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**PHYSICAL PROPERTIES MODIFICATION OF ASPHALT WITH
CASHEW NUT SHELL LIQUID**



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สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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ได้สังเคราะห์คาร์บอนอล-ฟอร์แมลดีไฮด์เรซิน จากปฏิกิริยาของฟอร์แมลดีไฮด์และคาร์บอนอลที่แยกมาจากสารสกัดจากเปลือกเมล็ดมะม่วงหิมพานต์ที่ผ่านปฏิกิริยาดีคาร์บอกซิเลชัน โดยมีโซเดียมไฮดรอกไซด์อยู่ด้วย พิสูจน์เอกลักษณ์ด้วยอินฟราเรดสเปกโทรสโกปีและนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี ยางมะตอยดัดแปรด้วยสารเติมแต่งเตรียมได้โดยปฏิกิริยาระหว่างยางมะตอย (5 ชั่วโมง, 150 องศาเซลเซียส) กับคาร์บอนอล-ฟอร์แมลดีไฮด์เรซิน มาเลอิกแอนไฮไดรด์ มาเลอิกเรซินและพาราฟอร์แมลดีไฮด์ โดยศึกษาอิทธิพลความเข้มข้นของสารเติมแต่ง ยางมะตอยดัดแปรด้วยสารเติมแต่งนำไปทดสอบสมบัติทางกายภาพด้วยไดนามิกเชิยรรีโอมิเตอร์ และพีเนโทรมิเตอร์

ผลการศึกษาสมบัติทางกายภาพของยางมะตอยดัดแปรด้วย คาร์บอนอล-ฟอร์แมลดีไฮด์เรซิน พบว่าลดความว่องไวต่อการเปลี่ยนแปลงอุณหภูมิ (ดัชนีพีเนทรชันเพิ่มขึ้น) และมีความยืดหยุ่นมากกว่า (มูมเฟสลด) เมื่อเทียบกับยางมะตอยที่ไม่ดัดแปร และที่ดัดแปรด้วยมาเลอิกแอนไฮไดรด์ มาเลอิกเรซินและพาราฟอร์แมลดีไฮด์ และสามารถใช้งานทางได้ถึงอุณหภูมิ 64 องศาเซลเซียส โดยไม่เกิดการเสีรูอย่างถาวร งานวิจัยนี้แสดงให้เห็นว่า คาร์บอนอล-ฟอร์แมลดีไฮด์เรซินเป็นสารเติมแต่งที่ไม่เหนียวและสามารถปรับปรุงสมบัติทางกายภาพได้

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AMORN RAT SURIYACHOT: PHYSICAL PROPERTIES MODIFICATION OF ASPHALT WITH CASHEW NUT SHELL LIQUID. THESIS ADVISOR: PROFESSOR SOPHON ROENGSUMRAN, Ph.D. 100 pp, ISBN 974-17-4121-9

Cardanol-formaldehyde resin was synthesized from a reaction of formaldehyde and cardanol separated from decarboxylated cashew nut shell liquid in the presence of sodium hydroxide and characterized by infrared spectroscopy and nuclear magnetic resonance spectroscopy. The physical properties of asphalt, modified through reaction (5 h, 150 °C) with cardanol-formaldehyde resin (CF), maleic anhydride (MA), maleic resin (MR) and paraformaldehyde (PF), were investigated using dynamic shear rheometry and penetrometer. The results of physical properties indicated that the asphalt-CF reaction products were found to have reduced temperature sensitivity (increased penetration index) to more elastic in character (decreased δ) compared to asphalt cement, asphalt-MA, asphalt-MR and asphalt-PF products. The asphalt-CF products gave rutting resistance for pavement to 64 °C. This work showed that CF was a non-inert additive and improved basic physical properties.

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จุฬาลงกรณ์มหาวิทยาลัย

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ABBREVIATIONS

ASTM	:	American Society for Testing and Materials
AC	:	Asphalt Cement
°C	:	Degree Celsius
CF	:	Cardanol-Formaldehyde Resin
CNSL	:	Cashew Nut Shell Liquid
DSR	:	Dynamic Shear Rheometry
δ	:	Delta
G*	:	Complex Shear Modulus
h	:	Hour
IR	:	Infrared Spectrometer
NMR	:	Nuclear Magnetic Resonance Spectrometer
MA	:	Maleic Anhydride
Min	:	Minute
MR	:	Maleic Resin
PF	:	Paraformaldehyde
PI	:	Penetration Index
PMA	:	Polymer Modified Asphalt
rpm	:	Rounds per minute
SBS	:	Styrene-Butadiene-Styrene copolymer
sec	:	Second
TISI	:	Thai Industrial Standards Institute
wt	:	Weight

CHAPTER I

INTRODUCTION

Asphalt is defined by the American Society for Testing and Materials (ASTM) as "a dark brown to black cementitious material in which the predominating constituents are bitumens which occur in nature or are obtained in petroleum processing." As cement, asphalt is especially valuable to the engineer because it is strong, readily adhesive, highly waterproof, and durable. It provides limited flexibility to mixtures of mineral aggregates with which it is usually combined. It is also highly resistant to the reaction with most acids, alkalis, and salts. Although a solid or semi-solid at ordinary atmospheric temperatures, asphalt may be readily liquefied by applying heat, by dissolving it in petroleum solvents, or by emulsifying it in water.[1]

The first documented use of rock asphalt as a sidewalk surfacing occurred in France in 1802 and later in Philadelphia in 1838. In 1870, the first asphalt pavement was constructed in Newark, New Jersey. The first sheet asphalt (fine sand mix) pavement was built in Washington, D.C. in 1876 with imported lake asphalt. Finally, in 1902, asphalt began to be refined from petroleum, which led to the development of the asphalt paving industry in the US. This rapid growth in asphalt usage is shown in Figure 1.1.[2]

More than 90 percent of the paved highways and streets in the world are paved with hot-mix asphalt, which involves significant expenditures for construction, rehabilitation and maintenance. Asphalt cement is the primary binder for hot-mix asphalt pavement, thus the properties of asphalt cement are a very important variable that affects the pavement performance. There are three primary modes of distress, which affect hot-mix asphalt pavements. These modes of distress are 1) permanent deformation, 2) thermal (non-load) cracking, and 3) fatigue (repeated load) cracking. In addition, aging and moisture susceptibility are also influencing factors, which have

an impact on these principal distress modes. Although these distresses may be caused by many factors including inadequate asphalt (cement) quality, improper air void content, improper asphalt quantity, poor mix design, poor quality control during construction, *etc.*

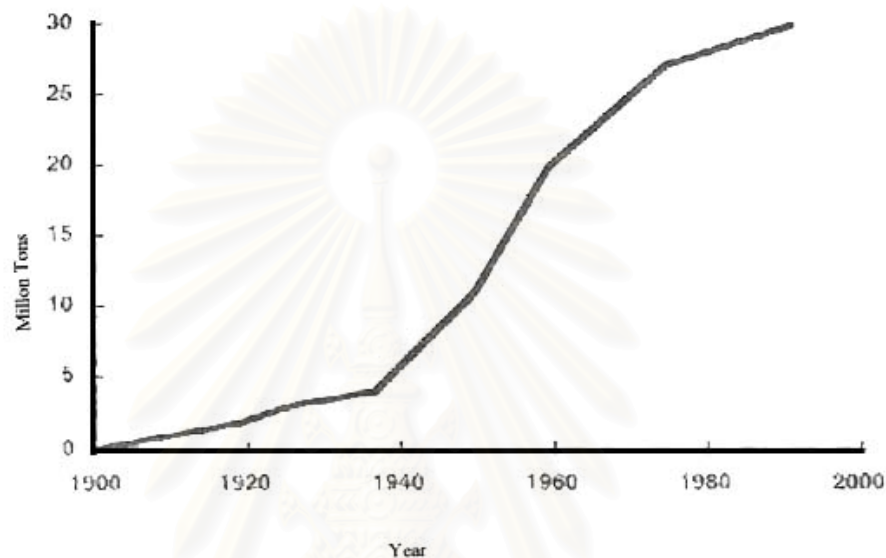


Figure 1.1 Annual asphalt usages.

There are many variables that affect asphalt quality including the sources of crude oil and the refinery process. Consequently, difficulties are encountered in the production of asphalt cement that meets the specifications for paving grade asphalt cement. This is a reason for encouraging the asphalt modification. In fact, the concept of asphalt modification has been used for many years, but the interest is especially high at this time for a number of reasons. They include at least the following [3];

1. Traffic loadings have significantly increased and include heavier loads, higher volume, higher tire pressures, new tire designs and changes in suspension systems.

2. There is also a high possibility that the costs of crude oil and asphalt cement will increase.
3. Environmental and economic pressure to dispose of certain industrial waste materials (*i.e.* tire, glass, ash, etc.) has prompted efforts to use them as asphalt additives.

To modify the asphalt cement or asphalt-aggregate mixture to enhance performance and minimize pavement distresses, it is necessary to understand the mechanism by which each pavement modifier interacts with asphalt cement in order to select the type of asphalt modifiers to be used.

Objective

The objective of this research is to study physical properties of asphalt modified with cashew nut shell liquid (CNSL).

Scope of investigation

The investigation procedures were carried out as follows:

1. Literature survey and in depth study of this research work.
2. Designed and preparation of apparatus and chemical substance
3. Decarboxylation of CNSL and purification of CNSL
4. Synthesis of cardanol-formaldehyde resin by oxidation polymerization
5. Mixing of asphalt with additives such as cardanol-formaldehyde resin, paraformaldehyde, maleic resin, maleic anhydride. The appropriate reaction condition was determined by changing the concentration of additives.
6. Characterization of CNSL, cardanol, cardanol-formaldehyde resin, by IR and NMR.
7. Testing of physical properties such as penetration, softening point and ductility.
8. Summarization of the results.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Asphalt

2.1.1 Introduction [2,4]

Asphalt cement is refined from crude petroleum, which is primarily formed by nature from plant life. The process of transformation from plant life to crude oil occurs over millions of years under various temperature and pressure conditions. Although all petroleums are basically hydrocarbons (chemical combinations of carbon and hydrogen), the amount and nature of hydrocarbons varies from crude to crude. Since the asphalt cement is obtained by distillation from the crude, its chemical composition and properties also vary from source to source.

Presently, the commercial types of asphalt cement can be broadly classified into two categories: natural and petroleum asphalts. The majority of the paving asphalt cement used today is obtained through a distillation process from crude petroleum. At ambient temperature, asphalt cement is a black, sticky semisolid and a highly viscous material. It is strong and durable cement with excellent adhesive and waterproofing characteristics. It is also highly resistant to the action of most acids, alkalies and salts.

2.1.2 Elemental Composition and Molecular Structure

Carbon and hydrogen are the principal elements present in asphalt cement molecules. Sulfur is the next most abundant element. Nitrogen and oxygen are usually present in very small amounts. Heavy metals, such as vanadium and nickel, may also

be present in trace amounts. Elemental contents of four types of representative petroleum asphalt cements are given in Table 2.1.

Most asphalt molecules consisting of carbon and hydrogen contain one or more of the following so-called heteroatoms: sulfur, nitrogen and oxygen. The type of molecular structure is more important than the total amount of each element. Since the petroleum is transformed from diverse living organic matters under different conditions, asphalt cements have extremely diverse molecular structures depending on the crude source.

Asphalt cements contain a combination of the following three arrangements by which the carbon atoms are linked with each other (Figure 2.1):

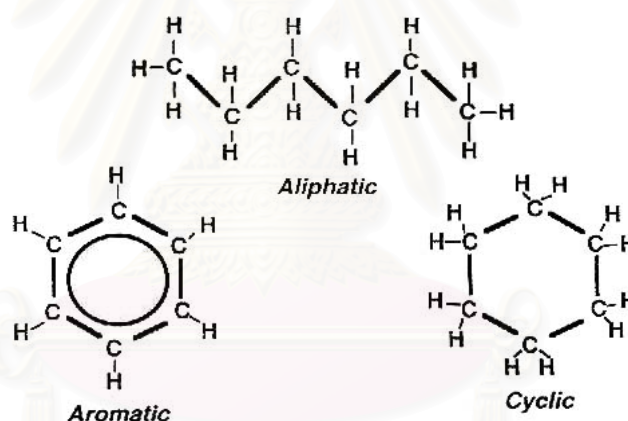


Figure 2.1 Types of asphalt molecules.

1. Straight or branched chains. Such asphalt cements are generally called “aliphatic” or “paraffinic” types.

2. Simple or complex saturated rings. “Saturated” means the highest possible hydrogen/carbon ratio in the asphalt molecules. These asphalt cements are usually referred to as “naphthenic” types.

3. One or more stable six-carbon condensed, unsaturated ring structures. These asphalt cements are called “aromatic” types. Benzene and naphthalene have such structures.

Table 2.1 Elemental Contents of Representative Petroleum Asphalts. [4]

	B-2959	B-3036	B-3051	B-3602
Elements	Mexican Blend	Arkansas-Louisiana	Boscan	California
Carbon, % w/w	83.77	85.78	82.90	86.77
Hydrogen, % w/w	9.91	10.19	10.45	10.93
Nitrogen, % w/w	0.28	0.26	0.78	1.10
Sulfur, % w/w	5.25	3.41	5.43	0.99
Oxygen, % w/w	0.77	0.36	0.29	0.20
Vanadium, ppm	180	7	1380	4
Nickel, ppm	22	0.4	109	6

Table 2.2 Sulfur, Nitrogen, and Oxygen Compounds. [4]

Sulfur Compounds	Polysulfides
	Sulfides
	Thiols
	Thiophenes
Nitrogen Compounds	Pyridines
	Pyrroles, indoles, carbazoles
	Porphyrins
Oxygen Compounds	Carboxylic acids/ naphthenic acids
	Phenols
	Ketones
	Esters
	Ethers
	Anhydrides

2.1.3 Functional or Polar Groups

As previously mentioned, heteroatoms (sulfur, nitrogen and oxygen) are attached to carbon atoms in asphalt molecules in different configurations and in the form of different compounds. These configurations (molecules) are polar because there is an imbalance of electrochemical forces within the molecule, which produces a dipole. Therefore, each polar molecule has electropositive and electronegative characteristics similar to a magnet, which has north and south poles. Since like charges repel each other and unlike charges attract each other, molecular interactions are induced in asphalt cements, which strongly influence their physical or “engineering” properties and performance. These configurations of heteroatoms thus impart functionality and polarity to asphalt molecules and are therefore called functional or polar groups.

Also, the non-polar components of asphalt cement, which act as solvents or dispersants for the polar or functional groups, play a major role in determining the effect that the polar groups will have on physical and aging properties of the asphalt cement. The types of sulfur, nitrogen, and oxygen compounds, which have been identified in asphalt cements, are given in Table 2.2.

2.1.4 Compositional Model [4,7]

Presently, there are two models of asphalt composition: micellar model and SHRP model. The micellar model is based on the premise that asphalt cements are made up of asphaltenes, resins, and oils, and has been widely accepted as providing the best available explanation of how asphalts are structured for along period of time. In recent years, the researchers of the Strategic Highway Research Program (SHRP) have achieved an entirely new understanding of asphalt that has resulted in the development of a new asphalt model that provides another understanding and explanation of asphalt performance.

2.1.4.1 Micellar model

Previously, the composition of asphalt cement was described in terms of the separation method of Corbett and Rostler, with primary components of asphaltenes and maltenes, which included resins and oils. (Figure 2.2)

Asphaltenes. Asphaltenes are generally dark brown, friable solid. The type of nonpolar solvent used to precipitate the asphaltenes affects determination of its total amount in the asphalt cement. Higher amounts are precipitated by *n*-pentane than by *n*-heptane because the number of carbon atoms in *n*-pentane is less than that in *n*-heptane. Asphaltenes are the most complex components with the highest polarity. Therefore, they have a very high tendency to interact and associate. They are mixtures of many compounds that have a strong tendency to associate in conglomerates. Asphaltenes play a major role as the viscosity-building (“bodying”) component of asphalt cements.

Resins. Resins are generally dark and semi-solid or solid in character. They are fluid when heated and become brittle when cold. They work as agents that disperse (or “peptize”) the asphaltenes throughout the oils to provide a homogeneous liquid. They are soluble in *n*-pentane, but adsorb on fuller’s earth or alumina. On oxidation resins yield asphaltene type molecules.

Oils. Oils are usually colorless or white liquid. They are soluble in most solvents. They have paraffinic and naphthenic structures without oxygen and nitrogen usually present. On oxidation they yield asphaltene and resin molecules.

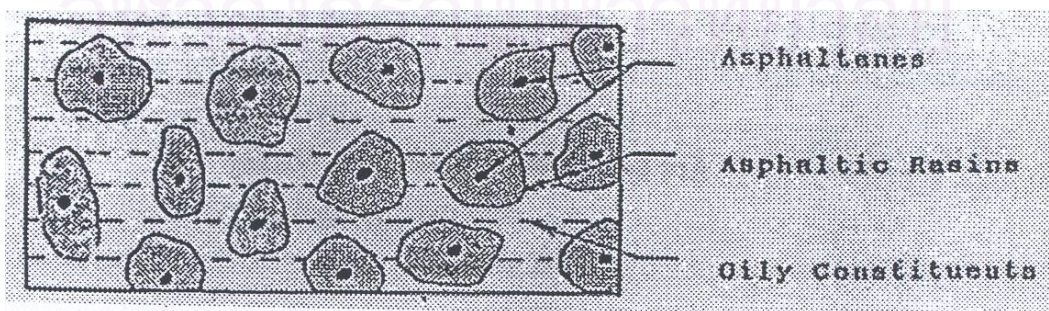


Figure 2.2 Micellar model. [5]

2.1.4.2 SHRP model

In 1987, a 5.5 year asphalt research program was established by the Strategic Highway Research Program in an effort to improve the quality of hot-mix asphalt pavement. Since its inception, the large efforts of numerous researchers at different institutions have resulted in a new model to explain asphalt's chemistry-physical property-performance relationships. This new microstructural model of asphalt has made the micellar model out-of-date and explains many of the anomalies that exist in the earlier asphalt models.

The SHRP model proposes that asphalt cement is a single-phase homogeneous mixture of many different molecules, which may be differentiated into two broader classes: polar and non-polar. The non-polar molecules serve as a matrix or solvent for the polar molecules, which form weak "networks" of polar-polar associations that give the asphalt its elastic properties. There are no micelles or "cores" of asphaltenes in asphalt. The polar materials are uniformly distributed throughout the asphalt, and upon heating the weak interactions are broken to yield the newtonian fluid, When agitated these interactions break and reform to produce a new combination of interactions that gives a new asphalt. Good asphalts need to have a proper balance of polar and non-polar molecules. The true molecular weight of the non-polar molecules is also important in asphalt performance, especially in low-temperature performance. Asphalts that have too much polar material are too stiff and are subject to fatigue cracking in thin pavements, brittleness, and thermal cracking. On the other hand, asphalts that have too much non-polar material, or asphalts in which the non-polars are too low in molecular weight, are highly flexible and suffer from fatigue cracking in thick pavements, moisture sensitivity, and rutting. At the time that this work is written, however, the SHRP asphalt research program are still in the progress of expanding understandings of and determining the link between asphalt chemistry and pavement performance.

2.1.5 Distresses in hot-mix asphalt pavement [6]

Prior to the discussion of asphalt modifications, the problems in pavement performance today are described to further justify the central goal of modifications.

The distresses, occurring in hot-mix asphalt pavement due to the properties of asphalt cement, are discussed below. The distresses are expected to occur as a result of the environment and repeated traffic loads. It is important to recognize that a distress occurs at the surface can have a number of different causes each of which must be properly identified before the proper type of asphalt modifiers (or additives) can be selected for use. In addition, it is possible that the visible manifestation of the problem at the surface looks the same but the solution of each cause may be different. Therefore, if the remedial action is effective, the cause of the problem should be understood and identified correctly. Presently, the three principal modes of distress affecting hot-mix asphalt pavements include:

1. Permanent deformation
2. Thermal cracking
3. Fatigue cracking

In addition, moisture damage and aging are influencing factors, which have an impact on these principal distress modes. Each of these deficiencies will be discussed briefly below.

2.1.5.1 Permanent deformation

Permanent deformation is a permanent change or distortion in the shape of the pavement or pavement layer. It can occur in any layer of a pavement structure. This distress generally is recognized as surface depressions in wheel paths. Permanent deformations can be caused by consolidation or plastic flow in the asphalt pavement layers and is exaggerated during periods of high ambient temperature. Surface distortion caused by consolidation of one or more layers or plastic flow as a result of repetitive shear stress is referred to as rutting. Generally, on rural highways wheel path rutting is the most common type of permanent deformation, but in urbanized areas and at intersections, where heavy vehicles move slowly or stop frequently, both rutting and shoving can also occur. Plastic flow is related to the properties of asphalt cement binder, even though the aggregate may have a dominant effect in most cases. Nevertheless of primary interest is the benefit of modification



Figure 2.3 Rutting along the wheel path in HMA pavement.[6]

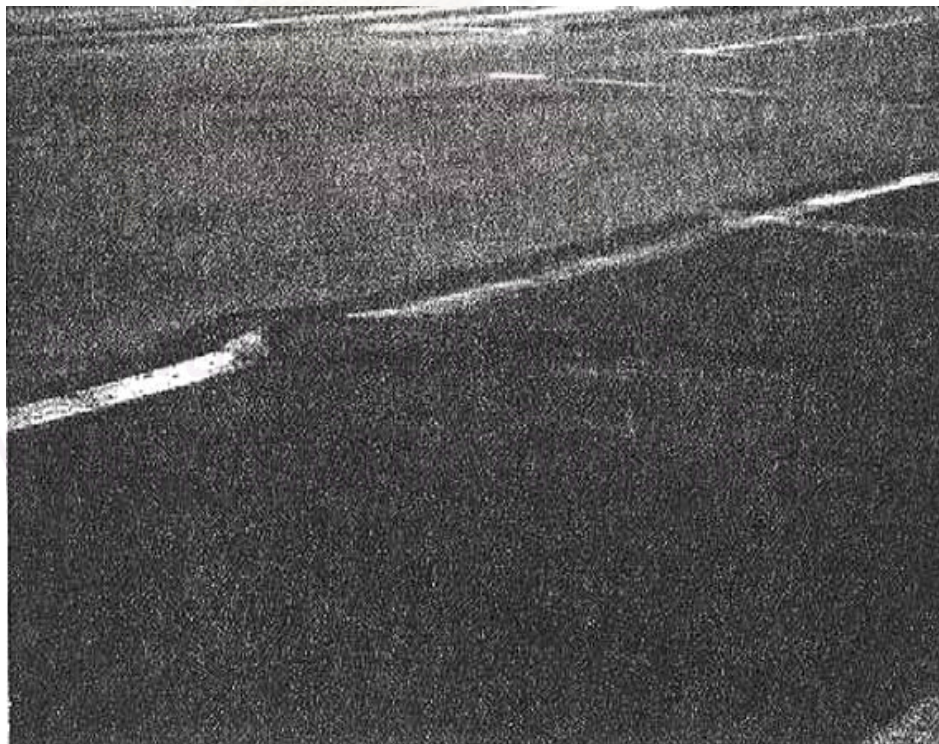


Figure 2.4 Shoving at the intersection in HMA pavement.[6]



Figure 2.5 Transverse cracking due to temperature change.[6]

2.1.5.2 Thermal cracking

Thermal (non-loading) cracking in hot-mix asphalt pavement is caused by thermally induced tensile stresses produced by high cooling rates and low temperatures. When these stresses exceed the tensile strength of the pavement material, thermal cracking occurs. It manifests itself through transverse shrinkage cracking similar to fatigue cracks.

In asphalt concrete pavements, the thermal cracking behavior is controlled primarily by properties of the asphalt cement at low temperatures. Asphalt cements are temperature susceptible, viscoelastic materials. Under moderate temperature and normal operating conditions, asphalt cement can relieve stresses caused by temperature changes in the pavement through viscous flow. At low temperatures, all asphalts reach a point when viscous flow stops and their behavior becomes purely elastic. The temperature at which asphalt reaches this maximum stiffness varies with its grade, crude source, age and its strain rate. When asphalt cement experiences low temperature and rapid temperature change, strains induced by temperature change

may not be relieved through viscous flow and brittle failure occurs. Although generally considered a low temperature phenomenon, temperature induced cracking is also observed in age-hardened pavements in desert climates. Within a given grade, the more temperature susceptible the asphalt, the greater the tendency for thermal cracking.

