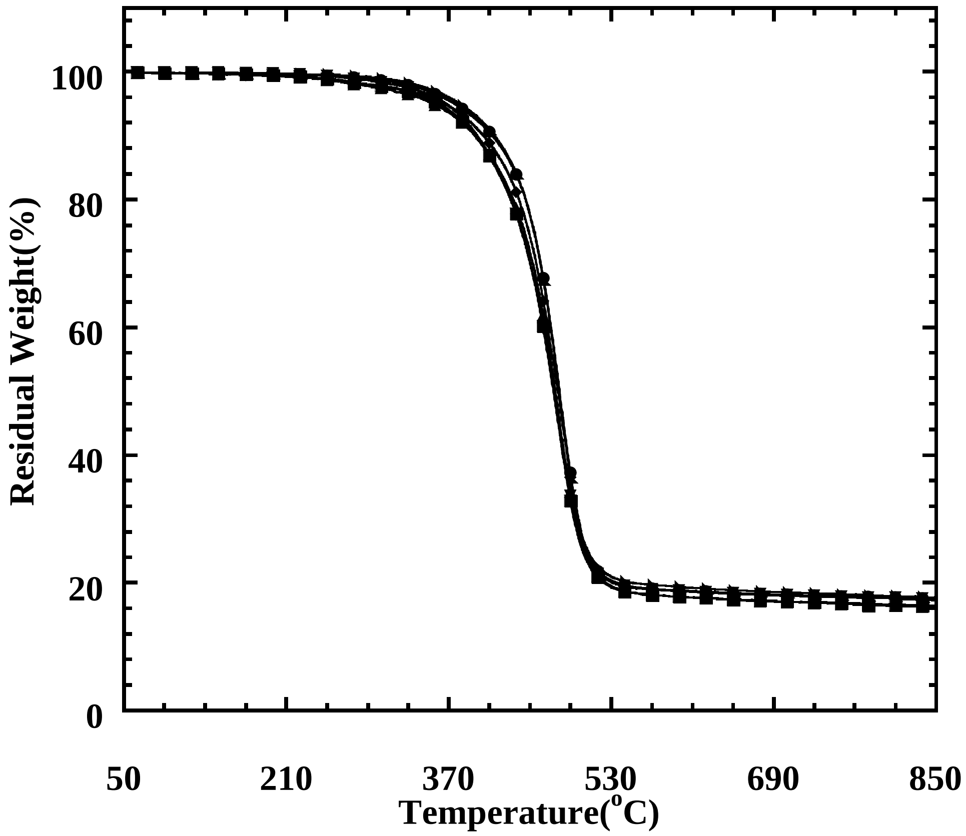


Figure 5.4 TGA thermograms of benzoxazine-modified asphalt: (▲) neat asphalt, (■) 1wt%, (♦) 3wt%, (▼) 5wt%, (●) 7wt%, (◣) 9wt%.

Table 5.1 Thermal characteristics of benzoxazine-modified asphalt.

Resins	Degradation Temperature (^{o}C) at 5% weight loss	Solid residue (%) at 800^{o}C
Neat asphalt	354	16.4
1wt% BA-a asphalt	359	16.5
3wt% BA-a asphalt	365	17.0
5wt% BA-a asphalt	367	17.5
7wt% BA-a asphalt	375	17.6
9wt% BA-a asphalt	380	17.9

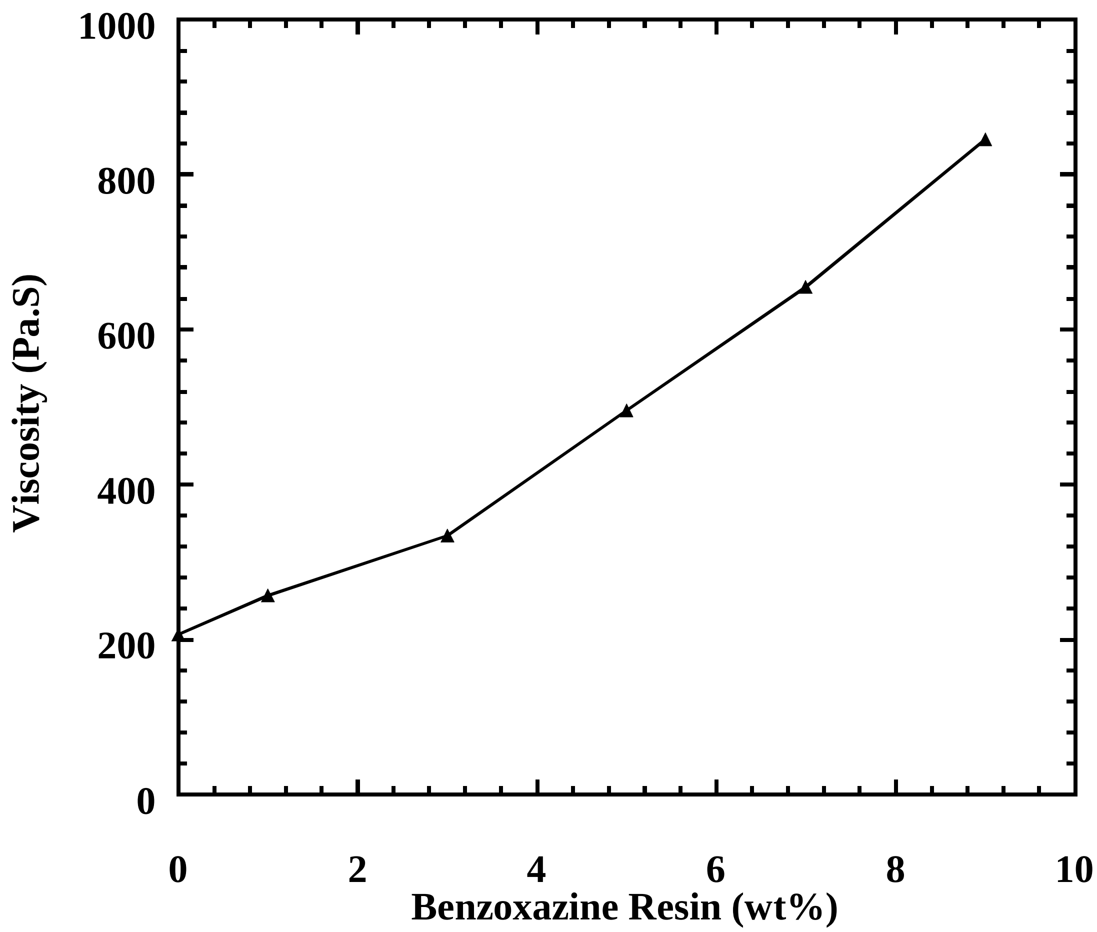


Figure 5.5 Viscosity of benzoxazine-modified asphalt as a function of benzoxazine contents at 60°C.