2.1.5.3 Fatigue cracking

Fatigue cracking in asphalt pavement structures occurs as a result of repeated loads or stress. Cracks are initiated by the repeated loads and propagate vertically through the pavement layer. Factors, which influence the development of fatigue cracks, are: 1) structural design of the pavement, 2) asphalt cement properties, 3) asphalt content, 4) air voids and aggregate characteristics in the asphalt mix, 5) in-place properties of foundation soils, 6) temperature and 7) traffic. However, only asphalt cement properties will be discussed here.

Fatigue testing has been conducted for many years in controlled strain or controlled stress modes. Controlled strain experiments are considered to be more representative of overlays and thin lift construction, which is the dominant type of asphalt construction taking place today. Controlled stress experiments are more related to thicker structures. For thin pavements, using controlled strain testing, low-stiffness asphalt cement is associated with longer fatigue life. On the other hand, for thick pavements, using controlled stress testing; stiffer asphalt cements exhibit longer fatigue lives. For both controlled strain and controlled stress testing, stiffness of the mixture is the principal property affected by the asphalt cement, which affects the fatigue life of the asphalt pavement.

2.1.5.4 Moisture damage

As previously discussed, moisture damage, while not a distress, is an influencing factor which has an impact on these principal distress modes. Moisture damage involves the removal of the asphalt film from the aggregate surface in the presence of water. Moisture damage induces the hot-mix asphalt pavement distresses in a number of types, including:

1. Flushing may occur when the excess asphalt works to the surface as the results of asphalt and rater combining to form an unstable soft matrix.
2. Ravelling may result from the reduced asphalt-aggregate adhesive strength at the surface.
3. Cracking and rutting may be induced from the resulting decrease in strength and volume resulting from the stripping of asphalt from the aggregate at the bottom of the bituminous layer.

Although several factors can affect water-induced damage in asphalt-aggregate mixes and contribute to the distresses in the hot-mix asphalt pavement, the chemical and physical properties of the asphalt cement and aggregate are still a primary factor. A variety of approaches have been considered for improving asphalt pavement resistance to moisture damage. These approaches include the use of antistripping additives, surfactants. Hydrated lime, aggregate pretreatment, aggregate coatings, and modified asphalt cements. The effectiveness of the treatment usually varies with the aggregate. Generally, resistance to moisture damage has been evaluated in terms of the ability of the mixture to retain strength after moisture conditioning. The specimen strengths have been characterized using static and dynamic, indirect tensile and compressive strength tests.

2.1.5.5 Aging

Aging is another influencing factor, which is not a distress, but can lead to modes of cracking. Aging or age hardening of asphalt cement in HMA pavement results in progressively lower penetration or higher viscosity. This causes a progressive increase in the brittleness, hardness and lack of binder characteristics of asphalt cement. Although this result from aging is good to resist deformations in pavement, excessive aging can initiate early cracking in pavement and sometime disintegration such as raveling may occur. One of the six reactions, as previously discussed, can induce aging in every step of HMA pavement construction from the short mixing period at the plant to the long service periodic the roadway. In addition, it should be noted that aging in service takes place at the accelerated rate if the HMA

pavement has a higher air void content than originally designed, or in the other word is lack of compaction, which provides for easy entry of air, water and light.

2.1.6 Ideal asphalt cement properties [4]

To overcome the defective properties of asphalt cement that can lead to hot-mix asphalt pavement distress, the idealized asphalt cement properties are needed to be modeled as a goal for the asphalt modification. The idealized asphalt cement binder properties are as follows:

1. At high temperatures (>100 °F), the modified asphalt cement should be stiffer than the conventional asphalts in order to reduce rutting and/or shoving.
2. At cold ambient temperatures (<40 °F), the modified asphalt cement should be less stiff than conventional asphalt to reduce low temperature cracking.
3. At the processing temperatures (280-325 °F), viscosity should be low enough to expedite spraying, pumping, mixing, and compaction.
4. The adhesion between the asphalt cement binder and aggregate should be strong enough to reduce moisture damage.
5. The age hardening of asphalt has to be reduced to minimize cracking.

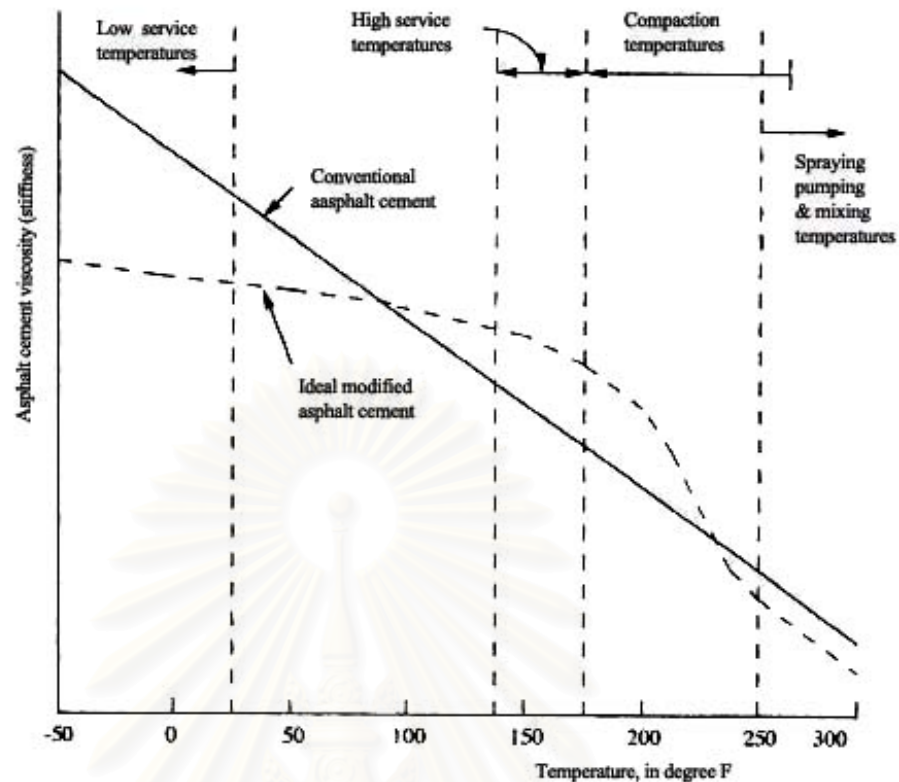


Figure 2.6 Viscosity-temperature Relationship of Ideal modified asphalt.[4]

2.2 *Anacardium Occidentale* [8,9]

2.2.1 The Cashew Tree

The cashew tree, *Anacardium occidentale* Linn., is a native plant of Brazil, the tree grows in the coastal areas of Asia and Africa. It is now found widely in other parts of tropical South and Central America. The generic name, *Anacardium*, is bestowed upon it because it describes the heart-like shape of the nut. The specific name, *occidentale*, is used because the nut comes from the Western Americas.

The cashew plant is a jungle or semi-jungle tree by nature. The tree, which is an evergreen, naturally grows up to 12 metres in height and has a spread of 25 metres. Its light colored foliage readily recognizes it. The yellow-green leaves, revealing distinct veins, are elliptic in shape and approximately 4 to 6 inches in length and 2 to 3 inches in width. They feel leathery to the touch.

2.2.2 Cashew apple and Cashew nut

The cashew nut is attached to the bottom of the cashew apple, with the size of 2 to 4 inches in length and 1.5 to 2 inches in width. It has a waxy yellow, red or orange skin. Broadly conical or pear-like in shape, it is called a cashew “pear” or cashew “apple”.



Figure 2.7 A picture of cashew apple and cashew nut. [10]

The whole cashew nut is from 2.5 to 4 cm long; 1.9 to 2.2 cm broad at the base; and 1.3 to 1.6 cm thick at the stem-end. It is gray brown and shapes more like the kidney than the heart from which its generic name is derived. The shell is about 0.3 cm thick, having a soft leathery outer skin and a thin hard inner skin. Between these skins is the honeycomb structure containing the phenolic material popularly called “Cashew Nut Shell Liquid (CNSL)”. Inside the shell is the kernel wrapped in a thin brown skin, known as the testa.

The nut thus consists of the kernel (20-25 %), the shell liquid (20-25 %), and the testa (2 %), the rest being the shell.

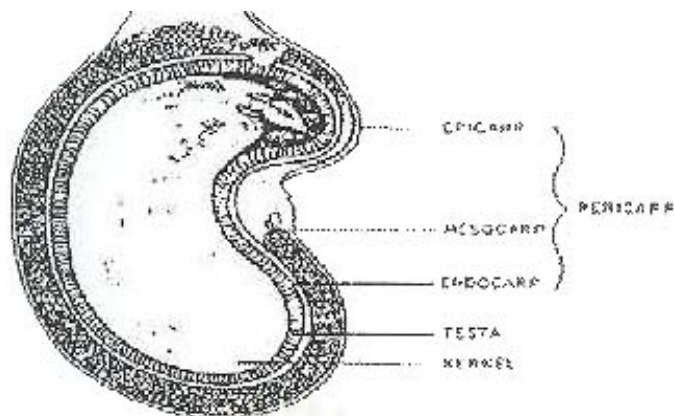


Figure 2.8 A cross section of a cashew nut. [11]

2.2.3 Cashew Nut Shell Liquid

2.2.3.1 Introduction [12,13]

Cashew nut shell liquid (CNSL) occurs as a reddish brown viscous liquid in the soft honeycomb structure of the shell of cashew nut and is reported to occur in the fresh shell to the extent 15 to 20 and 20 to 30 percent by weight for African nuts and Indian nuts, respectively. CNSL is extremely caustic and a strong vesicating agent.

2.2.3.2 Extraction of CNSL [14]

In the production of cashew kernels for edible purposes, CNSL is extracted from the outer shell of the cashew nuts before they are decorticated in order that the kernels may be removed without becoming contaminated by the liquid. There are three main methods to obtain this liquid:

1. Hot oil bath method

This is the most common method of commercial extraction. The raw nuts are passed through a bath of hot CNSL (180-200 °C) itself, when the outer part of the shell bursts open and releases CNSL (50 % recovery). Another 20 % could be extracted by passing the spent shells through an expeller and the rest by solvent extraction techniques.

2. Expeller method

Some factories have introduced manually operated cutting machines in which shells of lightly roasted nuts are cut, keeping the kernel intact. The shells are then fed to an expeller to recover 90 % of the oil.

3. Kiln method

The nuts are shelled after sun drying or after drum roasting. The liquid obtained is, however, crude and contaminated.

CNSL, extracted with low boiling petroleum ether, contains about 90 % anacardic acid and about 10 % cardol. CNSL, on distillation, gives the pale yellow phenolic derivative cardanol. Natural CNSL contains 80.9 % anacardic acid, 10-15 % cardol and small amounts of other materials, notably the 2-methyl derivative of cardol. The chemical structures of major compounds in natural CNSL are shown in Figure 2.8. The side chains exist in saturated ($n = 0$), monoene ($n = 2$), diene ($n = 4$) and triene ($n = 6$) forms with *cis* configuration.

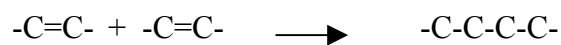
In the roasting process, some polymerization as well as decarboxylation occurs, because of the highly unsaturated nature of CNSL. Thus, a typical product could contain polymer (20-25 %), cardanol (60-65 %), cardol (10-12 %) and other minor components. The characteristics of cardanol and IS specification for CNSL are given in Tables 2.3 and 2.4, respectively. [14]

2.2.4 Resin from CNSL [15]

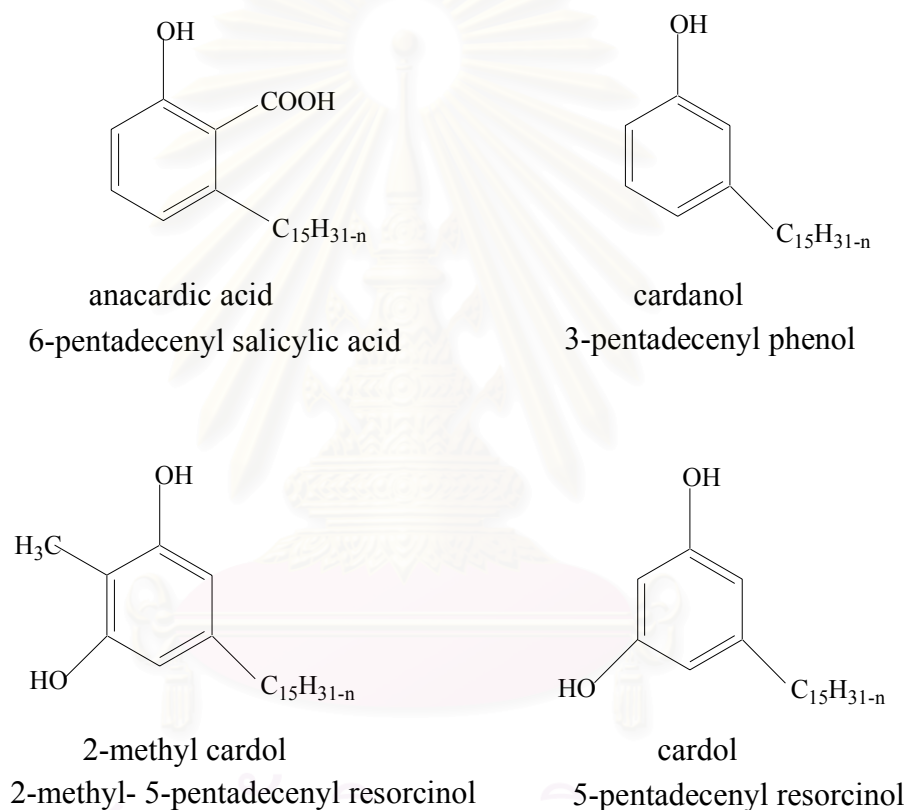
CNSL has a dual functionality in resin-forming reactions, because it is both phenolic and olefinic in character. It can therefore be:

(a) Condensed with formaldehyde through the phenolic nuclei with acid or base catalyst that give straight chain polymer.

(b) Polymerized through the unsaturated side chain ($-C_{15}H_{31-n}$) by addition polymerization



Both reactions are used in making commercial products from CNSL and its derivatives.



Where $n = 0, 2, 4$ or 6

Scheme 2.1 Chemical structures of major compounds in natural CNSL. [9]

Table 2.3 Characteristics of Cardanol. [14]

Characteristics	
Boiling point, °C	228-235 (3.4 mm Hg)
Color (Livibond, 1 cm cell)	red (1.0-3.0)
(Freshly distilled)	Yellow (1.5-3.5)
Viscosity, 30 °C (cP)	40-60
Specific gravity 30/30 °C	0.93-0.95
Ash content	negligible
Volatile loss, % by wt (max)	2.0
Acid value	1.9-2.0
Iodine value (Wij's method)	210-220
Hydroxyl value	180-200

Table 2.4 IS Specification* for Cashew Nut Shell Liquid. [14]

Characteristics	Requirement
Specific gravity 30/30 °C	0.950 to 0.970
Viscosity at 30 °C, cP (max)	550
Moisture, % by wt (max)	1.0
Matter insoluble in toluene, % by wt (max)	1.0
Loss in wt on heating, % by wt (max)	2.0
Ash, % by wt (max)	1.0
Iodine value (max)	
a) Wij's method	250
b) Catalytic method	375
Polymerization	
a) Time, min (max)	4
b) Viscosity at 30 °C, cP (max)	30
c) Viscosity after acid washing	200
at 30 °C, cP (min)	

*IS 840:1964

2.2.5 The Advantages of Resin from CNSL [15]

The principal features of all resinous products based on CNSL arise from the presence of the long unsaturated carbon-chain substituent. These can be summarised as:

1. Internal plasticity of the cured aldehyde condensation products, i.e., the resin has more flexibility, especially at elevated temperature, than straight phenolic resins.
2. Solubility or compatibility with substances of a hydrocarbon nature, e.g., aromatic and aliphatic solvents, natural and synthetic rubbers, and drying oils, similar to resins based on p-alkylphenols.
3. Resistance to alkalis and acids, probably because of the strongly hydrophobic nature of the hydrocarbon chain.

2.2.6 Uses and Applications [11,14]

The CNSL is an undesirable by-product of the cashew kernel industry. This is an effective replacement of source and expensive petrochemicals. CNSL is described often as a versatile industrial raw material. It has wide application in the manufacture of numerous industrial products.

The CNSL is second only to the cashew kernel or nutmeat in economic importance. In its nature state, it serves as a protection to the kernel against insect attack. If used in combination with kerosene or diesel oil, it is an effective insecticide against mosquito larvae. Made into a varnish it is a preservation of wooden floors and fine carved woods, protecting them from insect destruction. For many year, fishermen have used the liquid to waterproof and preserve their fishnets, fishing lines and boats.

With recent advances in chemical technology, the CNSL is finding many new industrial applications. It is used commercially as a phenolic raw material for the manufacture of certain resins and plastics. In particular, it is used as a friction

modifier in the manufacture of brake linings and clutch facings. It has the property of absorbing the heat generated by friction in the braking action while retaining their braking efficiency longer. Apart from low 'fade' characteristics, cashew-based friction materials again give a much quieter braking action and also are more efficient for 'cold wear'. These materials are ideal for use in low speed automobiles where the temperature generated does not exceed 250 °C. It is also used in rubber compounds, where it acts as reinforcing fillers, which tensile strength, hardness and abrasion-resistance are improved. The resins from CNSL are used in laminating for papers, cloths and glass fibers, or impregnating materials where oil or acid resistance is required. Other uses include the manufacture of lacquers, paints, printing inks, electrical insulation material, an anti-corrosive for metals, water proofing compounds and adhesives.

2.3 Phenolic Resins

2.3.1 Introduction [15, 16, 17, 18]

Phenolic resin (phenol-aldehyde polymer) are polymers formed by the interaction of a phenol and/or substituted phenol and aldehyde with strong acid or alkaline catalysts. The phenols of commercial importance are phenol (III) itself, cresols (IV), xylenols (V), resorcinol (VI) and higher homologues of phenol, i.e., para-tertiary-butyl phenol (VII), p-tert-amyl phenol (VIII), p-tert-octyl phenol (IX) and p-phenyl phenol (X); also, a product derived from Cashew Nut Shell Liquid (CNSL), which is a mixture of phenol derivatives (Figure 2.10.). It may be noted that several aldehydes other than formaldehyde (XI) have been used to prepare phenolic polymers but none has attained appreciable commercial significance (Scheme 2.2).

Phenolic resins find practical utilization mainly in the form of network polymer. The polymerization is normally carried out in two separate operations. The first operation involves the formation of a low molecular weight fusible, soluble resin, and the second operation involves curing reactions, which lead to the cross-linked product. Various types of initial low molecular weight resin is produced commercially, resol and novolac resins. The thermosetting (i.e., nonsubstituted) phenolic resins are employed as structural adhesives for laminating, and for bonding applications: bonded and coated abrasives, friction materials, fiber bonding, foundry

use, and wood bonding. The resins based on para substituted phenols are not capable of crosslinking to a thermoset state. These resins are employed as tackifiers in contact, pressure sensitive, and hot-melt adhesives. The meta substituted isomer is trifunctional, and, therefore, crosslinking will occur. Substituted phenols provide improved compatibility with rubbers (in adhesives) and drying oils (in varnishes).

2.3.2 Factors Influencing the Course and Speed of the Reaction [16]

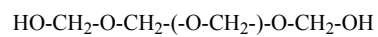
Precise control of the course, speed and extent of the reaction is essential for the manufacture of products. Factors important for achieving this control include:

1. molar ratio of phenol to formaldehyde;
1. kind and amount of catalyst;
2. reaction time and reaction temperature;
3. modification with other aldehydes and phenols;
4. modification with other compounds.

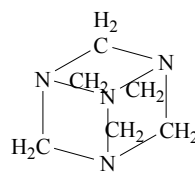
The phenol:formaldehyde molar ratio, coupled with the type of catalyst use, determine whether the polymer will be phenol terminated or methylol (-CH₂OH) terminated. If phenol terminated, the resin is referred to as a novolac or a two-step resin. Such a resin is not heat-reactive until a second ingredient is added that supplies the formaldehyde needed to effect cure. The most widely used curing agent is hexamethylenetetramine (II). If methylol terminated, the resin is referred to as a resol or a one-step resin. This type is heat-reactive. In both resols and novolacs, the resinous state is due to the presence of isomers and of homologous products with a wide range of molecular size, rather than to the presence of large molecules such as is found in most of the ethenoid polymers.

2.3.3 Resol-Resin [16, 19]

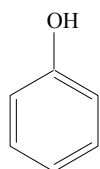
Resol are obtained by reaction of phenols and aldehydes under alkaline conditions, where the aldehyde is used in excess. Phenol-formaldehyde ratios of between 1:1.0 and 1:3.0 are usually used. Common alkaline catalysts are NaOH, Ca(OH)₂ and Ba(OH)₂. This excess may be small or large according to the type of resin required. It should be noted that resols cannot normally be made from the higher



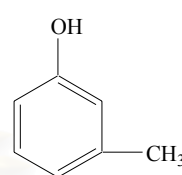
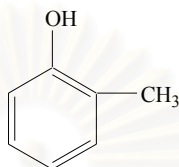
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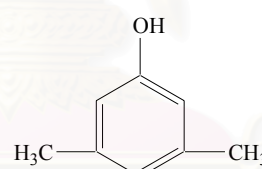
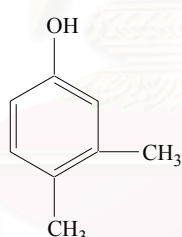
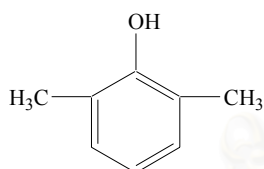
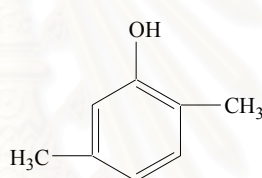
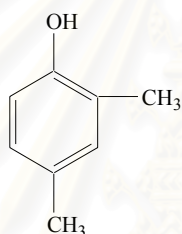
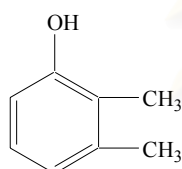
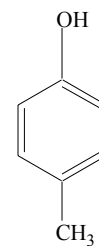
(II)



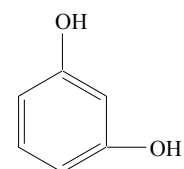
(III)



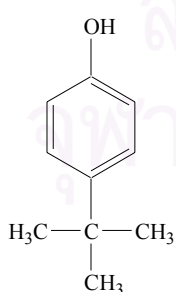
(IV)



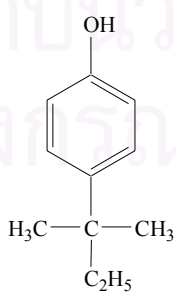
(V)



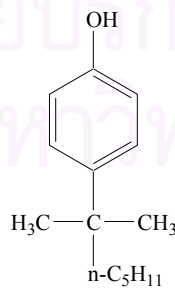
(VI)



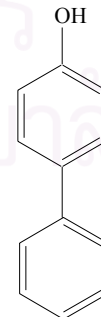
(VII)



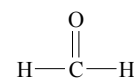
(VIII)



(IX)



(X)



(XI)

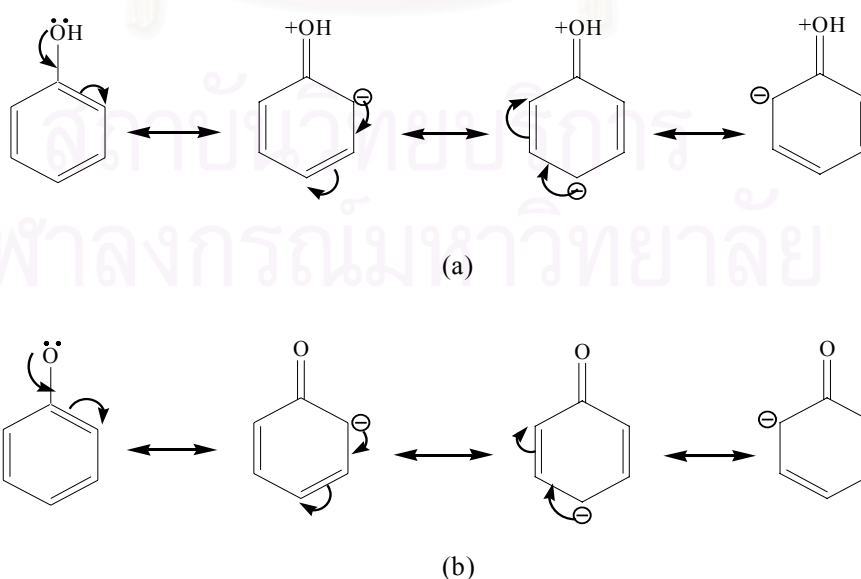
Scheme 2.2 Derivatives of phenols.

aldehyde. The molecules contains reactive methylol groups, heating causes the reactive resol molecules to condense together to form larger molecules, a result achieved without the addition of a substance containing reactive methylene (or substituted methylene) groups.