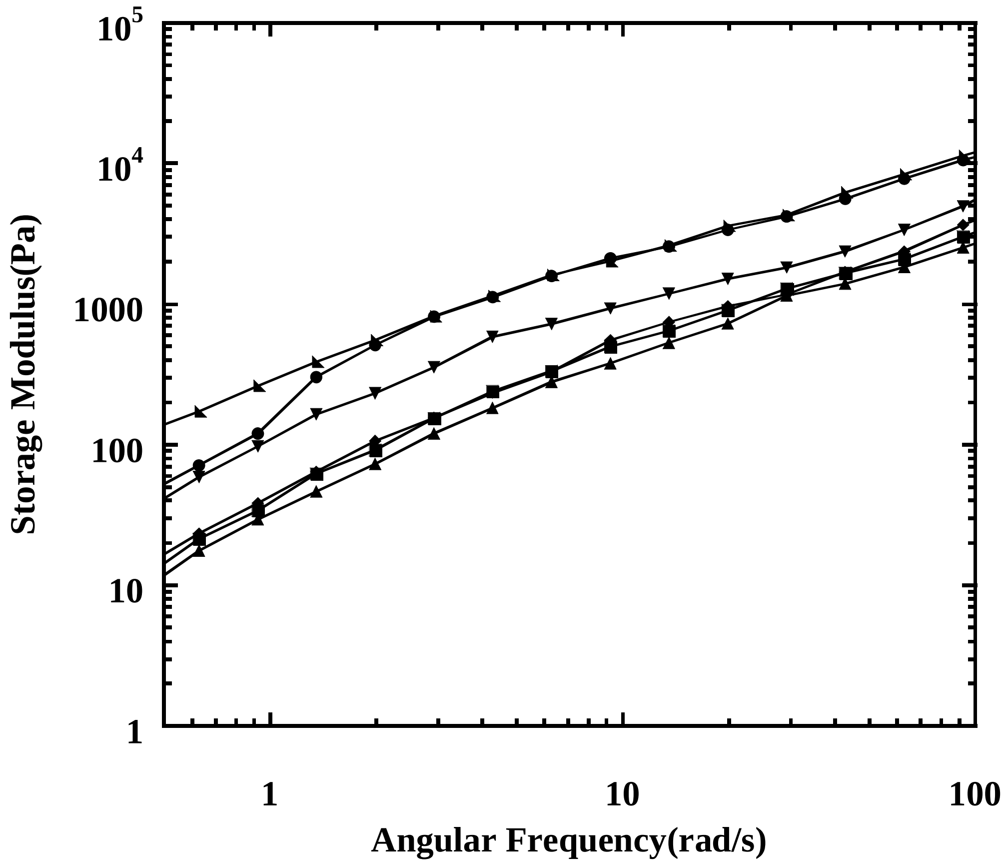


Figure 5.6 Storage modulus of benzoxazine-modified asphalt: (▲) neat asphalt, (■) 1wt%, (♦) 3wt%, (▼) 5wt%, (●) 7wt%, (◣) 9wt%.