2.3.3.1 Mechanism and Preparation [15, 19]

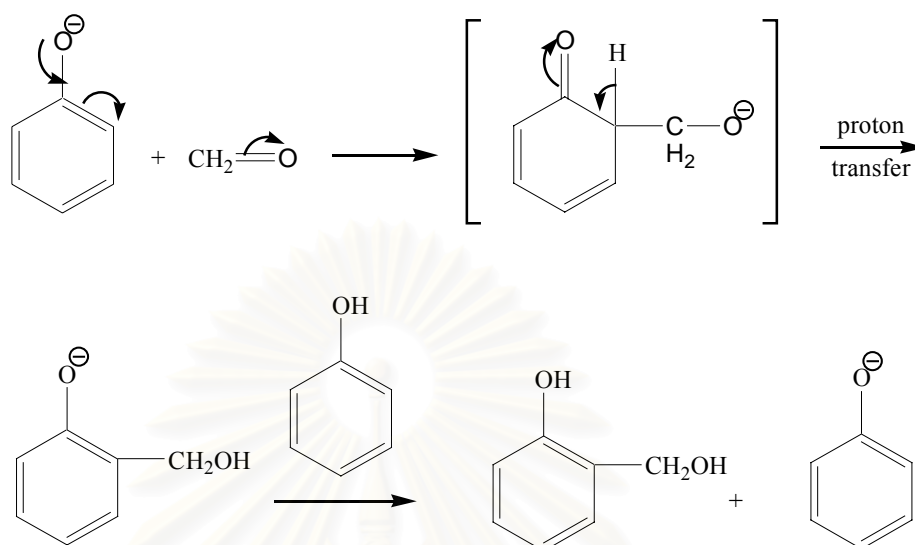
The reaction in making resols consists of an initial addition reaction between the phenol and formaldehyde to form phenol-alcohols (XII, XIII) follow by a condensation reaction of these, either with one another or with more phenol, and then in turn by successive further addition and condensation reactions.

In undissociated phenol, delocalization of an unshared electron pair on the oxygen atom results in increased electron densities at the ortho and para positions. This effect is larger than the decrease in electron density, which results from the inductive effect of the hydroxyl group (Scheme 2.3 a). Thus substituted of phenol by electrophilic reagent takes places at the o- and p-positions. In the phenoxide ion, similar delocalization occurs but because of the negative charge on the oxygen atom the inductive effect is greatly increased and reversed in direction so that electron density in the benzene ring is notably increased (Scheme 2.3 b). Thus phenol is more reactive and more o-/p-directing in alkaline solution than in neutral or acid solution.



Scheme 2.3 Resonance of phenol (a) and phenoxide ion (b).

The reaction of phenol and formaldehyde in alkaline conditions therefore results in the formation of *o*- and *p*-methylol groups (Scheme 2.4).

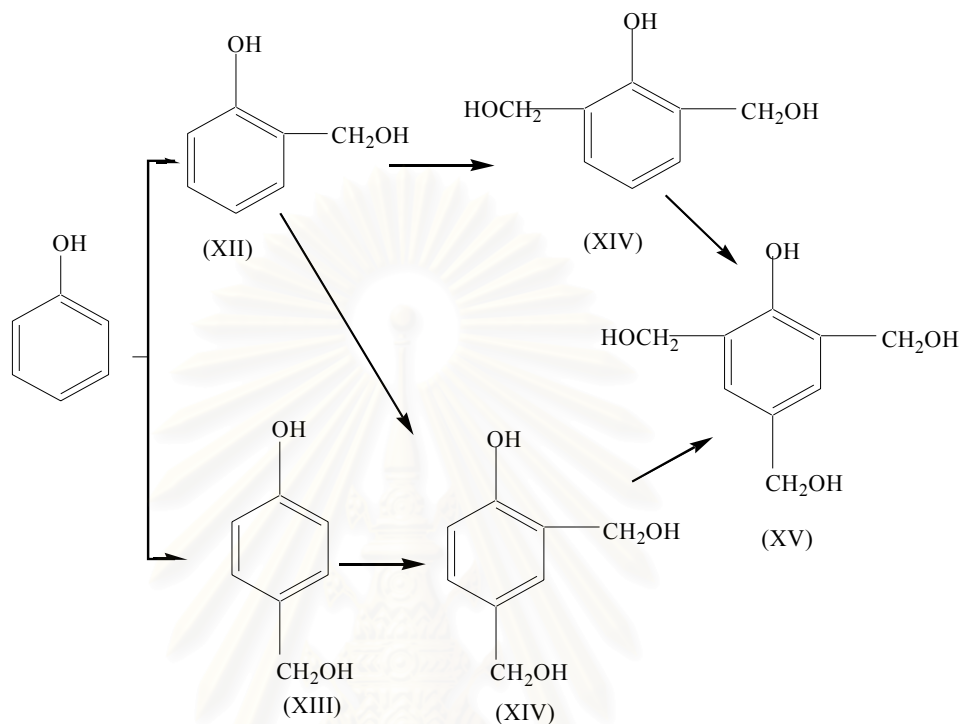


Scheme 2.4 Formation of *o*-methylolphenol.

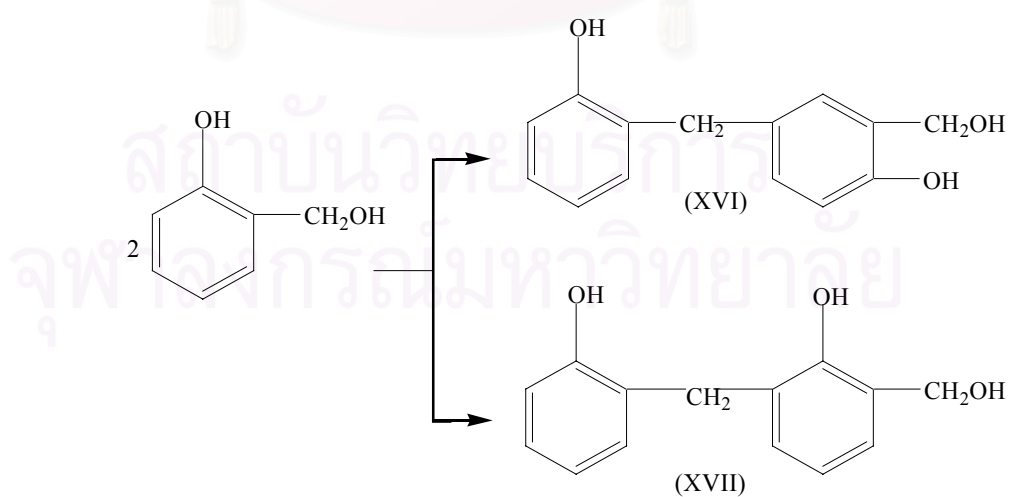
(It should be noted, however, that the identity of the actual hydroxyalkylating species has not been established and it is not clear how formaldehyde, as methylene glycol, reacts with the phenoxide ion.) The resulting *o*-(XII) and *p*-methylolphenols (XIII) are more reactive towards formaldehyde than the original phenol and rapidly undergo further substitution with the formation of di-(XIV) and trimethylol derivatives (XV). Since virtually no substitution occurs at the *m*-position, the possible products are as shown in Scheme 2.5. All of these compounds have been obtained from aqueous alkaline solutions of phenol and formaldehyde.

The methylolphenols obtained are relatively stable in the presence of alkali but can undergo self-condensation to form dinuclear and polynuclear phenols in which methylene groups link the phenolic nuclei. These products can arise from two different types of self-condensation; one involves two methylol groups and the other involves a methylolphenol. Examples of such reactions are provided by an investigation in which *o*- and *p*-methylolphenols were heated with aqueous sodium hydroxide at 80 °C and the products analysed by paper chromatography. *o*-Methylolphenol gave 3-methylol-2'4-dihydroxydiphenylmethane (XVI) by reaction

between a methylol group and a p-hydrogen atom together with traces of 3-methylol-2,2'-dihydroxydiphenylmethane (XVII) by reaction between a methylol group and an *o*-hydrogen atom, Scheme 2.6.



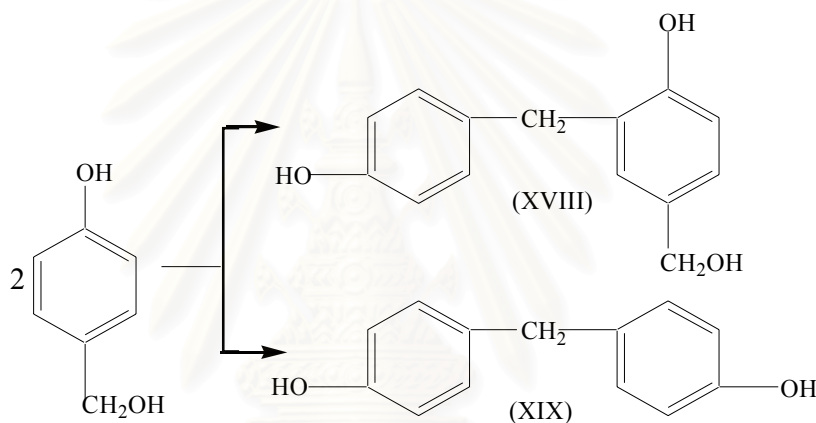
Scheme 2.5 Formation of di- and tri-methylolphenols.



Scheme 2.6 Self-condensation of *o*-methylolphenols yield polynuclear phenols.

p-Methylolphenol gives 5-methylol-2-4'-dihydroxydiphenylmethane (XVIII) by reaction between a methylol group and an *o*-hydrogen atom and 4,4'-dihydroxydiphenylmethane (XIX) by reaction between two methylol groups, Scheme 2.7.

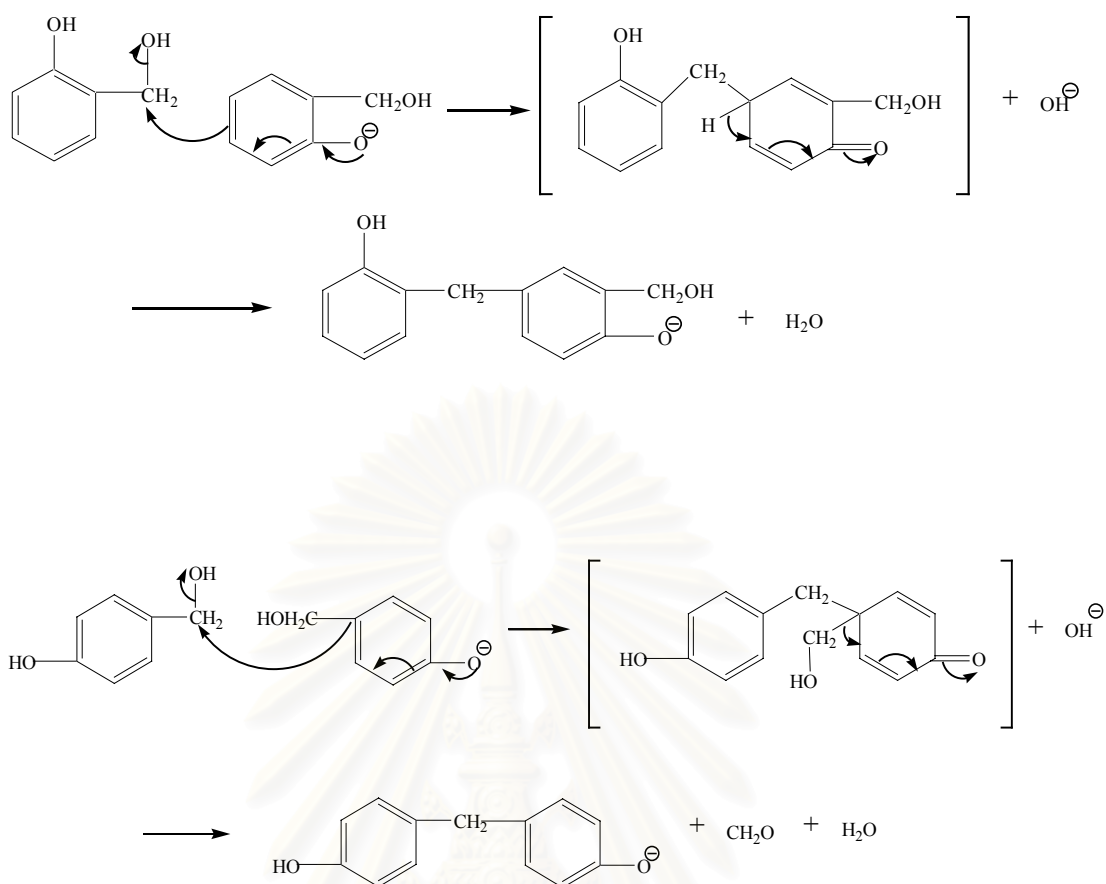
Possible mechanisms of these two types of self-condensation are shown below, Scheme 2.8. Both cases involve attack on a methylol group with displacement of a hydroxyl group. In the first case, a proton is subsequently eliminated and in the other a methylol group is subsequently eliminated (as formaldehyde). Which of these two types of reaction occurs in any particular case depends on the experimental conditions



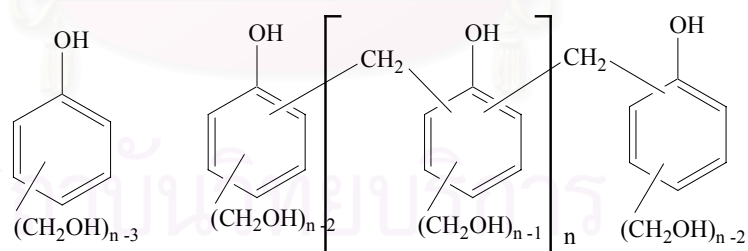
Scheme 2.7 Self-condensation of *p*-methylolphenols.

and the structure of the methylolphenol involved. Generally, *p*-hydrogen atoms and *p*-methylol groups are the predominant sites for the self-condensation of methylolphenols.

The above reactions, which are shown as leading to dinuclear phenols, may be repeated so that trinuclear phenols are formed, and so on. Thus the product obtained by the reaction of phenol and formaldehyde under alkaline conditions is a complex mixture of mono- and polynuclear phenols in which methylene groups link the phenolic nuclei. The structures of the components of such a mixture may be represented as follow in Scheme 2.9.



Scheme 2.8 Possible self-condensation mechanism of o- and p-methylolphenols.



Scheme 2.9 Mono- and poly-nuclear phenols.

In these general formulas, the methylol groups and methylene bridges are restricted to o- and p-positions and there is a tendency for o-methylol groups and p-methylene bridges to predominate. Typical commercial liquid resols have the average of less than 2 aromatic rings per molecule, whilst solid resols have 3-4. It is noted that the conversion of resol molecules into high molecular weight, cross-linked materials

may be accomplished by simply heating a resol, it being is often referred to as a “one-stage” process, since a quantity of formaldehyde sufficient to permit the formation of highly cross-linked material is present from the outset. Thus, during the preparation of a resol, polymerization is steadily advancing and there is a danger of gelation in the reactor of reaction is taken too far.

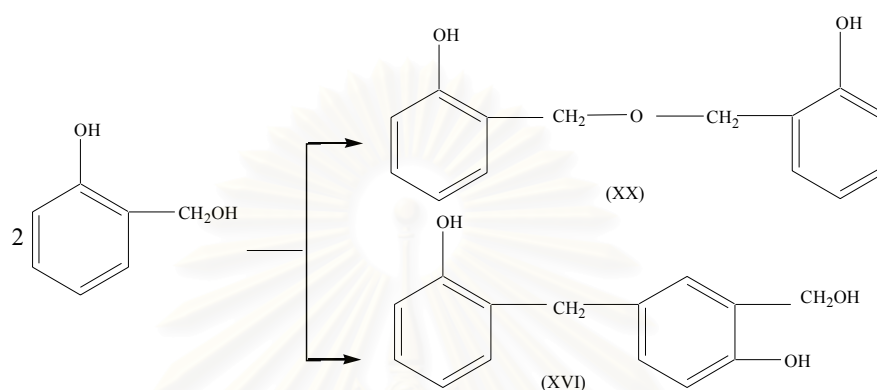
2.3.3.2 Cross-Linking of Resol Resin [19]

Resol, produced under alkaline conditions, are generally neutralized or made slightly acid before curing is carried out. Network polymer polymers are then obtained simply by heating. The curing of resol is extremely; involving a number of competing reactions each of which may be influenced by reaction conditions it is easy to unravel precisely what takes place. Also, the cured product, being infusible and insoluble, is not amenable to chemical investigation.

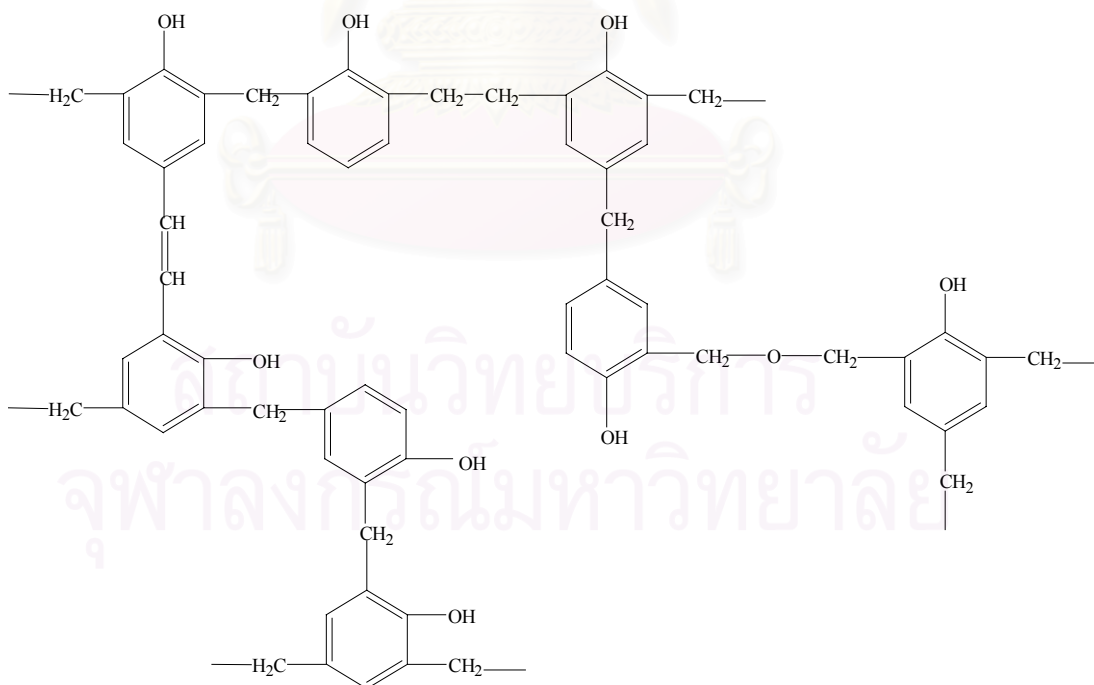
When pure (i.e. natural) o-methylolphenol is heated at 110 °C the main product is 2,2'-dihydroxydibenzylether (salireton, XX) with very little of the methylene compound (XVI), Scheme 2.10. It was also found in this investigation that when o-methylolphenol is heated at 70 °C in the presence of hydrochloric acid both compounds (XX) and (XVI) are produced but in the presence of sodium hydroxide only the methylene compound (XVI) is formed. Thus when a resol is cured, it is likely that both methylene and ether links are present in the product. It was been found that whilst methylene compounds are generally rather stable, dibenzyl ethers are not so stable and at temperature above about 150 °C (i.e. at temperature commonly used for curing resol) they undergo a number of illdefined reactions. The mechanisms of these secondary reactions have been extensively studied but are still rather poorly understood.

To summarize, it may be said that the network polymer obtained from a resol is composed principally of phenolic nuclei joined by methylene groups. However, there is the possibility of other types of linkages, the nature and extent of which depend on the nature of the resol and the conditions of cure. The possible structure of such a network is represented as in Scheme 2.11. It is noted that the relative amounts of the various linkages shown below are not intended to have any quantitative

significance. It is also noted that phenol-methylene chains are extremely irregular and their geometry precludes a large proportion of the theoretically possible cross-links. It may be mentioned that it is common practice to refer to resols as “A stage resins” and to the final network polymers as resites or “C stage resins”; intermediate materials are called resitols or “B stage resins”.



Scheme 2.10 Self-condensation of o-methylolphenol at 110 °C.

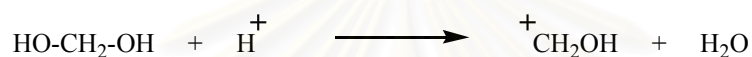


Scheme 2.11 Possible network structure of resol resin.

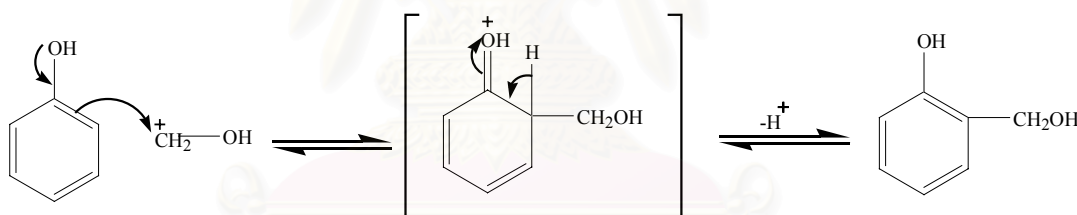
2.3.4 Novolac resins [16, 19]

2.3.4.1 Mechanism

Novolac resins are obtained by reaction of phenol and formaldehyde in the strongly acidic pH region. The reaction is usually carried out at a molar ratio of 1 mol (phenol) to 0.75-0.85 mol (formaldehyde). The reaction between phenol and formaldehyde under acidic condition proceeds through a mechanism different from the base-catalyzed reaction. The initial step involves the protonation of formaldehyde (methylene glycol) to give carbocation:

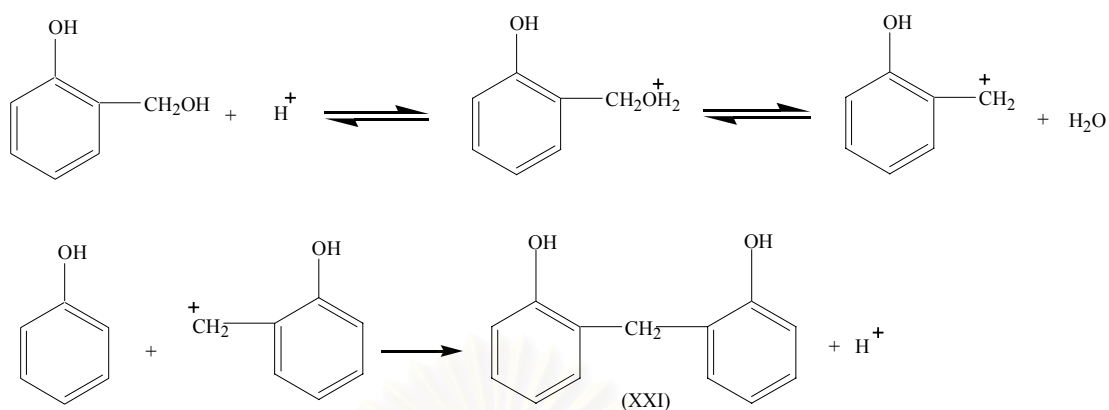


The phenol then undergoes electrophilic substitution with the formation of an *o*- and *p*-methylol group, e.g., Scheme 2.12.



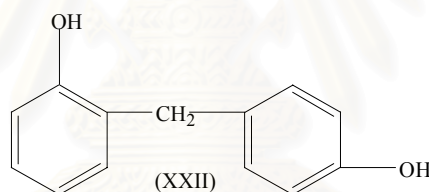
Scheme 2.12 Electrophilic substitution of phenol in acid catalyzed reaction.

In the presence of acid the initial products, *o*- and *p*-methylolphenols, are present only transiently in very small concentration. They are converted to benzylic carbocation which rapidly react with free phenol to form dihydroxydiphenylmethanes, e.g., Scheme 2.13.



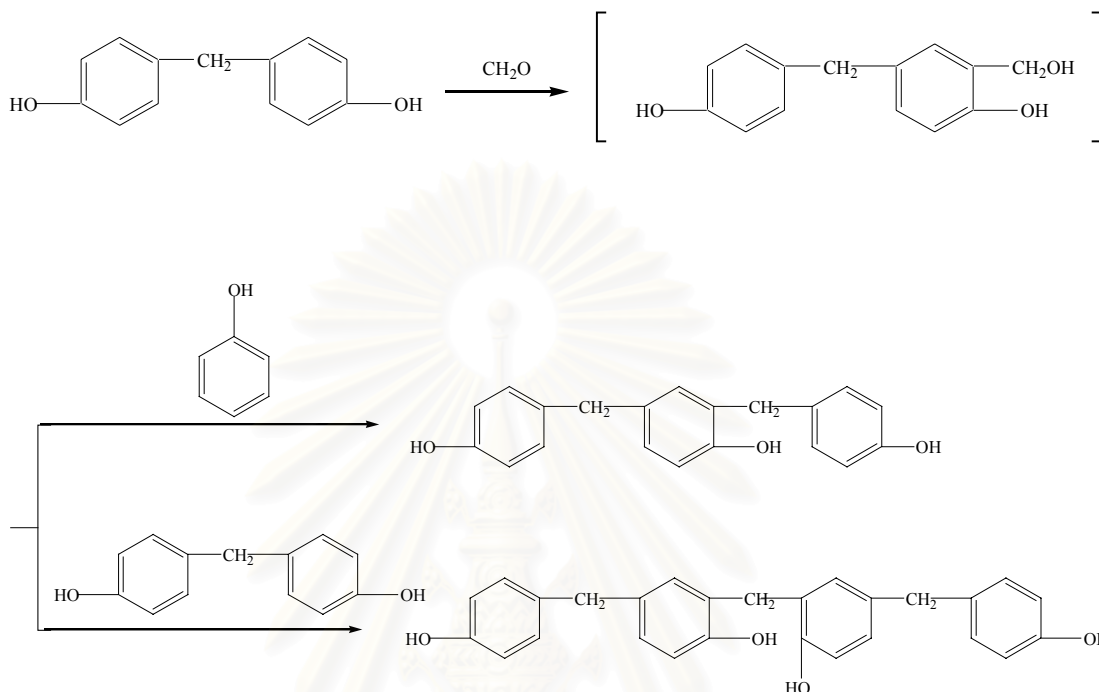
Scheme 2.13 Formation of dihydroxydiphenylmethane.

Since the phenol does not undergo substitution at m-position, there are possible three dihydroxydiphenylmethanes, namely 2,2'-(XXI), 2,4'-(XXII) and 4,4'-dihydroxydiphenylmethane (XIX).



The proportions in which the three isomers are formed depend on the condition used, particularly pH. Under strongly acidic conditions ($\text{pH} < 2$), such as are normally used in making novolacs, only the 2,4'- and 4,4'-isomers were isolated in any appreciable yield, whereas at higher pH (3-6) the 2,2'-isomer predominated. In the acid-catalyzed reaction between phenol and formaldehyde the first substitution in the phenolic nucleus substantially deactivates the ring against further substitution. Also, although the dihydroxydiphenylmethanes formed are activated in the same manner as the single phenolic nucleus, the activation is not so strong. Because of the aforementioned factors, there is an initial build-up in the concentration of dihydroxydiphenylmethanes.

The concentration of dihydroxydiphenylmethanes subsequently falls as polynuclear phenols are produced by further methylation and methylene link formation, e.g., Scheme 2.14.

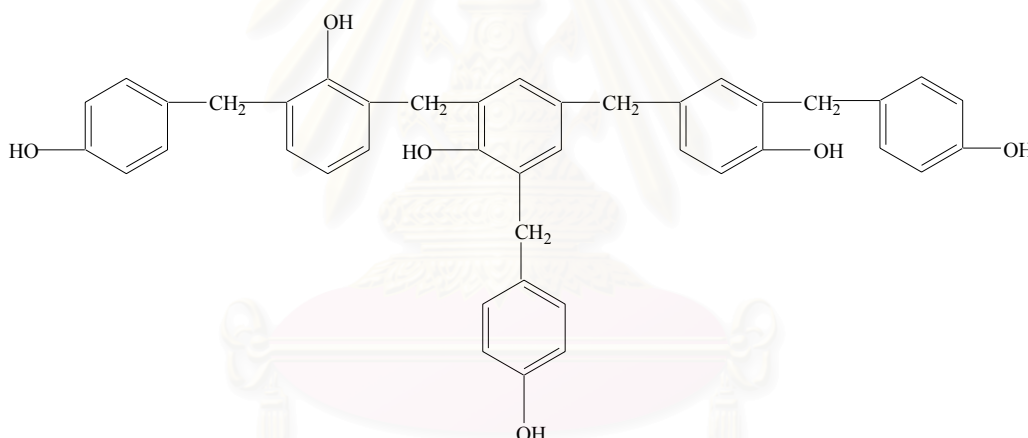


Scheme 2.14 Formation of polynuclear phenols.

Reaction of the below type continue until all the formaldehyde has been consumed. The final products therefore consist of a complex mixture of polynuclear phenol linked by *o*- and *p*-methylene groups. The average molecular weight, which is eventually attained, is governed by the initial molar ratio of phenol and formaldehyde. The average molecular weight (M_n) of a typical commercial novolac is about 600, which corresponds to about six phenolic nuclei per chain; the number of nuclei in individual chains is typically in the range 2-13. The potentially reactive third positions in the nuclei of a novolac are deactivated and thus the chains are essentially linear, although a small amount of branching occurs. The complexity of novolacs is illustrated by the fact that for a chain of eight phenolic nuclei there are 1485 possible unbranched isomers and around 11000-branched isomers. A typical novolac chain might be represented as follows in Scheme 2.15.

The essential feature of novolac is that they represent a completed reaction and they have no ability to continue increasing in average molecular weight. The resins are therefore permanently fusible and there is no danger of gelation during production. This is in contrast to resols, which contain reactive methylol groups and are capable of cross-linking on heating. In order to convert novolacs into network polymers the addition of an auxiliary chemical cross-linking agent is necessary. Because of this requirement, the preparation of novolac is often referred to as a “two-stage” process.

In conclusion, it is noted that novolacs can be prepared using mildly acidic catalysts such as zinc acetate. The resulting products have a high proportion of o-o'-links and are commonly called “high-ortho novolacs”. Such novolacs are more reactive than the normal resins and are sometimes preferred.



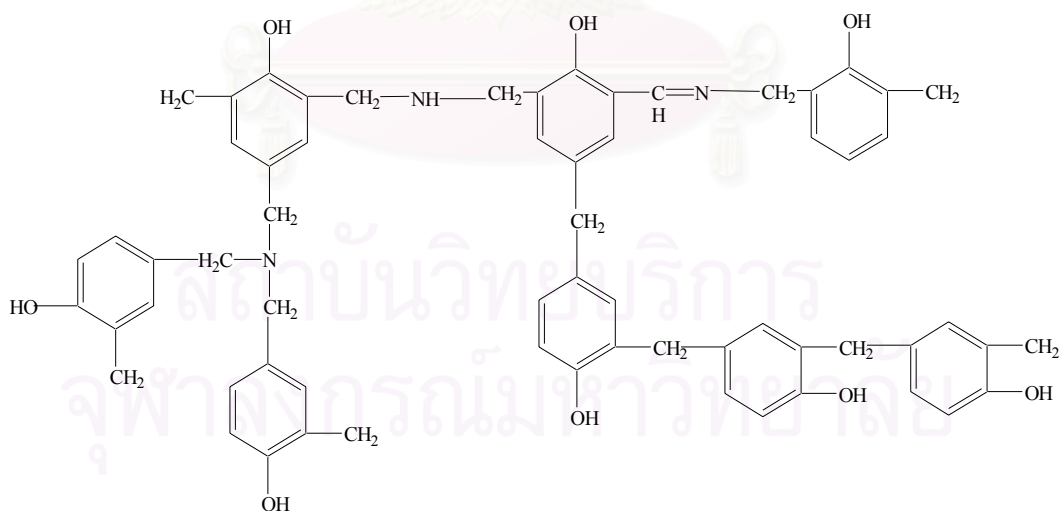
Scheme 2.15 A typical novolac resin.

2.3.4.2 Cross-Linking of Novolac Resin

As noted previously, the conversion of novolacs into network polymers can be accomplished only after the addition of a cross-linking agent. Although novolacs can be cross-linked by reaction with additional formaldehyde or with paraformaldehyde, hexamethylenetetramine is almost invariably used for this purpose. The mechanism of the curing process is not fully understood. The primary reaction between a novolac and hexamethylenetetramine (which in a typical commercial moulding powder is

present to the extent of only about 12 % on the weight of resin) leads to a complex structure containing secondary and tertiary amine links. On further heating most of these links break down to give methylene links and the resulting product has only small nitrogen content. Some azomethine links may be formed and may account for the characteristic brown colour of the cured material. A study of the novolac-hexamethylenetetramine reaction by differential thermal analysis and thermogravimetric analysis supports the view that the cross-linking reaction proceeds through dibenzylamines.

To summarize, it may be said that the network polymer obtained from a hexamethylenetetramine-cured novolac is composed of phenolic nuclei joined mainly by methylene groups with small numbers of various nitrogen-containing links. The possible structure of such a network might be represented as follow in Scheme 2.16. It is to be noted that the relative amounts of the various linkages shown above are not intended to have any quantitative significance. Thus the network polymer obtained from the novolac-hexamethylenetetramine reaction has a structure, which is predominantly similar to that of the network polymer derived from resol.



Scheme 2.16 Possible structure of network novolac resin.

2.4 Literature Reviews

Martinez-Boza *et al.* [20] studied the rheological characterization of model synthetic binders, and the influence of polymer (SBS) concentration exerts on their viscous and viscoelastic properties over an intermediate range of temperature. Their rheological characteristics were compared with those shown by unmodified bitumens, a polymer-modified (SBS) bitumen, and a commercial synthetic binder. The compositions of the two model binders studied are shown in Table 2.5.

Table 2.5 Compositions of the products used in the formulation of the synthetic binder samples studied.

Component	S1	S2
Oil (wt%)	45.9	33.3
Resin (wt%)	45.0	60.0
SBS (wt%)	9.1	6.6

They summarized that the synthetic binder with the highest resin concentration and therefore, lower polymer content (sample S2) and the unmodified bitumen present a quite similar higher thermal susceptibility. On the other hand, the system having high polymer concentration (sample S1) shown much lower thermal susceptibility in a temperature range between 278 and 308 K. A further increase in temperature produces a dramatic decrease in viscosity because SBS molecules are released from the rubbery network, and consequently, a continuous resin-rich phase develops.

Herrington *et al.* [21] studied the rheological properties of roading bitumens, modified through reaction (6 h, 150 °C) with maleic anhydride (MAH), succinic anhydride (SAH) and various straight chain dicarboxylic acids under various conditions. Bitumen-MAH reaction products were found to have reduced temperature sensitivity (in term of the ratio of the complex shear modulus (G^*) at 5 °C to that at 50 °C) and be more elastic in character (decreased $\tan \delta$), compared to the control bitumen. When the longer chain dicarboxylic acids were also found to increase G^* and decrease $\tan \delta$, the magnitude of the effects increasing with chain length. Values

of G^*/G^*_{50} for the dicarboxylic acids were slight reduce, however, the reduction in temperature sensitivity, achieved with the long chain di-acids, was similar to that obtained with SAH, but less than that achieved with acid groups from MAH. Also, the longer chain dicarboxylic acids had no effect on the reactions.

Lu *et al.* [22] studied the effect of polymer content/structure type on viscosity characteristics of styrene-butadiene-styrene (SBS) polymer modified bitumens. Results indicated that SBS polymer were not inert additives. In addition, an increase in kinematic and dynamic viscosities of the modified bitumens was not directly proportional to polymer content; a mark viscosity increase was observed when the polymer content increased from 3 to 6 % by weight of the blend. The base bitumens and modified bitumens containing 3 % SBS were observed to be essentially shear rate independent, while those containing 6 or 9 % SBS displayed shear-thinning behaviour. Compared to the modified bitumens with linear SBS, the modification with branched SBS demonstrated a higher degree of shear-thinning behaviour. These effects were dependent on ranges of shear rate and temperature.

Chaala *et al.* [23] studied the rheological properties of standard and modified bitumen with pyrolytic carbon black at concentrations ranging from 5 wt% to 30 wt%. The temperature susceptibility of the bitumen reduced, and the loss modulus G'' and the storage modulus G' increased significantly for the mixture with 30 wt% of CBp, mainly in the high-frequency region. Softening point, temperature susceptibility of penetration and temperature susceptibility of viscosity were improved for practical application by the addition of CBp. Results indicated that pyrolytic carbon black could be used as a filler to reduce the influence of temperature on physical response characteristics of the mixtures.

Perez-Lepe *et al.* [24] studied the optimization of the mixing process conditions and their influence on the mechanical properties of straight bitumen and modified binders with a number of polymers: high-density polyethylene (HDPE), low-density polyethylene (LDPE), SBS, ethylene-propylene-diene monomer (EPDM), and their mixtures. Polymer addition to bitumen enhances the mechanical properties of the modified binder, depending on the polymer nature and mixing process. The HDPE and HDPE/EPDM-modified binders, prepared in a rotor-stator device, showed

a remarkable enhancement of the mechanical properties, as compared to those modified with LDPE, EPDM and SBS. Less promising results were usually obtained with a lab-scale mixer. These results were attributed to a more effective dispersion of the polymer with the rotor-stator device, which would favour the generation of polymer-rich microphase. The interactions among them may become sufficiently strong, yielding a plateau region in the mechanical spectrum. Blends of polyethylene and EPDM showed that the major component in the polymer blend mainly determinates the rheological behaviour of the binder, being the influence on the rheological behaviour of the interactions among the molecules of EPDM and LDPE less important than the interactions among the molecules of EPDM and HDPE.

Kamiya *et al.* [25] studied compatibility role of styrene-butadiene-styrene triblock copolymer in asphalt. Results indicated that maltene, the soluble fraction extracted from asphalt by *n*-heptane, interacted preferentially with the polybutadiene unit (PB) of SBS, whereas asphaltene, insoluble fraction, predominantly with the polystyrene (PS) unit from DSC measurement. The components of asphaltene and maltene partially interacted with specific units of SBS, so that emulsifying effects of SBS resulted in phase inversion. Rheological and mechanical measurements demonstrated that viscosity, penetration and tensile strength of the composite were enhanced even at low SBS concentration (between 5-10 %).

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Asphalt Cement (AC 60-70) : Tipco Asphalt Public Co., Ltd.
2. Cashew Nut Shell Liquid (CNSL) : 25 Industrial Products Co., Ltd.
3. Maleic anhydride (MAH) : commercial grade
4. Maleic resin (MR) : commercial grade
5. Paraformaldehyde (PF) : Riedel
6. Formaldehyde : Lab Scan
7. Sodium hydroxide : Merck
8. Calcium hydroxide : Merck
9. Diethylenetriamine : Fluka
10. Petroleum ether : Fluka
11. Deuterated chloroform : Aldrich
12. Hexane : commercial grade
13. Methanol : commercial grade

3.2 Instruments and Apparatus

1. Infrared Spectrophotometer : Perkin Elmer, Nicolet (Impact 410)
2. Nuclear Magnetic Resonance Spectrophotometer : Bruker, ACF 200 MHz
3. Dynamic Shear Rheometer : JIKA
4. Penetration : HUMBOLDT MFG.CO, model H-1240
5. Ductility : FORMA SCIENTIFIC, model 2956
6. Toughness and Tenacity : ZWICK, model Z 010
7. Brookfield Digital Viscometer : model DV-II+
8. Thin Film Oven Test : Lindberg/ Blue M, model RS 18 A

3.3 Experimental Procedures

3.3.1 Preparation of Cardanol-Formaldehyde Resin

3.3.1.1 Preparation of Cardanol from CNSL

CNSL was decarboxylated to give cardanol in the presence of calcium hydroxide as a catalyst. Calcium hydroxide (4 g) and hexane (200 ml) as solvent were charged into a 1000 ml 2-neck round bottom flask, equipped with condenser and thermometer, containing 200 g of natural CNSL. The mixture was refluxed with stirring for 3 hours. The reaction was stopped and the mixture was cooled down. Calcium hydroxide was filtrated. After evaporation of the solvent, decarboxylated CNSL was obtained.

Decarboxylated CNSL (60 g), formaldehyde (19.4 g) and diethylenetriamine (2.57 g) were mixed in methanol (200 ml). An exothermic reaction took place after mixing the reactants. After 30 minutes, two phases were formed. The upper phase was decanted and treated with water (40 ml) followed by extraction with petroleum ether. The petroleum ether extract was distilled to recover hydrocarbon solvent. A reddish residue of cardanol (45 g, 80 % w/w) was obtained [12,13]. IR and NMR spectra of the resulting product are shown in Appendix B indicate that the carboxylic acid group was removed completely.

3.3.1.2 Synthesis of Cardanol-Formaldehyde Resin

Cardanol 200 g and formaldehyde 50 g (molar ratio of 1 mol (phenol) to 2.5 mole (formaldehyde)) were mixed together in the reaction kettle, which was equipped with a thermometer and a mechanical stirrer. A sodium hydroxide solution (2.0 g NaOH in 10 ml of water, mole NaOH/mole cardanol = 0.2) was then added. The mixture was stirred at temperature of 95 °C with agitation rate of 250 rpm for 60 minutes. The product was red-brown semi solid. IR and NMR spectra of the resulting product are shown in Appendix B.

3.3.2 Preparation of Asphalt mixture

A series of mixtures composed of asphalt and additives at different concentrations ranging from 0.5 to 10 wt %. In preparation, 800 g of the asphalt was heated to 100 – 110 °C and continuously stirred before the additives were added in small amounts up to desired concentration. Stirring was maintained until a homogeneous mix (150 °C, agitation rate 450 rpm, 5 hr) was obtained. After completion, the modified asphalt was cooled to room temperature; the mixtures were stored in metallic containers.

3.4 Physical testing

3.4.1 Penetration [26]

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

The penetration test is an empirical test used to measure the consistency of asphalt cement. The standard penetration test is shown in Figure 3.1. A container of asphalt cement is brought to the standard test temperature (25 °C) in a thermostatically controlled water bath. The sample was placed under a needle of prescribed dimensions. The needle was loaded with a 100 g weight and is allowed to penetrate the asphalt cement sample for 5 seconds. The depth of penetration was measured in units of 0.1 mm and was reported as a penetration unit.

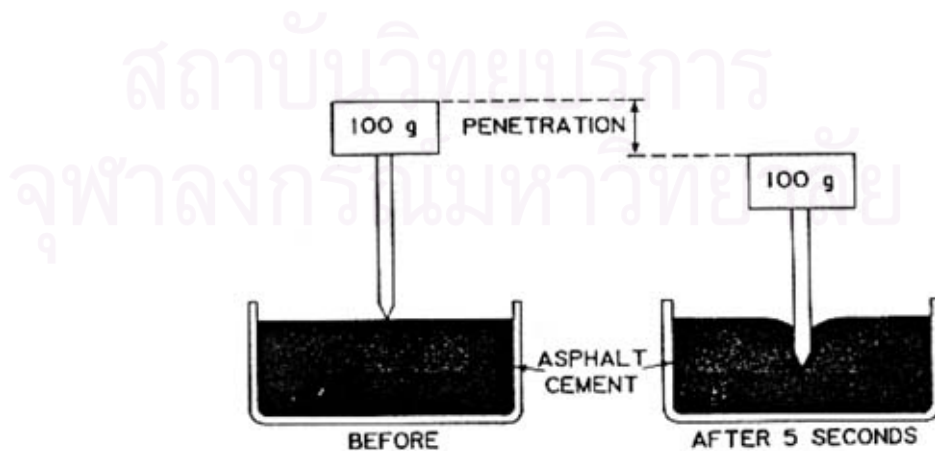


Figure 3.1 Penetration Test.

3.4.2 Softening Point [27]

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

The softening point of an asphalt cement may be defined as that temperature at which an asphalt attains a particular degree of softness under specified conditions of test. As shown in Figure 3.2, the test consists of taking a brass ring filled with asphalt cement and suspending it in a beaker filled with water. A steel ball of specified dimensions and weight was placed in the center of the sample. The bath was heated at a controlled rate of 5 °C/minute. When the asphalt cement softens, the ball and asphalt cement sink toward the bottom of the beaker. The temperature was recorded at the instant when the softened asphalt cement sank the prescribed distance and touches the bottom plate. Asphalt does not have a definite melting point, but rather it changes gradually from a harder to a softer material with increasing temperature. For this reason, melting characteristics are described as the softening point as defined by this procedure.

The condition in testing of the softening point of asphalt cement in the range from 30 to 157 °C using the ring and ball apparatus immersed in distilled water and the bath was heated at a controlled rate of 5 °C/min.

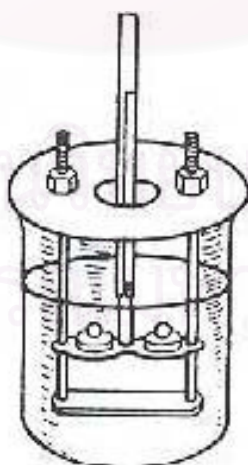


Figure 3.2 Softening Point Test.

3.4.3 Ductility [28]

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

The ductility of asphalt cement is expressed as the distance in centimeters, which a standard briquet can be elongated before breaking (Figure 3.3). The cross section of the briquette at its smaller dimension is one square centimeter. The test sample was brought to temperature in a water bath, maintained at the temperature 13 °C and 25 °C. The two ends of the sample were separated at the rate of 5 cm/minute until rupture. The water must be at the same specific gravity as the asphalt to prevent floating or sinking of the stretched sample. Salt was added to increase the specific gravity, and alcohol was added to decrease the specific gravity of the water.

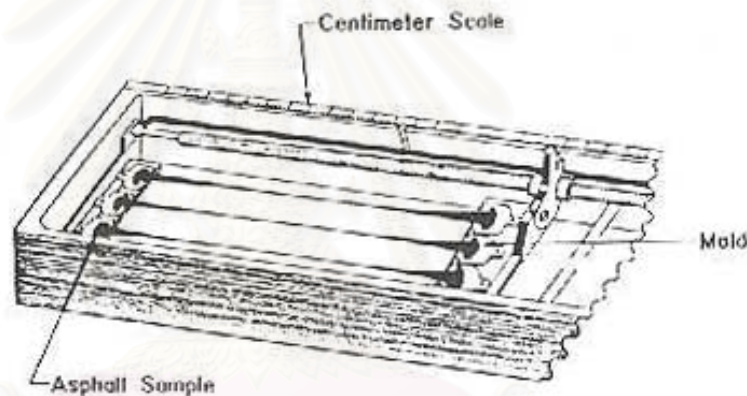


Figure 3.3 Mold for Ductility Test Specimen.