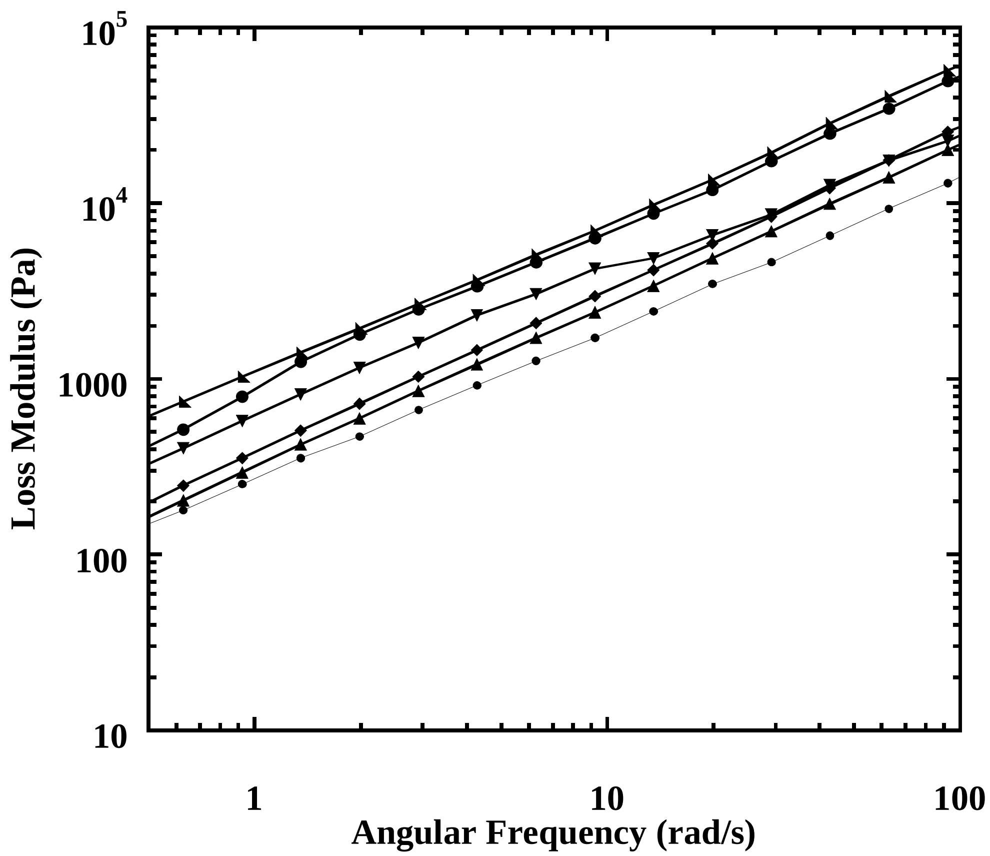


Figure 5.7 Loss modulus of benzoxazine-modified asphalt: (▲) neat asphalt, (■) 1wt%, (♦) 3wt%, (▼) 5wt%, (●) 7wt%, (◣) 9wt%.

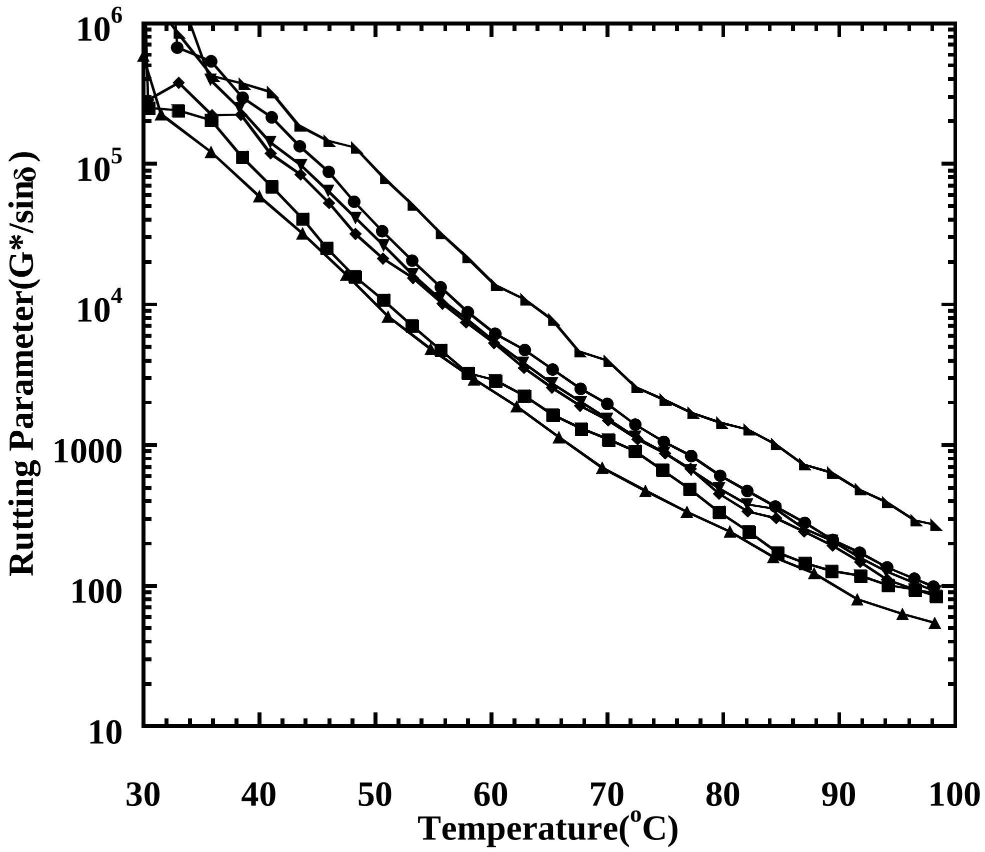


Figure 5.8 Rutting parameter of benzoxazine-modified asphalt: (▲) neat asphalt, (■) 1wt%, (♦) 3wt%, (▼) 5wt%, (●) 7wt%, (◣) 9wt%.

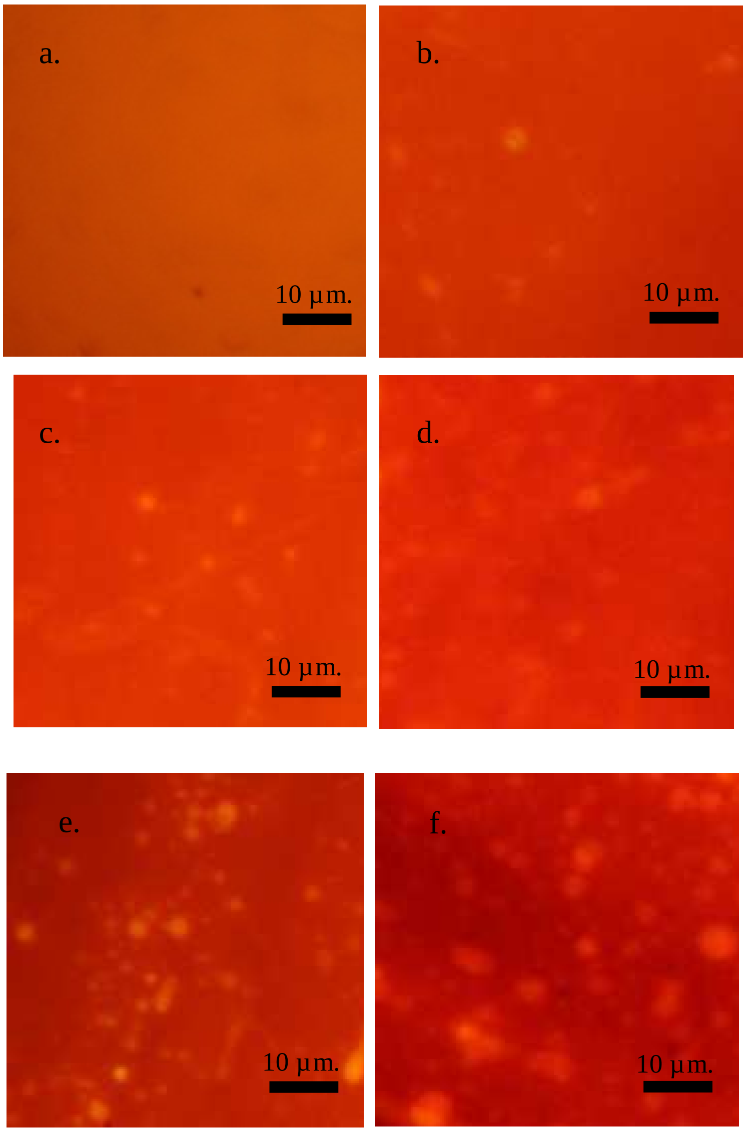


Figure 5.9 Optical microscope of benzoxazine-modified asphalt: (a) neat asphalt, (b) 1wt% benzoxazine-modified asphalt, (c) 3wt% benzoxazine-modified asphalt, (d) 5wt% benzoxazine-modified asphalt, (e) 7wt% benzoxazine-modified asphalt, (f) 9wt% benzoxazine-modified asphalt.