3.4.4 Viscosity [29]

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

The Brookfield Thermosel Viscometer can be used to measure the viscosity of asphalt at elevated temperatures. The torque on a spindle rotating in a special thermostatically controlled sample holder containing a small sample of asphalt is used to measure the relative resistance to rotation. A factor is applied to the torque dial reading to yield the viscosity of the asphalt in centipoises (cP). The condition used in testing are shown as following:

Temperature	:	135 °C and 165 °C
Spindle number	:	21
Shear rate	:	18.6 s

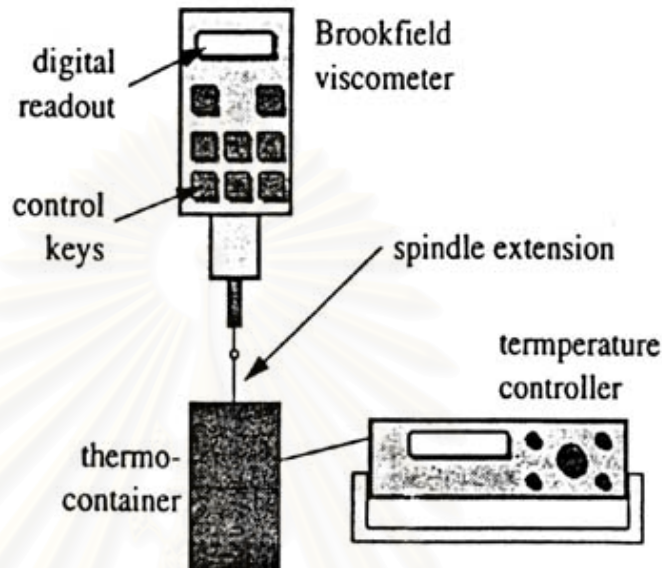


Figure 3.4 Rotational Viscometer.

3.4.5 Toughness and Tenacity [30]

(ESM NE 31/91 Determination of Toughness and Tenacity of bituminous materials)

The present standard covers the determination of the tensile properties of bituminous mixtures and in particular of polymer modified bitumens. In Figure 3.4, there are typical curves, for normal and polymer modified bitumens. In analyzing the curve a tangent line is extended from the right side of the force vs. elongation curve as it decreases from its maximum value. Determine the following:

- Toughness: total area under the curve.
- Tenacity: area under the curve to the right of the tangent line.

The conditions of toughness and tenacity are the following temperature of 25 °C, speed of testing 500 mm min⁻¹.

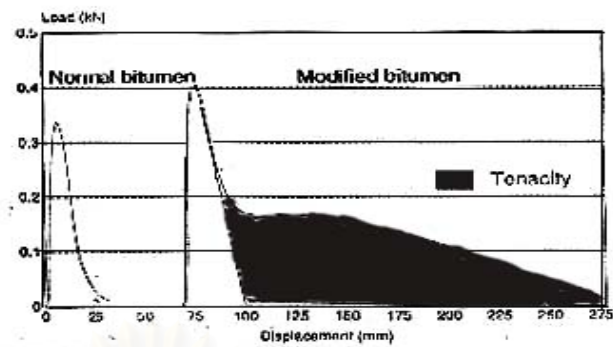


Figure 3.5 Toughness and Tenacity.

3.4.6 Flash Point [31]

(ASTM D92 Standard Test Method for Flash and Fire Points by Cleveland Open Cup)

The flash point of an asphaltic product can be defined as the temperature to which it must be heated in order to give off sufficient vapor to form an inflammable mixture with air. The Cleveland method involves heating the asphalt in a brass cup at the rate of 10 °F /minute until a test flame causes a flash to appear at any point on the surface of the material being tested. The flash point was an indication of fire hazard although it was frequently used to indicate whether a given product has been contaminated with materials of lower flash point.

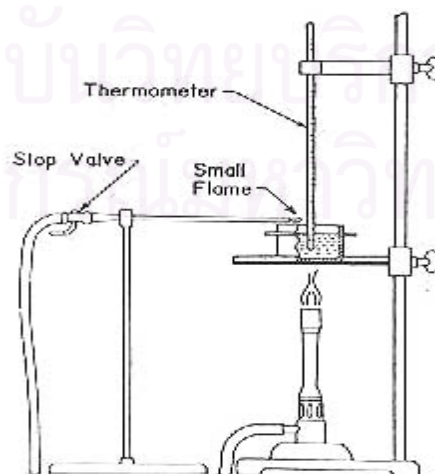


Figure 3.6 Cleveland Open Cup Apparatus.

3.4.7 Thin Film Oven Test [32]

(ASTM D1754 Standard Test Method for Effects of Heat and Air on Asphaltic Materials (Thin-Film-Oven Test))

This test method covers the determination of the effects of heat and air on a film of semisolid asphaltic materials. The effects of this treatment were determined from measurements of selected asphalt properties before and after the test. Thin Film Oven Test shown in Figure 3.7

The thin film oven test was conducted by placing a 50 g sample of asphalt cement in a cylindrical flat-bottom pan. The asphalt cement layer in the pan was about 3 mm deep. The pan containing the asphalt cement sample was transferred to a shelf in a ventilated oven maintained at 163 °C (Figure 3.7). The shelf rotates at 5 to 6 revolutions per minute. The sample was kept in the oven for 6 hours, and then transferred to a suitable container for measuring softening point, penetration, mass, and ductility of the aged asphalt cement.

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

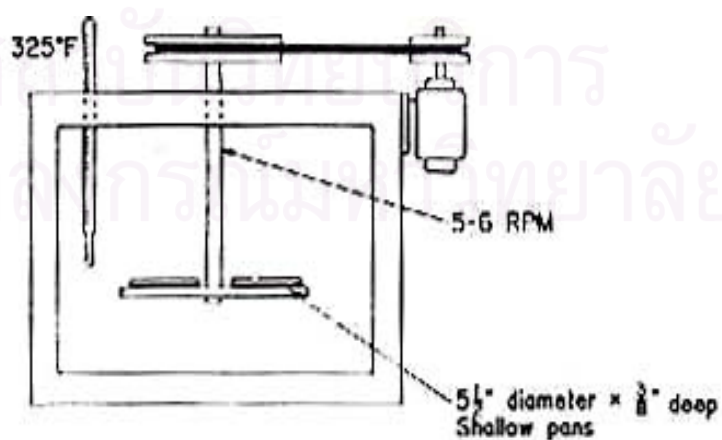


Figure 3.7 Thin Film Oven Test.

3.4.8 Dynamic Shear Rheology [33]

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

The dynamic shear rheometer (DSR) is used to characterize the viscous and elastic behavior of asphalt mixtures at high and intermediate service temperature. The DSR measurements the complex shear modulus (G^*) and phase angle (δ) of asphalt mixture at the desired temperature and frequency of loading. Complex shear modulus (G^*) can be considered as the total resistance of the mixture to deformation when repeatedly sheared. Complex shear modulus (G^*) consists of two components: (a) storage modulus G' or the elastic part, and (b) loss modulus G'' or the viscous part. The parameter phase angle (δ) is used as a measure of the relative elasticity of the mixtures studied and the complex shear modulus (G^*) is used as a measure of the stiffness or resistance of asphalt mixture to deformation under load. Thus, the lower the value of δ ($\delta = 0^\circ$), the more elastic the system and the lower G^* ($\delta = 90^\circ$), the lower the stiffness of the system.

The Superpave specification defines and places requirements on a rutting factor, $G^*/\sin \delta$, which represents a measure of the high temperature stiffness or rutting resistance of the asphalt binder. To minimize rutting, $G^*/\sin \delta$ must be a minimum of 1.00 kPa for the original asphalt binder.

Like permanent deformation, G^* and δ are also used in the Superpave binder specification to help control the fatigue of asphalt pavements. Since fatigue generally occurs at low to moderate pavement temperatures after the pavement has been in service for a period of time. The fatigue cracking factor is $G^* \sin \delta$. The Superpave binder specification has a maximum value of 5000 kPa for $G^* \sin \delta$.

The test procedure was given in AASHTO TP5. As shown in Figure 3.8, the asphalt mixture sample was sandwiched between a fixed plate and an oscillating plate. At the test temperature ranging from 25 to 70 °C, measurements were carried out using 8 mm diameter parallel stainless steel plates with a 2 mm gap at a frequency of 10 rad s⁻¹ (1.5 Hz). Test temperatures were 25, 30, 35 and 40 °C. And using 25 mm diameter parallel stainless steel plates with a 1 mm gap at a frequency of 10 rad s⁻¹

(1.5 Hz), test temperature were 46, 52, 58, 64 and 70 °C. Sample was annealed at 90 °C for 30 min before analysis.

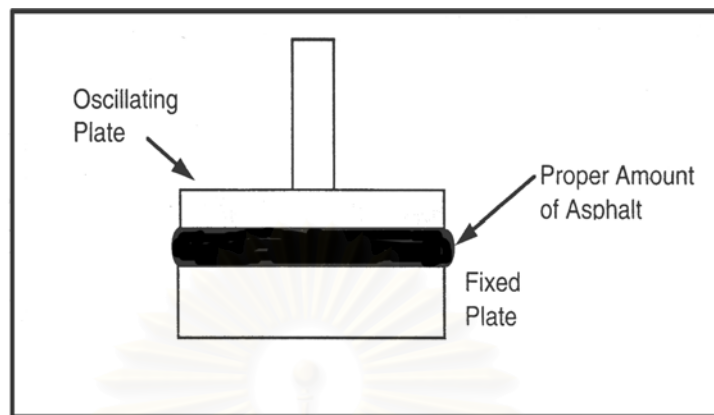


Figure 3.8 Asphalt Sample Configurations in DSR.

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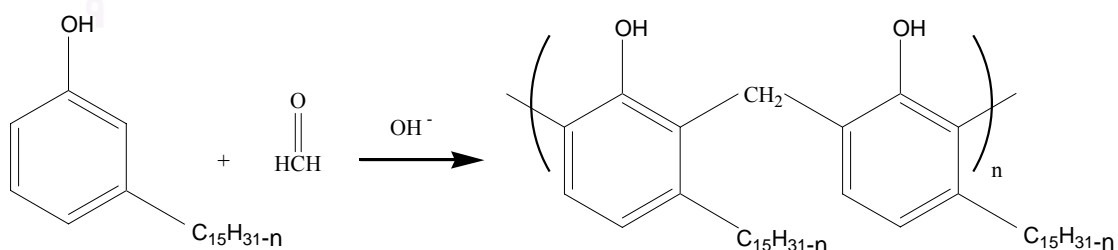
CHAPTER IV

RESULTS AND DISCUSSION

The modification of the asphalt was carried out in two steps: In the first step, cardanol-formaldehyde resin (CF) was synthesized from cardanol and formaldehyde in the presence of sodium hydroxide, and then the CF product was characterized by infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR). In the second step, the asphalt mixture was prepared by directly mixing the CF in a reactor kettle. Effects of various concentrations of cardanol-formaldehyde resin, maleic anhydride, maleicresin, and paraformaldehyde, have been taken into account. Physical properties were investigated to determine optimum ingredients and conditions for preparation of proper properties of the modified asphalt.

4.1 Preparation and Characterization of Cardanol-Formaldehyde Resin (CF)

Cardanol-formaldehyde resin (CF) was obtained from a reaction between cardanol and formaldehyde with a mole ratio of 1:2.5 in the presence of NaOH as the catalyst. The reaction was carried out at temperature of 95 °C with agitation rate of 250 rpm for 60 minutes. The product was red-brown solid. IR and NMR were used for cardanol-formaldehyde resin characterization. The condensation reaction was represented as the following:



Scheme 4.1 Formation of cardanol-formaldehyde resin.

4.1.1 Infrared Spectra

Perkin Elmer, Nicolet (Impact 410) infrared spectrophotometer was used for characterization of cardanol and CF. The IR spectra of cardanol and CF are given in Appendix A. The IR spectrum of cardanol was similar to that of CF resin. The broad band at the 3342 cm^{-1} indicates the presence of the hydroxyl group. The peak at 3001 cm^{-1} is due to =CH- stretching of phenol. The peaks between 2843 cm^{-1} and 2935 cm^{-1} is belonged to -CH- stretching of alkyl side chain and -CH- stretching of aromatic, respectively. The peak at 1591 cm^{-1} and 1449 cm^{-1} is due to the vibration of the aromatic -C=C- linkage. The peak at 1259 cm^{-1} is due to -CO- stretching of phenol and the peak at 1150 cm^{-1} showed -CO- stretching of tertiary alcohol. For CF resin, the intensity of the peak at 1150 cm^{-1} is stronger than cardanol.

4.1.2 Nuclear Magnetic Resonance Spectra

Bruker, ACF 200 MHz nuclear magnetic resonance spectrophotometer is used for characterization of cardanol and CF. The ^1H -NMR spectrum of resin in CDCl_3 was determined. The NMR spectrum showed the presence of aromatic protons and methyl protons. Aromatic protons appeared as a multiplet in the range of 6.64-7.25 ppm. Olefinic protons appeared in the range of 4.81-5.43 ppm. Methylene protons appeared in the range of 0.89-2.79 ppm. The peak at 4.35 ppm is due to methylene proton between aromatic rings. The ^1H -NMR spectrum of cardanol in CDCl_3 also showed the presence of aromatic protons and methyl protons similar to those of the CF, which all of chemical shifts referred to the protons in the benzene ring and alkyl side chain. Unlike CF, the spectrum of cardanol showed the absence of the peak at 4.35. Thus, the formation of CF is confirmed by the appearance of the peak at 4.35 ppm. The ^1H -NMR spectra of cardanol and CF are shown in Appendix A.

4.2 Preparation of asphalt mixture

The asphalt mixture was prepared from asphalt and additives such as cardanol-formaldehyde resin (CF), maleic resin (MR), paraformaldehyde (PF), and maleic anhydride (MA). A reaction temperature of 150 °C was used maintained for 5 hours. The additive contents used were 0.5, 1, 2, 4, 6, 8, and 10 % by weight of asphalt. Physical properties of the asphalt mixture were investigated by penetration, softening point, ductility, toughness and tenacity, viscosity, Thin Film Oven test, and dynamic shear rheometry measurement.

4.3 Effect of CF, MA, MR and PF Concentration on Physical Properties.

The CF-, MA-, MR- and PF-modified asphalt were prepared from asphalt and additives at concentration ranging from 0.5 % to 10 % by weight of asphalt at 150 °C for 5 hours. The details of all data are shown in Appendix B.

4.3.1 Penetration

The penetration test is used as a measure of consistency of asphalt expressed as the distance in tenths of a millimeter that a standard needle vertically penetrates a sample of the material under a load of 100 g within 5 sec at 25 °C. The penetrability of additives modified asphalts (0.5%-10% of CF, MA, MR and PF) is shown in Figures 4.1-4.4. It is seen that the penetrability of CF-modified asphalt slightly decreases with increasing concentration of CF, compared to the asphalt cement (AC). On the other hand, asphalt modified with MA, MR and PF dramatically decrease with increasing concentration of additives. A decrease in penetrability indicates that the consistency of asphalt increases as a result of interaction between additives and components of asphalt. A lower penetration is good to resist deformation in pavement. The details of penetration are shown in Appendix B.

Figures 4.5-4.8 show the percentage of retained penetration in thin film oven test (TFOT) at 165 °C for 6 hours. The extent of age hardening can be quantified in terms of penetration (% retained penetration) as follow:

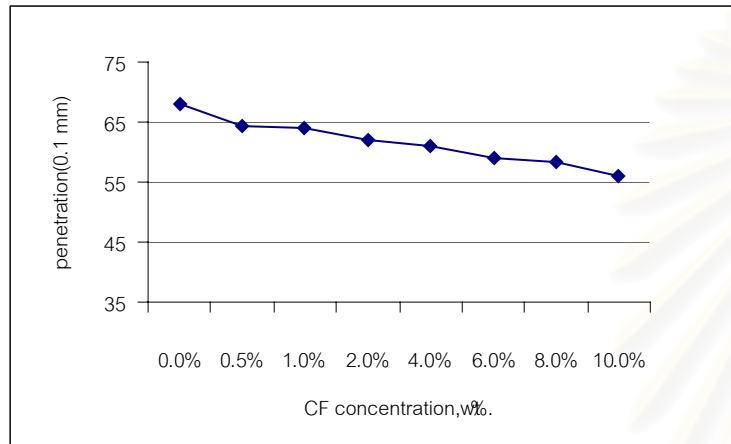


Figure 4.1 Effect of CF concentration on penetration.

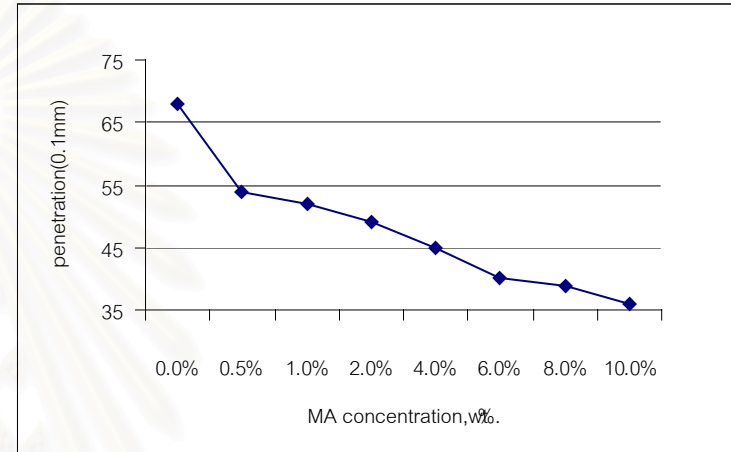


Figure 4.2 Effect of MA concentration on penetration.

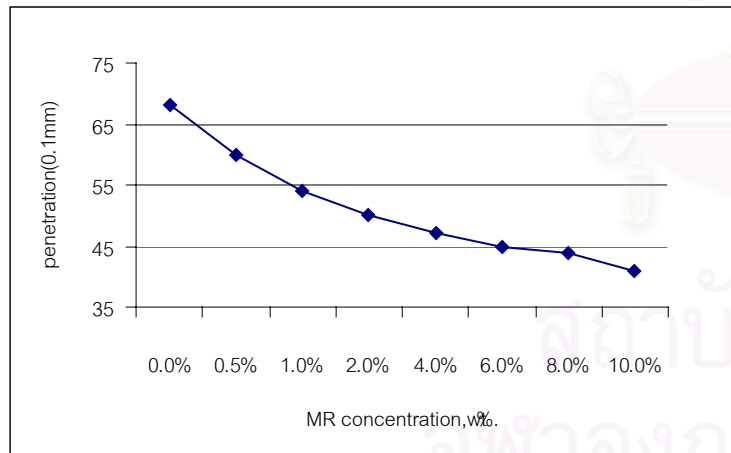


Figure 4.3 Effect of MR concentration on penetration.

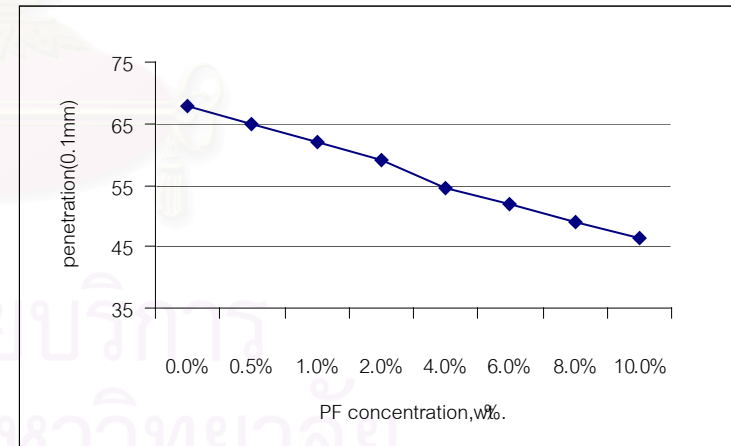


Figure 4.4 Effect of PF concentration on penetration.

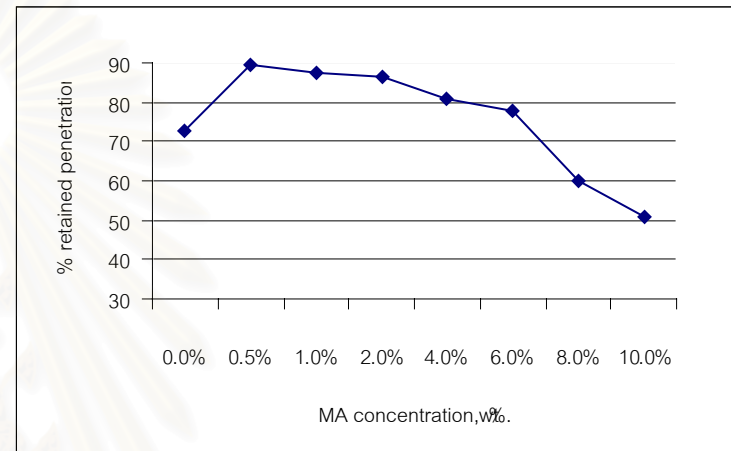
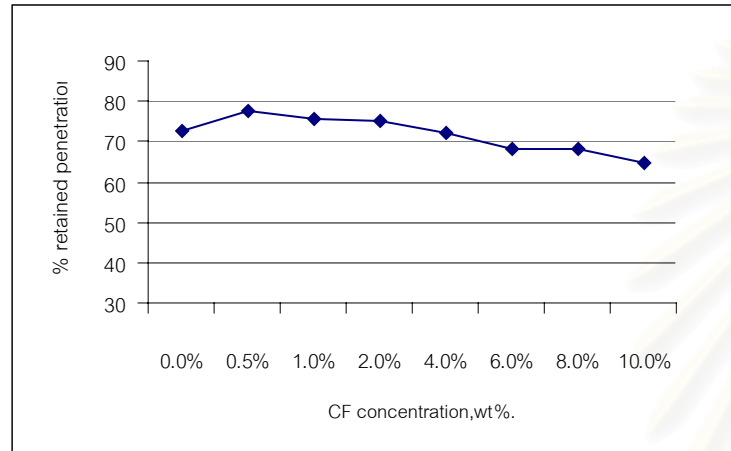


Figure 4.5 Effect of CF concentration on the % retained penetration. **Figure 4.6** Effect of MA concentration on the % of retained penetration.

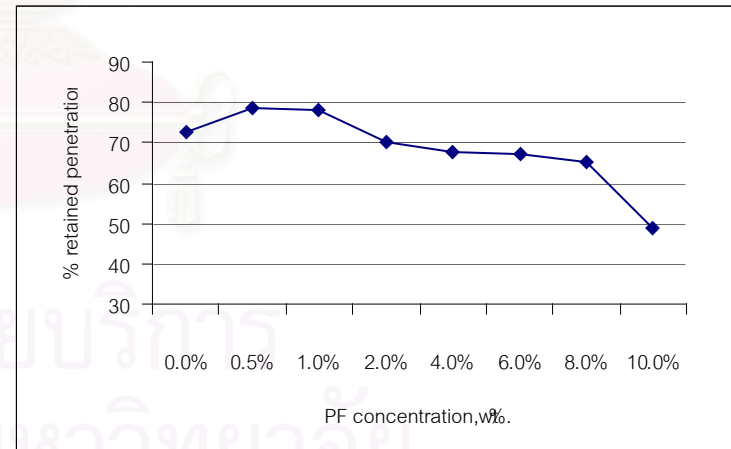
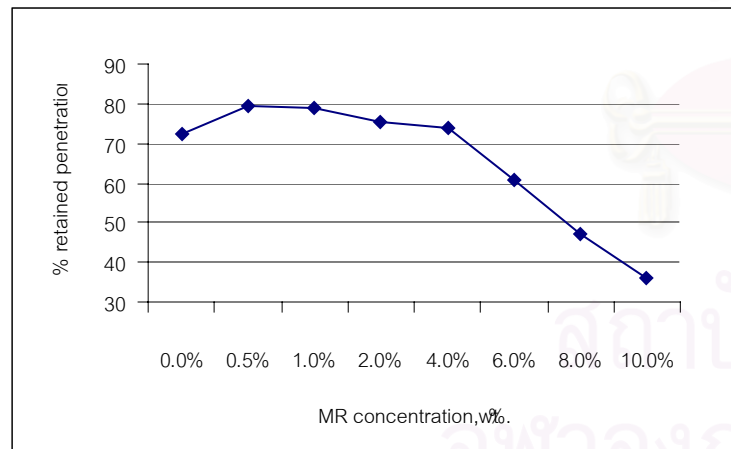


Figure 4.7 Effect of MR concentration on the % retained penetration. **Figure 4.8** Effect of PF concentration on the % of retained penetration.

$$\% \text{ Retained Penetration} = \frac{\text{Penetration of aged asphalt}}{\text{Penetration of original asphalt}} * 100$$

The percentage of retained penetration is used to evaluate relative aging of asphalt cements of different grades and sources. Figure 4.5 shows the percentage of retained penetration decreases when increasing concentration of CF. These results can be explained that when CF-modified asphalt is heated in TFOT, there is a crosslinking occurred. However, the asphalt containing MA, MR and PF more than 4 wt% has the percentage of retained penetration lower than does AC. A significant decrease in the retained penetration percentage indicates that additives modified asphalt increases stiffness. The details of the percentage of retained penetration are shown in Appendix B.