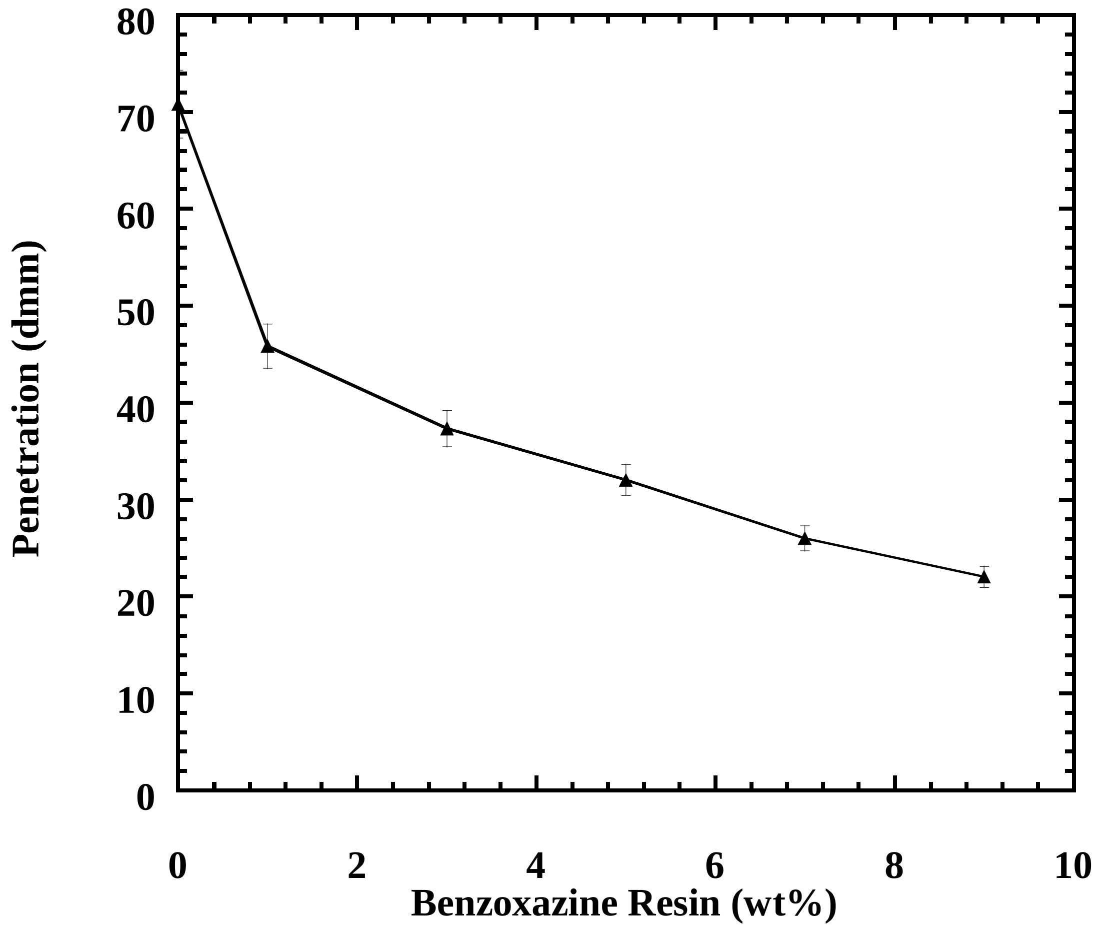


Figure 5.10 Penetration values of benzoxazine-modified asphalt as a function of benzoxazine contents.