4.3.2 Softening Point

The softening points of the additives modified asphalt are shown in Figures 4.9-4.12. The softening point was found increases with increasing concentration of additives. This indicates that additives modified asphalts reduce temperature susceptibility. It gradually becomes softer and less viscous as temperature rises. This could be explained in terms of ratio of the maltene and asphaltene contents in the asphalt. When the maltene oil content of the asphalt is high, the molecules of the asphalt components move freely and consequently, the system is fluid. The added additives adsorb a certain amount of maltene molecule, which in turn reduces the asphalt fluidity [23]. The details of softening point are shown in Appendix B.

4.3.3 Penetration Index (PI)

The relative temperature susceptibility of asphalt is often quantified using the penetration index, which is a relationship between values of penetration and softening point. The empirical expression in terms of PI as below [7,21]:

$$PI = \frac{20U - 300V}{U + 30V} \quad \text{where } U = (\log 4) * (T_{RB} - T_P)$$

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

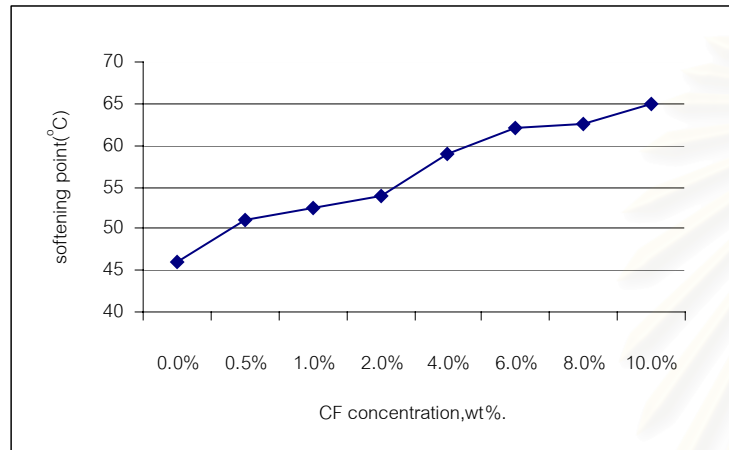


Figure 4.9 Effect of CF concentration on softening point.

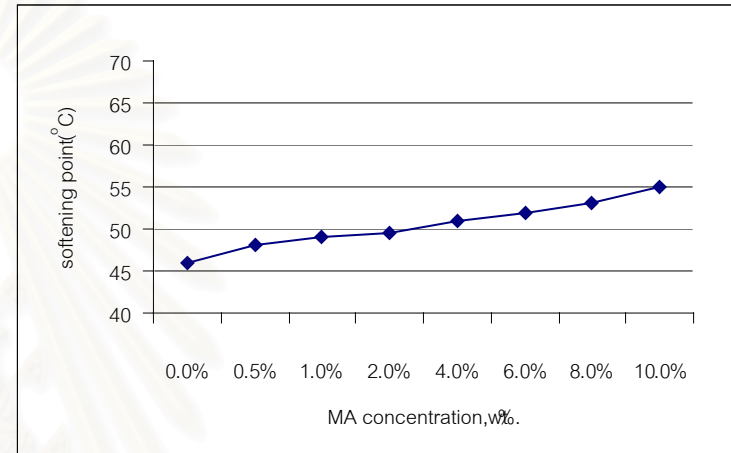


Figure 4.10 Effect of MA concentration on softening point.

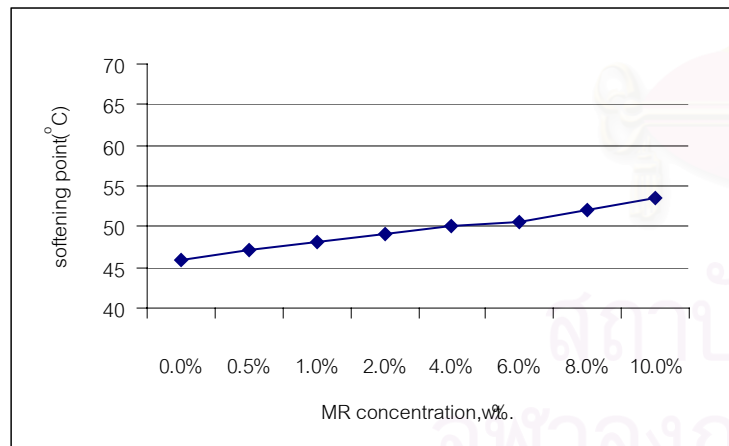


Figure 4.11 Effect of MR concentration on softening point.

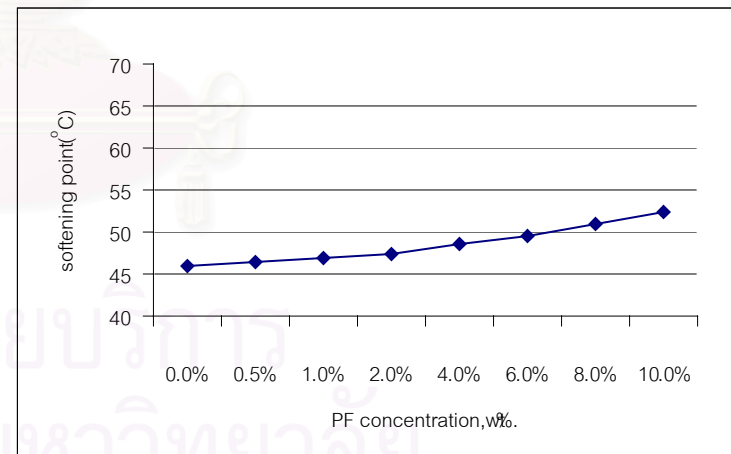


Figure 4.12 Effect of PF concentration on softening point.

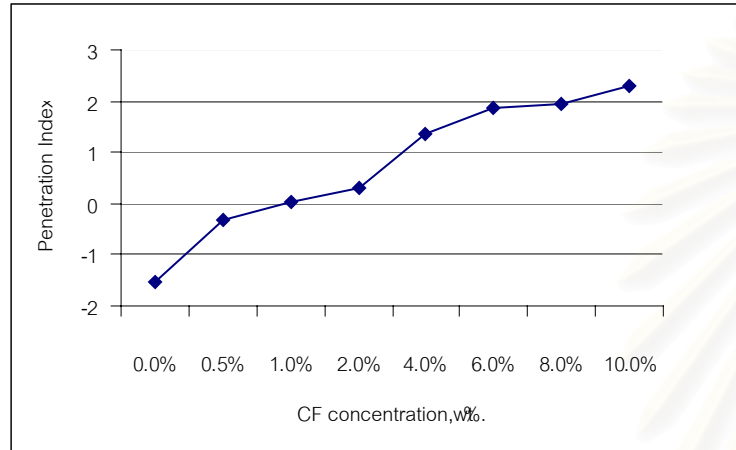


Figure 4.13 Effect of CF concentration on penetration index.

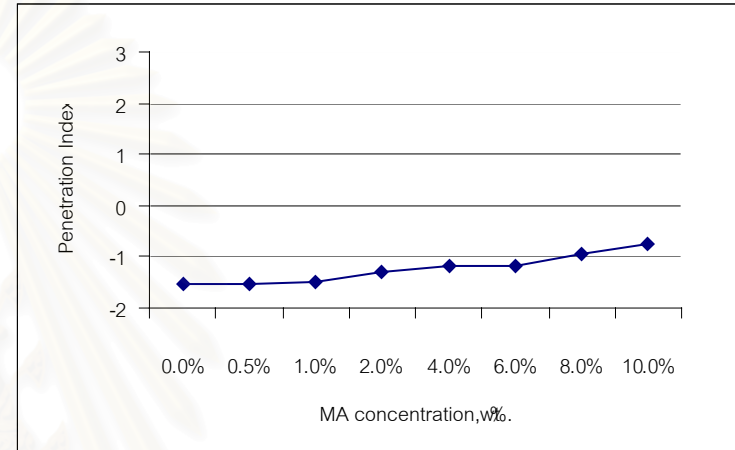


Figure 4.14 Effect of MA concentration on penetration index.

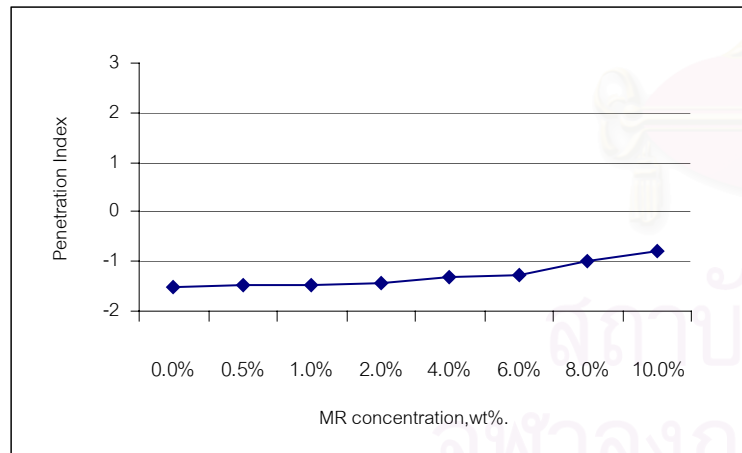


Figure 4.15 Effect of MR concentration on penetration index.

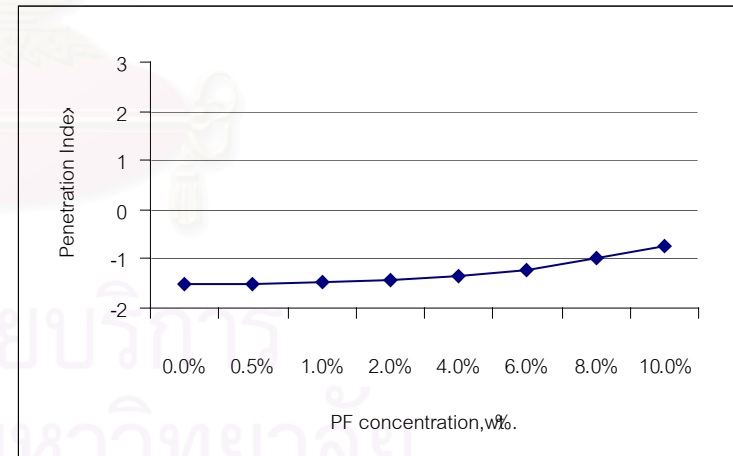


Figure 4.16 Effect of PF concentration on penetration index.

T_{RB} = The value of softening point ($^{\circ}\text{C}$)

T_p = The temperature of test penetration ($^{\circ}\text{C}$)

P_T = The value of penetration at T_p

The lower the PI value of an asphalt cement, the higher its temperature susceptibility. Most paving asphalt cements have a penetration index between +1 and -1. Asphalt cements with PI -2 are highly temperature susceptible, usually exhibit brittleness at low temperatures, and are very prone to transverse cracking in cold climates [4].

The PI of CF-modified asphalt is given in Figure 4.13. CF has significantly improved temperature susceptibility compared with the AC, even at a 0.5 % level. PI of the CF-modified asphalt increases with increasing concentration of CF indicates that the reduced temperature susceptibility typically shows a rubbery elastic behavior. PI for MA-, MR- and PF-modified asphalt is given in Figures 4.14-4.16, respectively. It indicates that the value of penetration index increases when increasing concentration of additives. But the value of penetration index of MA-, MR- and PF-modified asphalt lower than zero indicates that it's the highly temperature susceptibility. The details of penetration index are shown in Appendix B.

4.3.4 Ductility

The ductility of asphalt is measured by the distance to which it will elongate before breaking when two ends of a briquet specimen of the material. The values of ductility of CF-modified asphalt at 13 $^{\circ}\text{C}$ and 25 $^{\circ}\text{C}$, before and after heated with TFOT, are shown in Figure 4.17. At 13 $^{\circ}\text{C}$, the value of ductility slightly decreases with an increase of CF concentration. The TFOT is an aging model of asphalt cement; it is found that value ductility after heated is less than starting temperature due to a progressive increase in the brittleness and hardness of binder characteristics of asphalt cement. At 25 $^{\circ}\text{C}$, although CF concentration is increased, the value of ductility of CF-modified asphalt both before and after with thin film oven are more than 150 cm. This indicates that CF-modified asphalt does not has cracking behavior. The value of ductility for MA-, MR- and PF-modified asphalt is given in Figures 4.18-4.20, respective. At 13 $^{\circ}\text{C}$, the value of ductility of additives modified asphalt both before

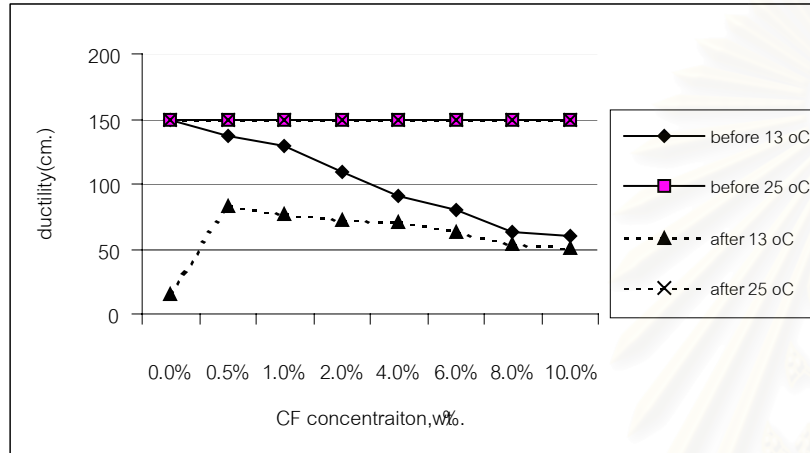


Figure 4.17 Ductility of CF before and after heating with TFOT.

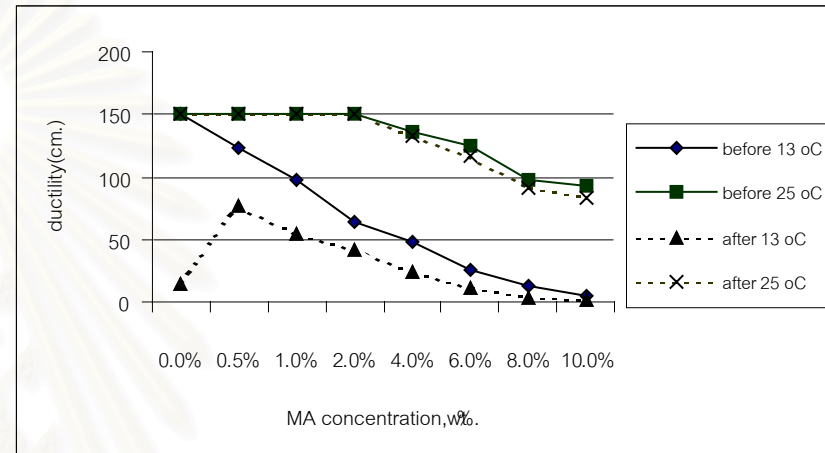


Figure 4.18 Ductility of MA before and after heating with TFOT.

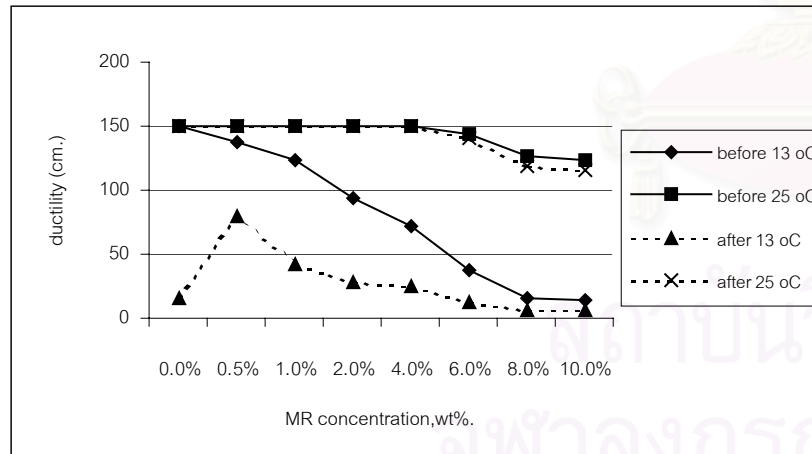


Figure 4.19 Ductility of MR before and after heating with TFOT.

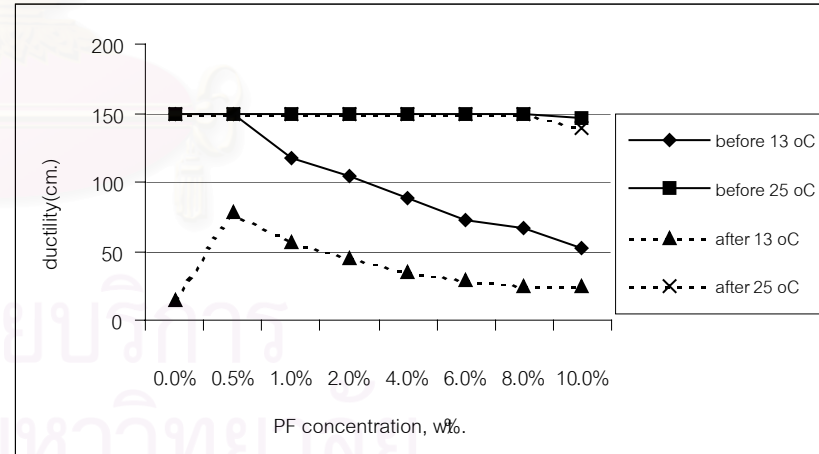


Figure 4.20 Ductility of PF before and after heating with TFOT.

and after heating with TFOT decreases when an increasing concentration of additives. If the MA, MR and PF concentrations are higher than 4 wt%, brittle can be occurred. However, a decrease of ductility of additives modified asphalt did not result in breaking at the temperature was used of 25 °C. The details of ductility are shown in Appendix B.

4.3.5 Toughness and Tenacity

Figures 4.21-4.24 show the toughness and tenacity of CF-, MA-, MR- and PF-modified asphalt at 25 °C. The toughness indicates energy required to completely breaking the specimen under stress and the tenacity indicated work performed from the maximum load point until breaking of the sample. The toughness and tenacity increase when additives concentration increases. This indicated that energy required completing breaking specimen increases when additives concentration increased. The details of toughness and tenacity are shown in Appendix B.

4.3.6 Brookfield viscosity

Figures 4.25-4.28 show the Brookfield viscosity of CF-, MA-, MR- and PF-modified asphalt. Increasing in viscosity of additives modified asphalt is due to a decrease of additives concentration. A somewhat marked change is observed when the additives content exceed 0.5 wt%. Results suggest that CF, MA, MR and PF be not an inert additive, i.e. certain molecular interactions may exist among additives molecules and asphalt components. During mixing, hot asphalt may penetrate the polymer particles; the polymer become solvated and/or swollen [22], depending on the asphalt composition. Under the influence of the shear action of mixer, the swollen polymer becomes mobile and disperses in the asphalt. A relatively small increase in the viscosity of the modified asphalt containing 0.5 wt% is probably attributable to weak interaction between polymer particles. The details of viscosity are shown in Appendix B.

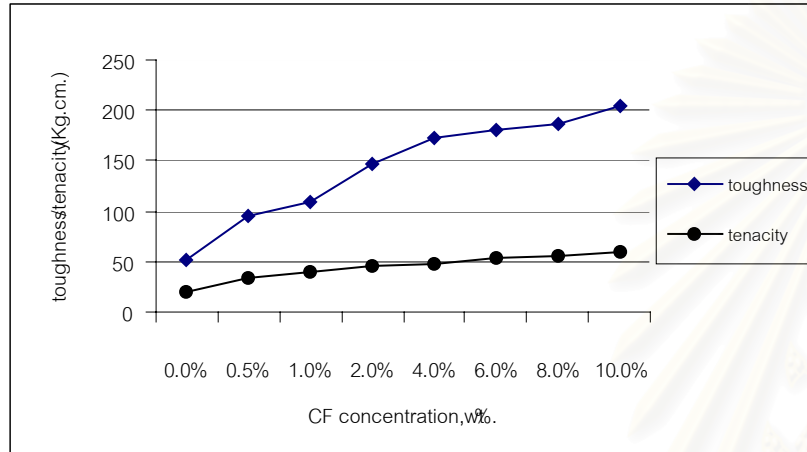


Figure 4.21 Effect of CF concentration on toughness and tenacity.

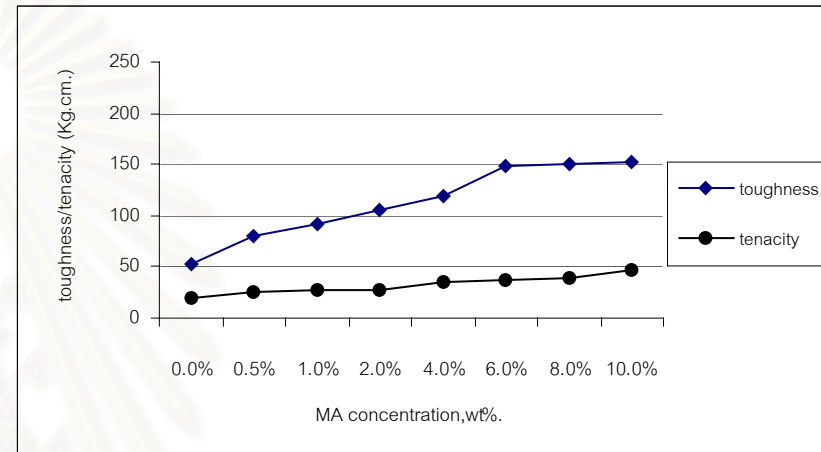


Figure 4.22 Effect of MA concentration on toughness and tenacity.

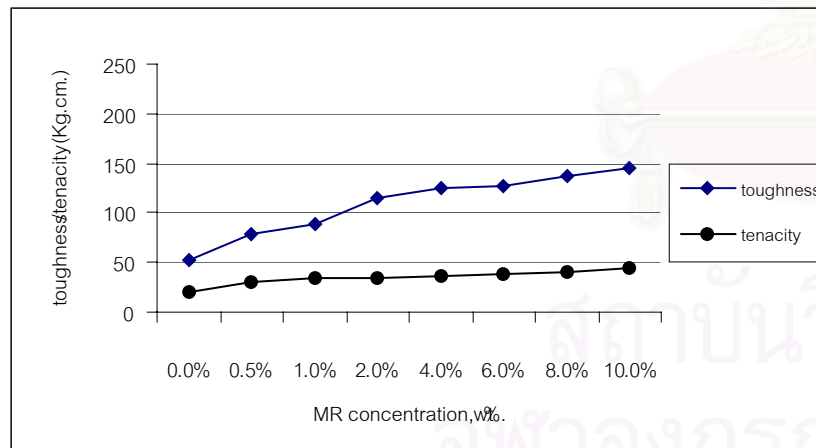


Figure 4.23 Effect of MR concentration on toughness and tenacity.