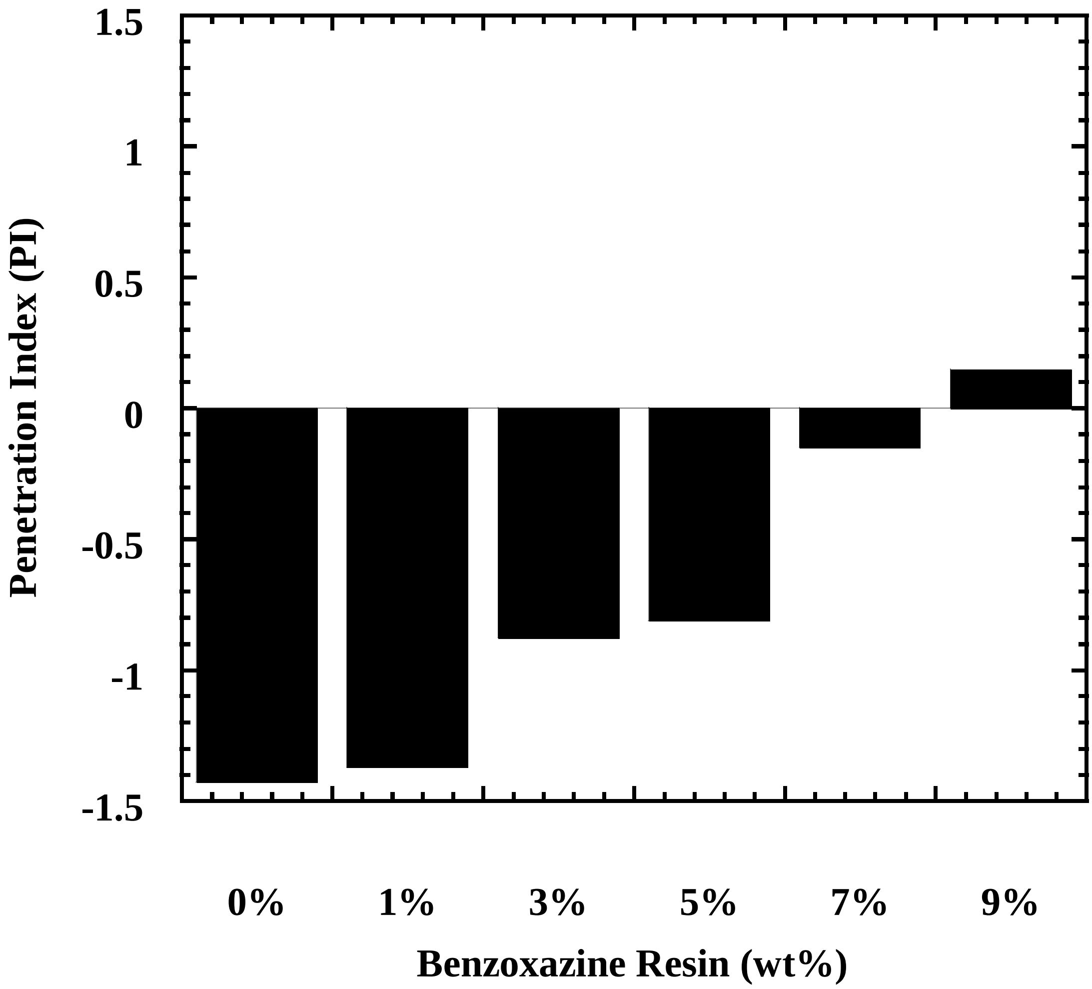


Figure 5.11 Penetration index of benzoxazine-modified asphalt as a function of benzoxazine contents.

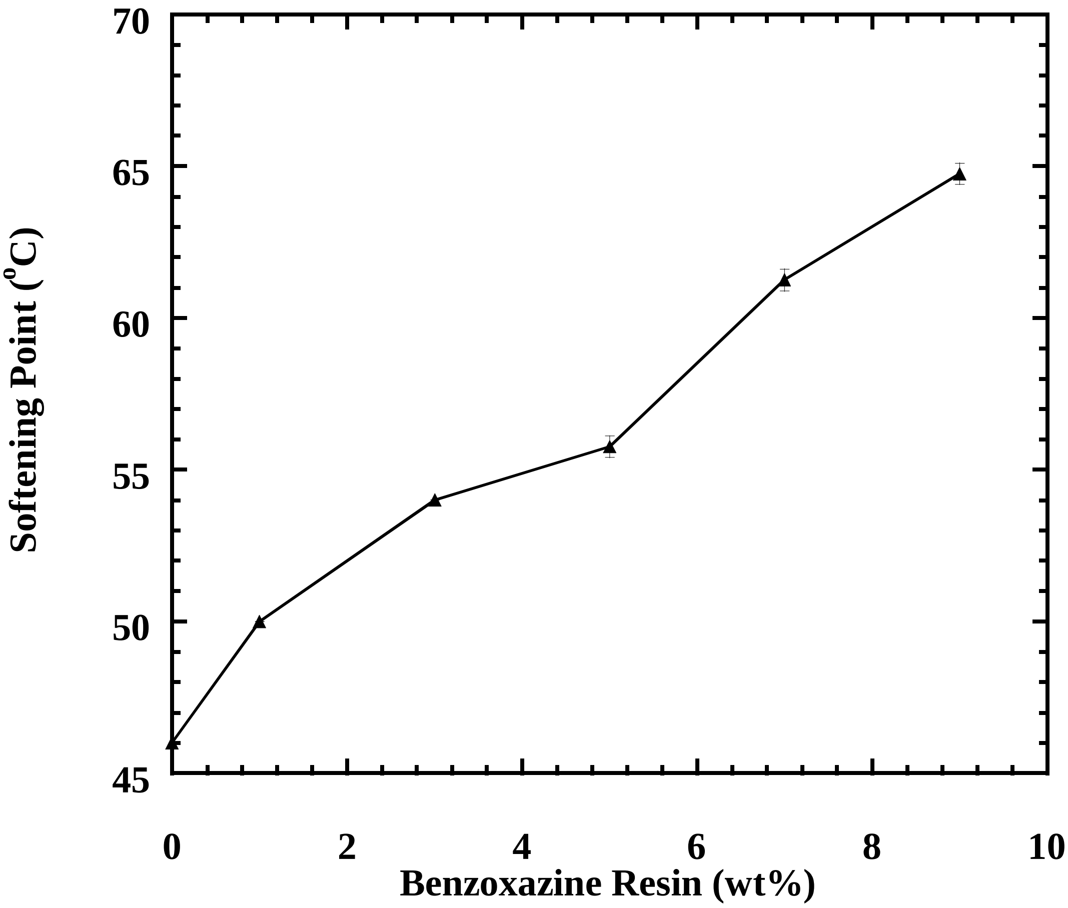


Figure 5.12 Softening point of benzoxazine-modified asphalt as a function of benzoxazine contents.

Table 5.2 Specific gravity of benzoxazine-modified asphalts.

Resins	Specific gravity at 25°C
Neat asphalt	1.034
1wt% BA-a asphalt	1.039
3wt% BA-a asphalt	1.040
5wt% BA-a asphalt	1.047
7wt% BA-a asphalt	1.048
9wt% BA-a asphalt	1.053

CHAPTER VI

CONCLUSIONS

The modification of asphalts by benzoxazine resin as a modifier can improve mechanical, thermal properties and conventional test for road pavement properties.

The DSC experiment revealed that the suitable curing condition for fully-cured sample of benzoxazine-modified asphalt was prepared by heating at 190°C for 1 hour in an air circulated oven. The mechanical and thermal properties of benzoxazine-modified asphalts were higher than unmodified asphalt and those increased when benzoxazine contents increased. The glass transition temperature was increased from -14.3°C to 4.4°C of 9%wt benzoxazine-modified asphalt. The degradation temperature (at 5% weight loss) and char residue (at 800°C) of benzoxazine-modified asphalts were increased with increasing benzoxazine contents. Morphology of benzoxazine resin and asphalt blends revealed the two phases between benzoxazine resin and the asphalt. The rheological properties show viscosity at 60°C, storage modulus and loss modulus of benzoxazine-modified asphalts were higher than unmodified asphalt and the rheological properties (the storage modulus and the loss modulus) increased when the benzoxazine contents increased. The result of rutting parameter of the Strategic Highway Research Program (SHRP) showed the maximum temperature increased with increasing benzoxazine contents. The specific gravity between benzoxazine-modified asphalt and unmodified asphalt were small different values and within specification of Highways department of Thailand. The penetration values were decreased while the penetration index and softening point temperature were increased when benzoxazine contents increased.

Appreciable, benzoxazine-modified asphalts decreased in formation of highly heavy traffic loads in rutting, bleeding and cracking deformation and can improve the road pavement properties as tropical countries requirement. This improvement is reduces the maintenance cost of road.

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APPENDIX

Characterization of Benzoxazine-Modofied Asphalts

Appendix A The storage modulus (E') at 35^{o}C and the glass transition temperature (Tg, loss modulus), of benzoxazine-modified asphalt at various benzoxazine contents which were determined from DMA.

Benzoxazine content (wt%)	Storage modulus (E') at 35^{o}C (MPa)	Glass transition temperature (^{o}C)
0	20	-14.3
1	20.2	-5.23
3	21	-4.4
5	23	-3.04
7	24	-2.6
9	25	4.4

VITA

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