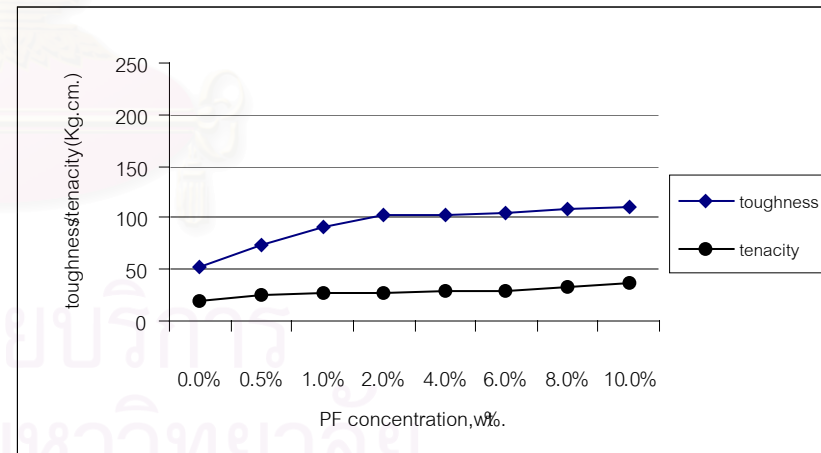


Figure 4.24 Effect of PF concentration on toughness and tenacity.

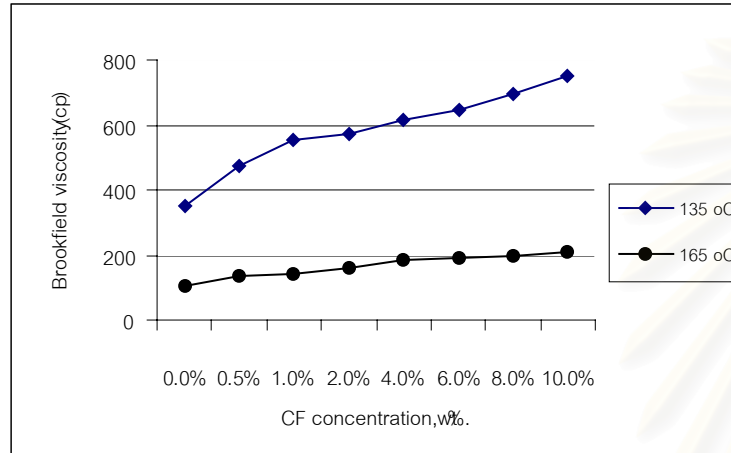


Figure 4.25 Effect of CF concentration on Brookfield viscosity.

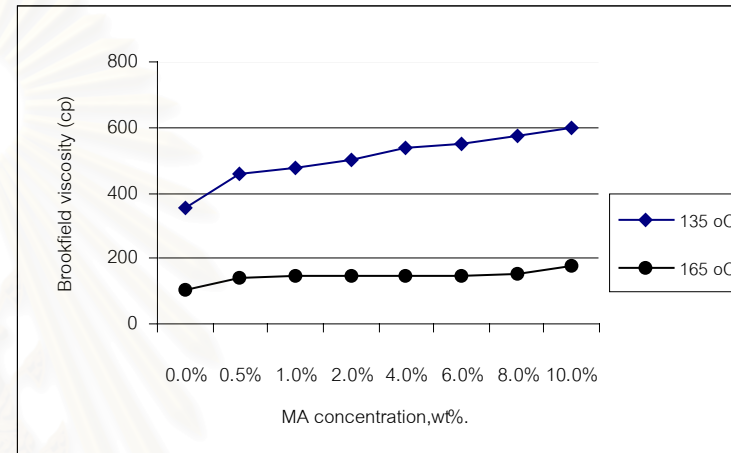


Figure 4.26 Effect of MA concentration on Brookfield viscosity.

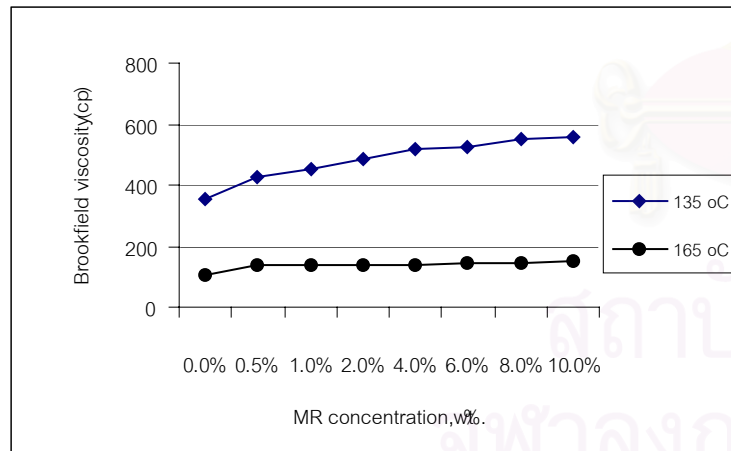


Figure 4.27 Effect of MR concentration on Brookfield viscosity.

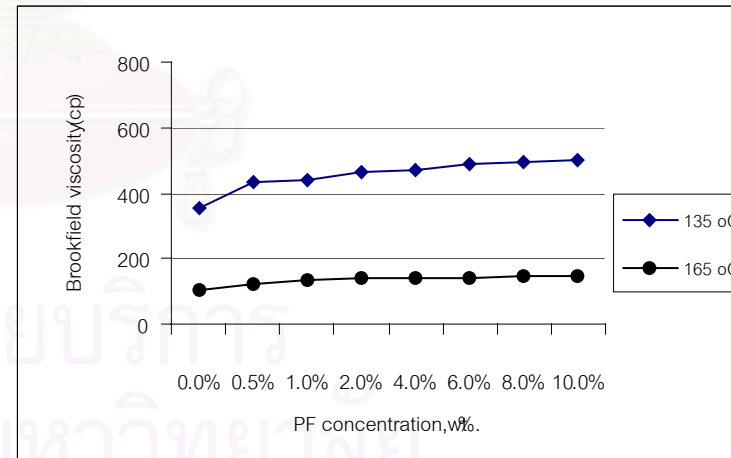


Figure 4.28 Effect of PF concentration on Brookfield viscosity.

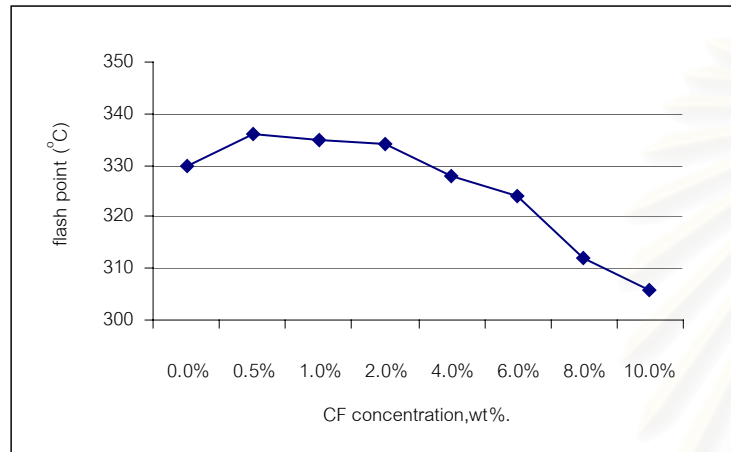


Figure 4.29 Effect of CF concentration on flash point.

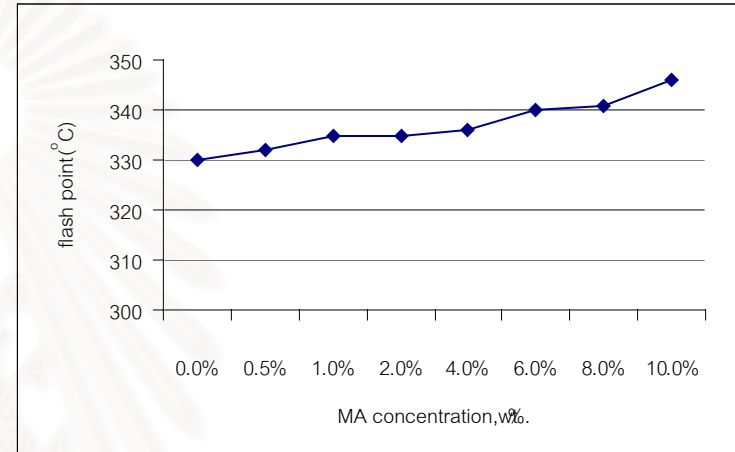


Figure 4.30 Effect of MA concentration on flash point.

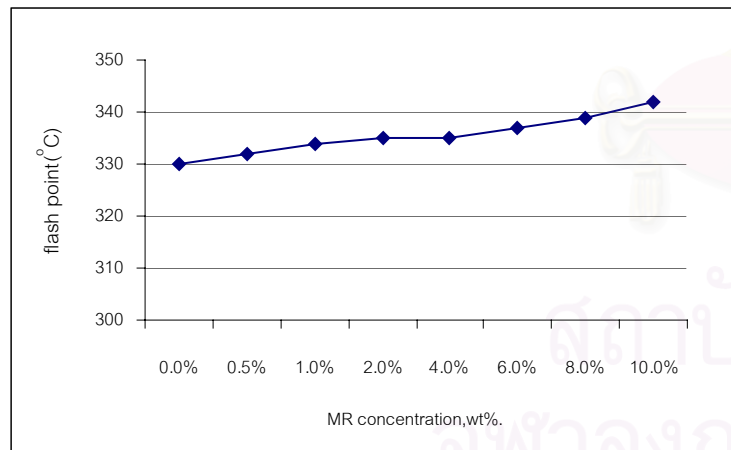


Figure 4.31 Effect of MR concentration on flash point.

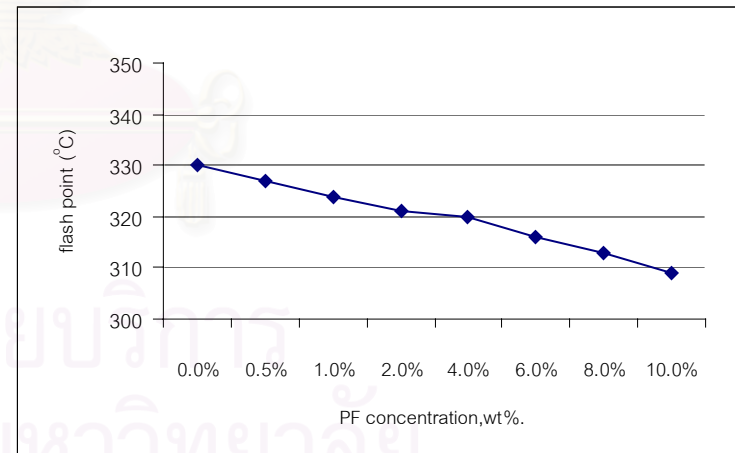


Figure 4.32 Effect of PF concentration on flash point.

4.3.7 Flash Point

Figures 4.29-4.32 show the flash points of CF-, MA-, MR- and PF-modified asphalt. The flash points of CF- and PF-modified asphalt slightly decreased with increasing CF and PF concentration and the flash point of MA- and MR-modified asphalt increase with increasing MA and MR concentration. However, the values of flash points decreased but they were still higher than standard value (220 °C). Therefore, the additives modified asphalt can be used without defect product. The details of flash point are shown in Appendix B.

4.3.8 Dynamic Shear Rheometry

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

The values of G^* and δ for asphalts are highly dependent on the temperature and frequency of loading. At high temperature, asphalts behave like viscous fluids with no capacity for recovering or rebounding. There would be no elastic component of G^* , since $\delta = 90^\circ$. At very low temperature, asphalts behave like elastic solids, which rebound from deformation completely. There is no viscous component of G^* , since $\delta = 0^\circ$.

The Superpave specification defines and places requirements on a rutting factor, $G^*/\sin \delta$, which represents a measure of the high temperature stiffness or rutting resistance of the asphalt binder. To minimize rutting, $G^*/\sin \delta$ must be a minimum of 1.00 kPa for the original asphalt binder. Like permanent deformation, G^* and δ are also used in the Superpave binder specification to help control the fatigue of asphalt pavements. Since fatigue generally occurs at low to moderate pavement temperatures after the pavement has been in service for a period of time. The fatigue

cracking factor is $G^* \sin \delta$. The Superpave binder specification has a maximum value of 5000 kPa for $G^* \sin \delta$. The details of all data are shown in Appendix C.

Figures 4.33-4.36 show the G^* of additives modified asphalt. G^* of additives modified asphalt is seen to increase with increasing additives concentration, but to decrease with increasing temperature. However, G^* of additives modified asphalt is higher than that of AC.

Figures 4.37-4.40 show phase angle (δ) of additives modified asphalt. δ of additives modification decreases with increasing additives concentration. On the other hand, CF modification increases with increasing temperature. This indicates that when the percentage of additives is increased, the additives modified asphalt behaves like elastic solid at intermediate temperature. Nevertheless, at the high temperature, additives modified asphalt behaves like viscous. From Figures 4.34 and 4.38, the magnitudes of G^* increase whilst δ decreases, possibly as a result of the formation of (or enhancement of existing) transient networks of asphalt species, linked by hydrogen bonding and dipole-dipole interaction [21].

Figure 4.41 shows all values of $G^*/\sin \delta$ of CF-modified asphalt at high temperature. To avoid rutting, $G^*/\sin \delta$ must be a minimum of 1000 Pa. Figure 4.41 also shows that at the CF concentration from 0.5 to 10 wt%, CF modified asphalt can be used at 64 °C compared to 58 °C for AC without rutting. Figures 4.42-4.44 also show that MA concentration from 4 to 10 wt%, MR concentration from 8 to 10 wt%, PF concentration from 8 to 10 wt%, MA-, MR- and PF-modified asphalt can be used at 64 °C. Figures 4.45-4.48 show the $G^* \sin \delta$ at intermediate temperature. None of $G^* \sin \delta$ exceeds 5000 kPa. This indicates that crack formation will not occur at the intermediate temperature.

From investigation of the physical properties of additives modified asphalt using various additives concentration, it can be concluded that the CF, MA, MR and PF could improve some physical properties of CF-, MA-, MR- and PF-modified asphalt. The optimum CF concentration of 4 wt%, MA concentration of 4 wt%, MR concentration of 8 wt% and PF concentration of 8 wt% were chosen to obtain the proper physical properties for CF-, MA-, MR- and PF-modified asphalt.

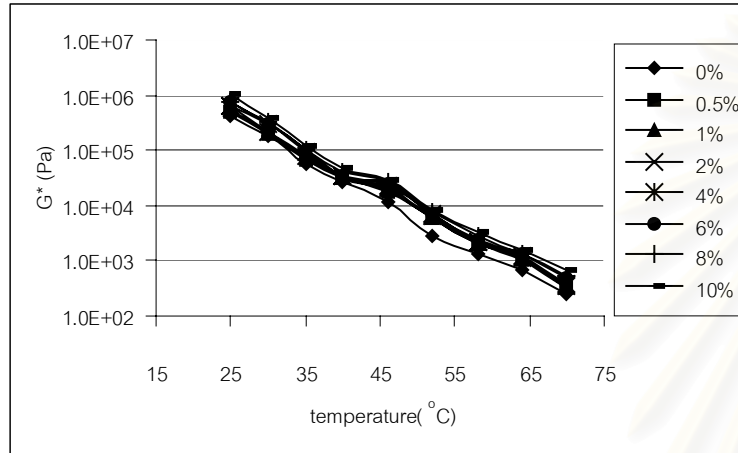


Figure 4.33 The G^* of CF-modified asphalt.

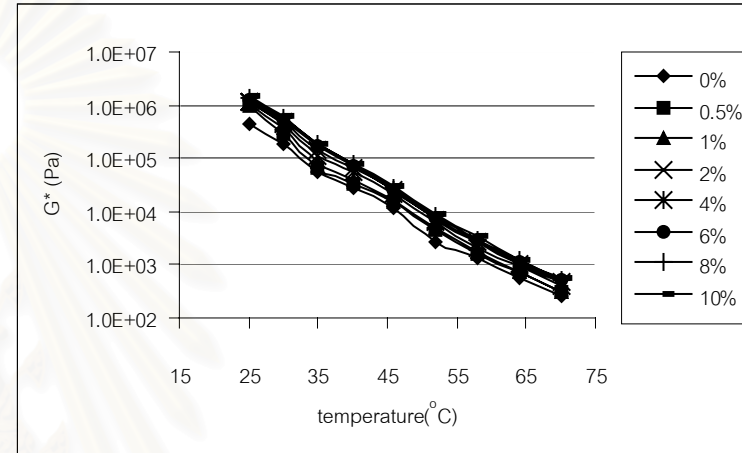


Figure 4.34 The G^* of MA-modified asphalt.

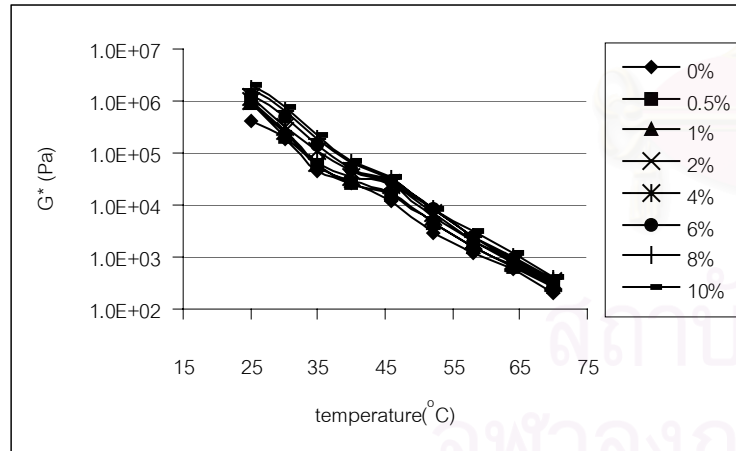


Figure 4.35 The G^* of MR-modified asphalt.

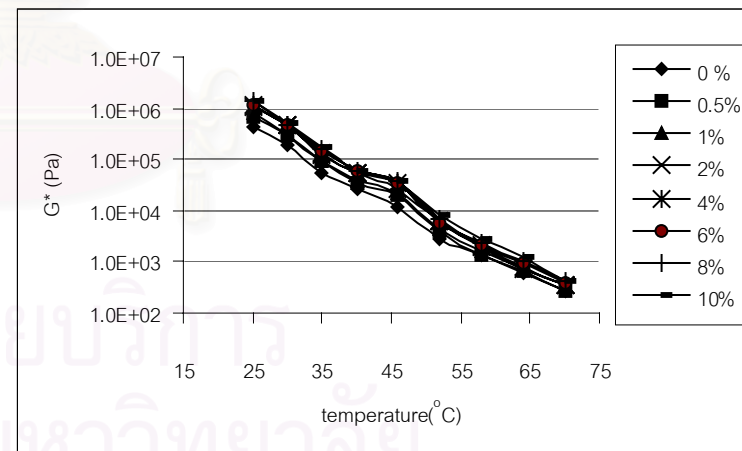


Figure 4.36 The G^* of PF-modified asphalt.

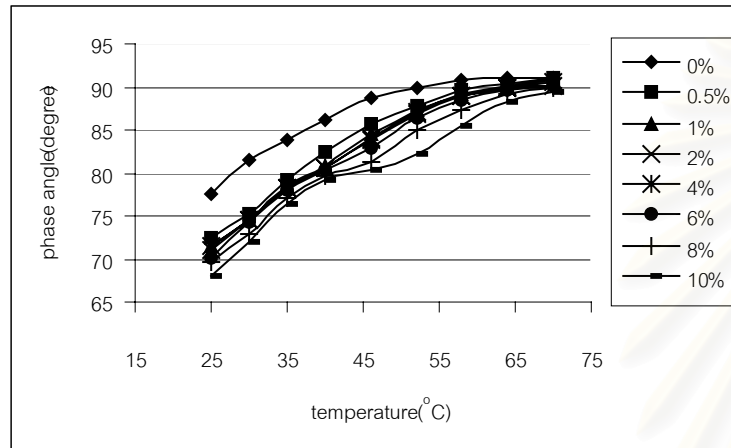


Figure 4.37 The δ of CF-modified asphalt.

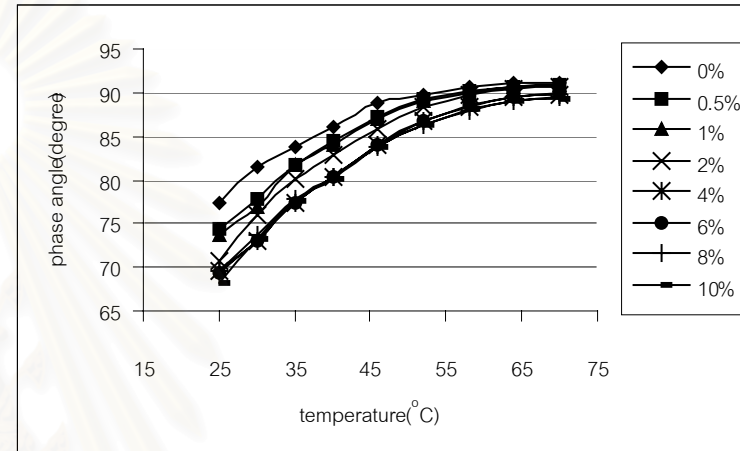


Figure 4.38 The δ of MA-modified asphalt.

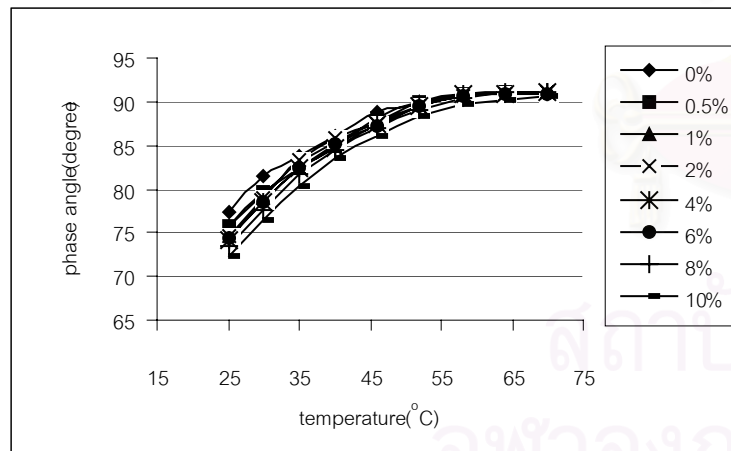


Figure 4.39 The δ of MR-modified asphalt.

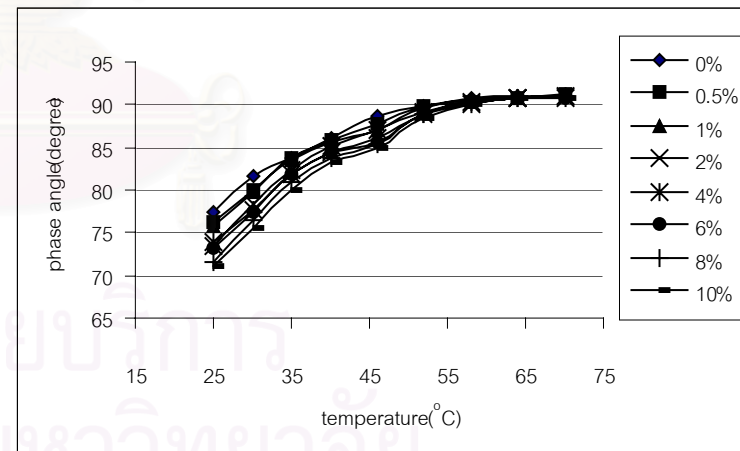


Figure 4.40 The δ of PF-modified asphalt.

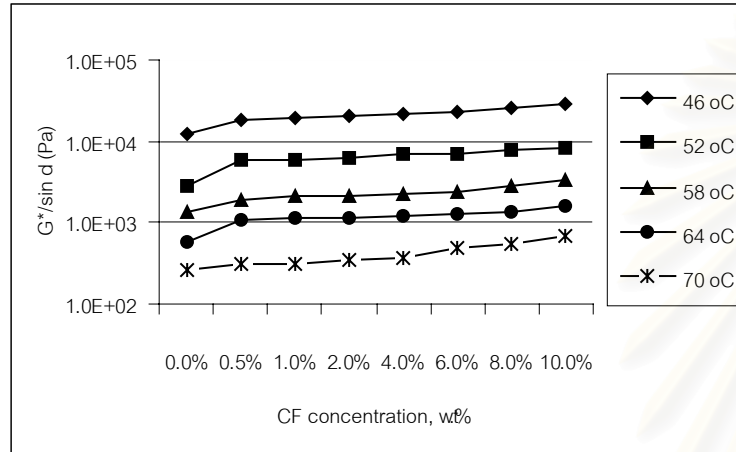


Figure 4.41 $G^*/\sin \delta$ of CF-modified asphalt.

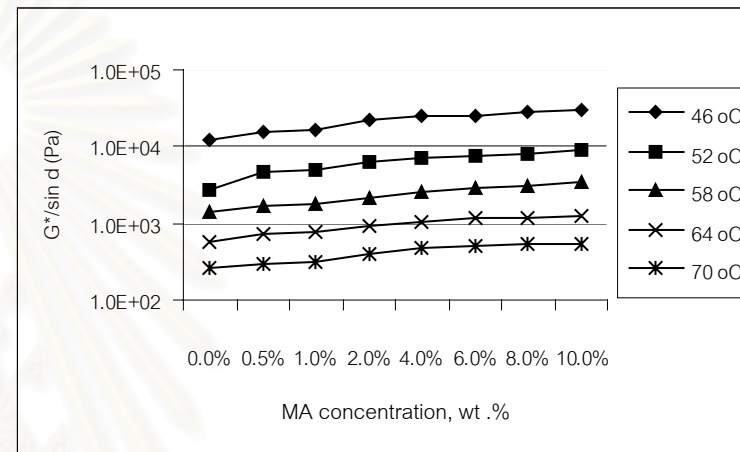


Figure 4.42 $G^*/\sin \delta$ of MA-modified asphalt.

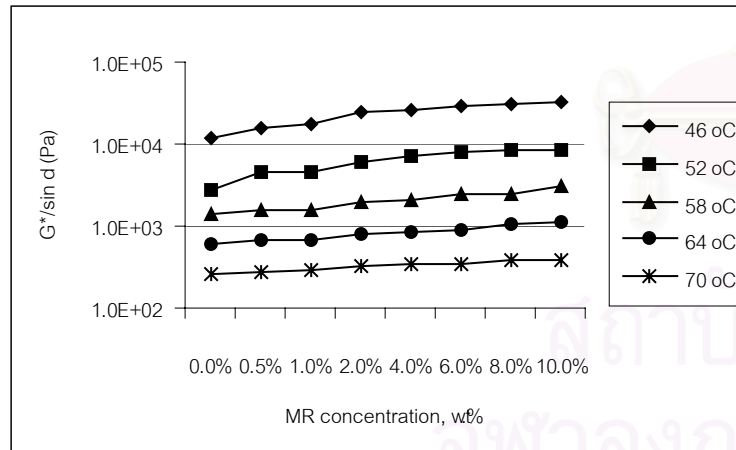


Figure 4.43 $G^*/\sin \delta$ of MR-modified asphalt.

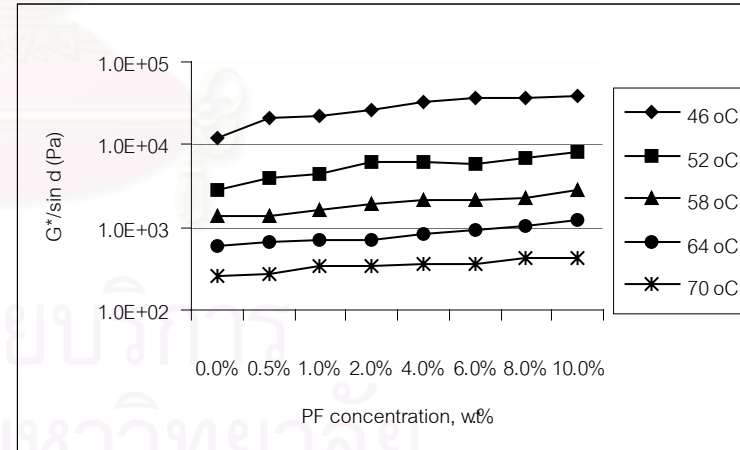


Figure 4.44 $G^*/\sin \delta$ of PF-modified asphalt.

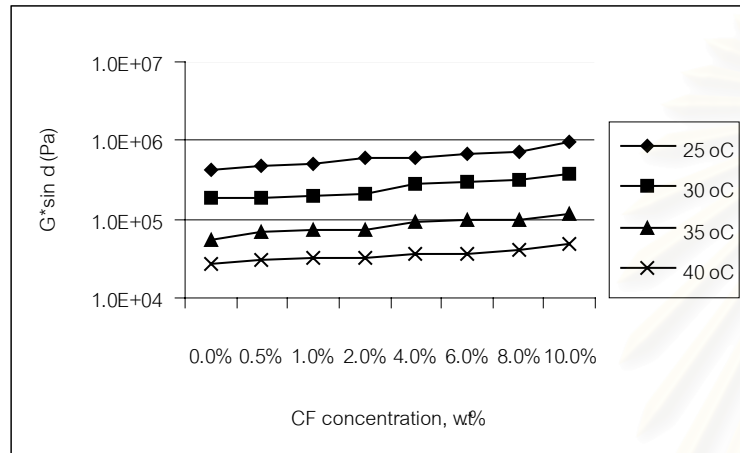


Figure 4.45 $G^* \sin \delta$ of PF-modified asphalt.

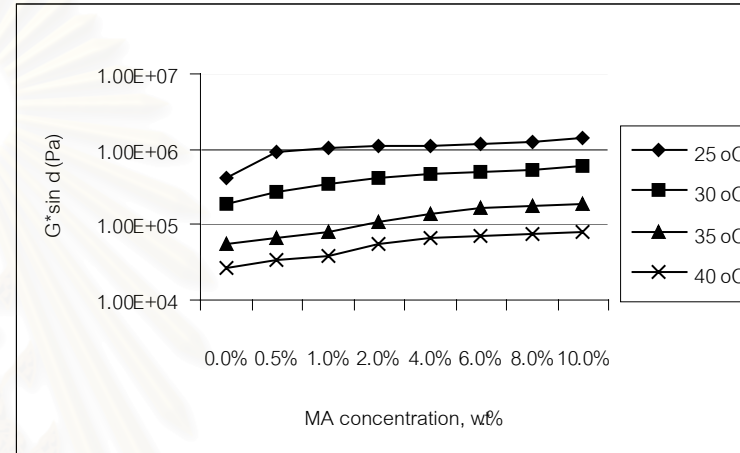


Figure 4.46 $G^* \sin \delta$ of PF-modified asphalt.

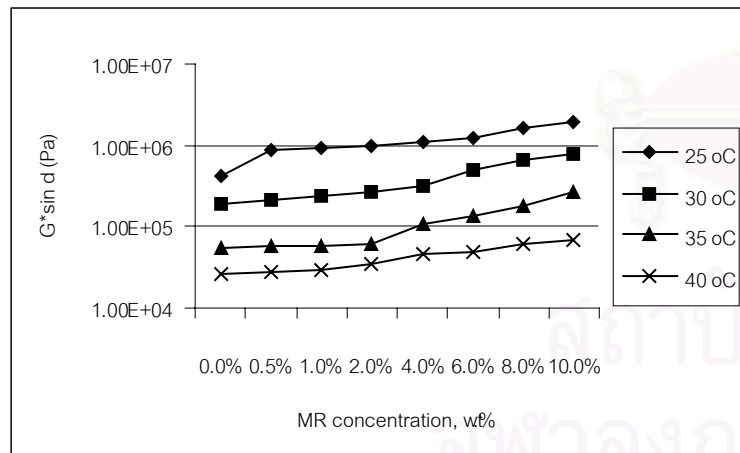


Figure 4.47 $G^* \sin \delta$ of PF-modified asphalt.

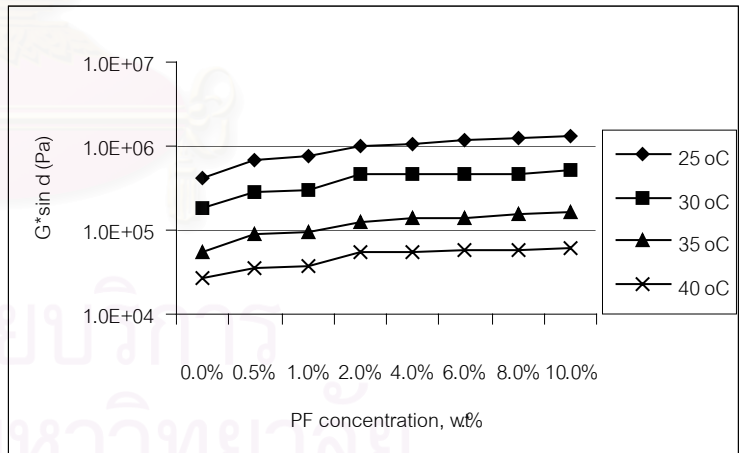


Figure 4.48 $G^* \sin \delta$ of PF-modified asphalt.

4.4 The Physical Properties Comparison of CF-, MA-, MR- and PF-modified asphalts Obtained from This Research with Standard Properties Specified by Thai Industrial Standard Institute (TISI)

Table 4.1 shows a comparison of physical properties of CF-, MA-, MR- and PF-modified asphalts and some asphalt cement for used in pavement construction of the Thai Industrial Standard Institute (TISI).

Results in Table 4.1 indicated that some physical properties of the modification of the asphalt with CF, MA, MR and PF from this investigation are poorer than styrene-butadiene-styrene (SBS) polymer modified asphalt (PMA) and the asphalt cement standard of TISI such as softening point and Brookfield viscosity. The PMA is thermoplastic elastomeric properties; the glassy styrene domains of SBS increase the stiffness of asphalt for high temperature use, whereas the rubbery butadiene midblocks resist thermal cracking at low service temperature. However, the physical properties of our samples are higher than the AC. Therefore, the CF, MA, MR and PF are able to modify the physical properties of asphalt. On the other hand, the CF, MR and PF are thermoset properties.

Table 4.1 The physical properties of modified asphalt are compared with the Thai Industrial Standard Institute.

No.	PROPERTIES	DH-SP 408/2536	AC 60-70	PMA	4%CF	4%MA	8%MR	8% PF
1.	Penetration at 25 °C, 100 g, 5 Sec., 0.1 mm	60-70	68	64	61	45	44	49
2.	Softening Point, Ring and Ball, °C	70 Min.	46	88.5	59	51	52	49.5
3.	Penetration Index	+3 Min.	-1.53	6.12	1.37	-1.4	-0.97	1.95
4.	Ductility at 13 °C, 5 cm/min., cm	55 Min.	>150	117	90.5	47.9	15	63
5.	Ductility at 25 °C, 5 cm/min., cm	100 Min.	>150	>150	>150	136	127	>150
6.	Toughness at °C, kg.cm	200 Min.	52.46	380.67	172.8	119.1	137.2	108.5
	Tenacity at 25 °C, kg.cm	100 Min.	19.53	340.27	48.26	34.79	41	32.01
7.	Brookfield viscosity, shear rate 18.6 s ⁻¹ , spindle 21							
	At 135 °C, cP	1,100Min.	352.35	1934	614.2	534.5	550	495
	At 165 °C, cP	300 Min.	102.5	506	184	147.5	142.5	145
8.	Flash point, Cleaveland Open Cup, °C	220 Min.	330	328	328	336	339	342
	Test on Residue from Thin Film Oven Test							
9.	Weight loss, % wt.	0.5 Max.	0.05	0.13	0.1	0.03	0.09	0.09
10.	Retained penetration at 25 °C, %	70 Min.	72.6	75.8	72.2	81	47	65
11.	Variation in softening point, °C	-4 to +6	4.5	-2	0.5	1.5	1.5	1
12.	Ductility at 13 °C, 5 cm/min., cm	40 Min.	15.1	84.4	70.2	23.7	7	25.3
13.	Ductility at 25 °C, 5 cm/min., cm	50 Min.	>150	>150	>150	132.5	119	>150

CHAPTER V

CONCLUSION

Cardanol-formaldehyde resin was synthesized from the reaction of cardanol with formaldehyde in the presence of sodium hydroxide (NaOH). A product from the reaction was characterized by infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR).

From our physical properties studies of AC, which modified with CF, MA, MR and PF at different level of concentration compared with AC and PMA, the following results have been found;

- Softening point, temperature susceptibility of penetration and temperature susceptibility of viscosity can be improved by the addition of CF, MA, MR and PF.

- Additives modified asphalt reduce aging, which can be observed from TFOT test. The differences of those additives before and after heated are not significant.

- Additives modified asphalt reduces temperature susceptibility. This is indicated by penetration index.

- The flash point of additives modified asphalt by all additives exceed standard, which means that the pavement can be done without danger.

- The results from DSR test indicate that additives increase elasticity, stiffness and at intermediate temperature, cracking will not occur. These additives modified asphalt can be used at the temperature of up to 64 °C.

To sum up, by comparing all results, CF is the most effective additives, which can be used at the range of 0.5-10 wt% while MA at 4 wt%, PF at 8 wt% and MR at 8 wt% as shown in Table 5.1. Although the physical properties of CF-modified asphalt are lower than PMA, CNSL can be found domestically at a cheaper price. Therefore, it is more economically to use CF instead of PMA.

Table 5.1 The physical properties of CF, MA, MR and PF modified asphalt.

PROPERTIES	4%CF	4%MA	8%MR	8% PF
Penetration at 25 °C	61	45	44	49
Softening Point	59	51	52	49.5
Penetration Index	1.37	-1.4	-0.97	1.95
Ductility at 13 °C	90.5	47.9	15	63
Ductility at 25 °C	>150	136	127	>150
Toughness at 25 °C	172.8	119.1	137.2	108.5
Tenacity at 25 °C	48.26	34.79		32.01
Brookfield viscosity				
At 135 °C, cP	614.2	534.5	550	495
At 165 °C, cP	184	147.5	142.5	145
Flash point	328	336	339	342
Test on Residue from TFOT				
Weight loss	0.1	0.03	0.09	0.09
Retained penetration at 25 °C	72.2	81	47	65
Variation in softening point	0.5	1.5	1.5	1
Ductility at 13 °C	70.2	23.7	7	25.3
Ductility at 25 °C	>150	132.5	119	>150

Suggestion for Future Work

1. The properties measured by especially transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS) and differential scanning calorimeter (DSC) of asphalt modifiers.
2. Investigating the effect of additives, such as natural rubber and carbon black, on this asphalt modifiers.



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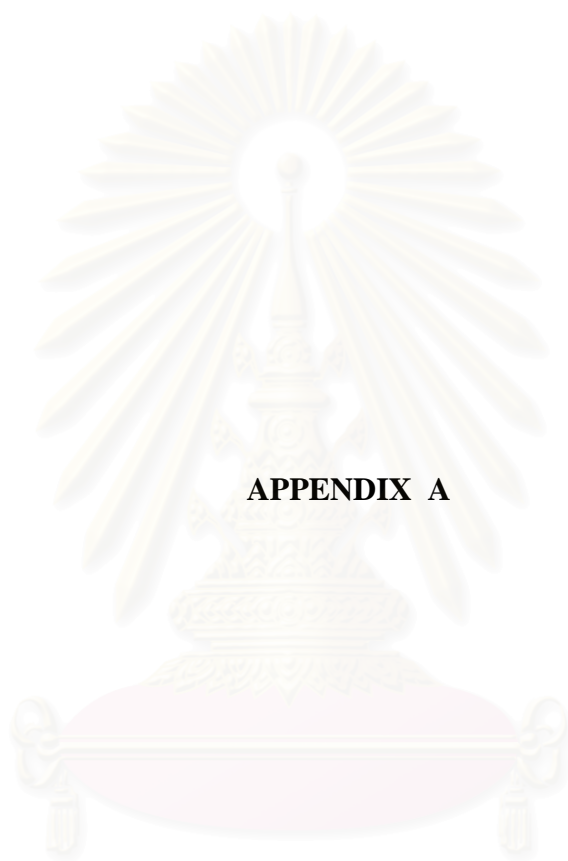
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APPENDICES

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



APPENDIX A

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

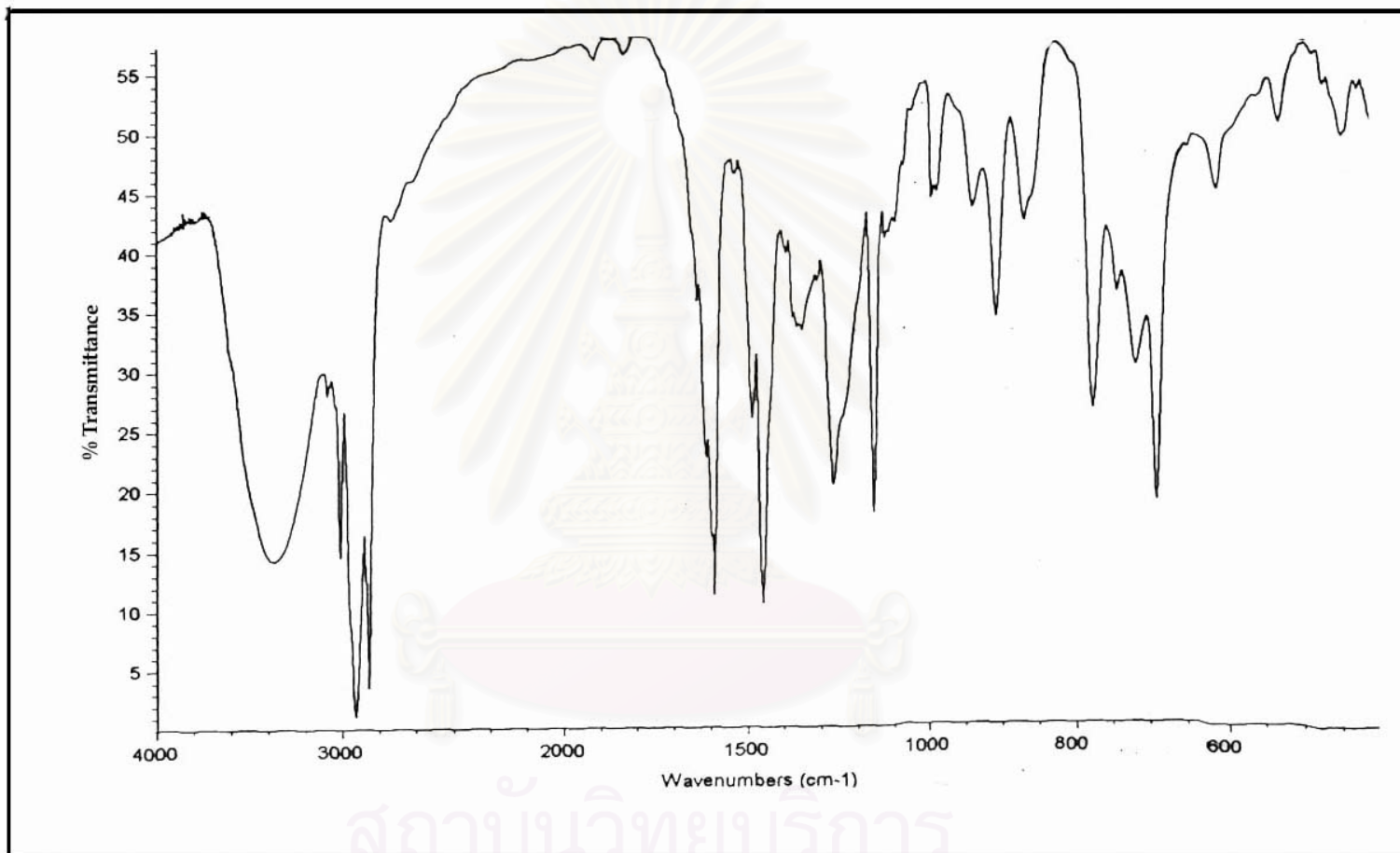


Figure A.1 Infrared spectrum of cardanol.

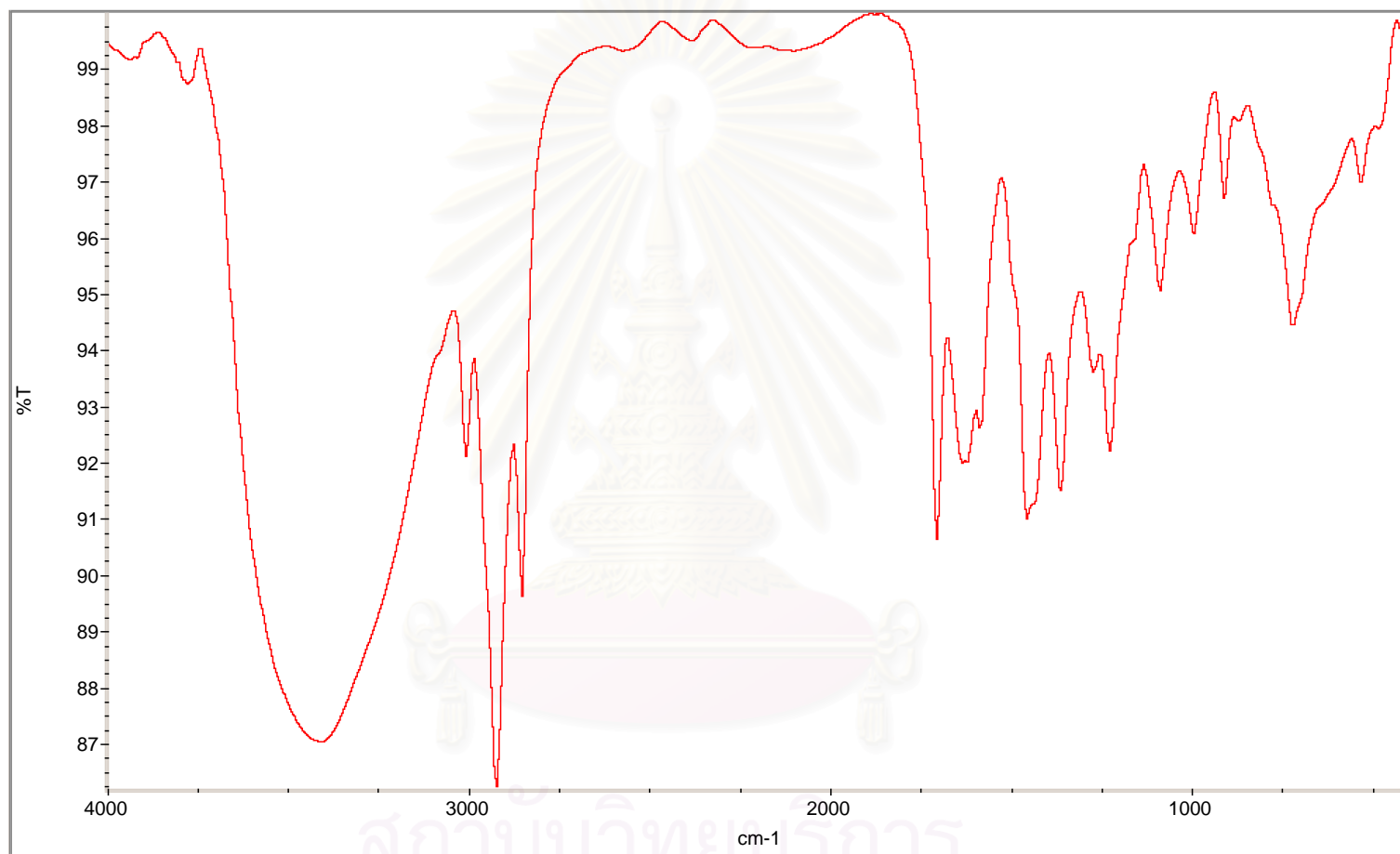


Figure A.2 Infrared spectrum of cardanol-formaldehyde resin.

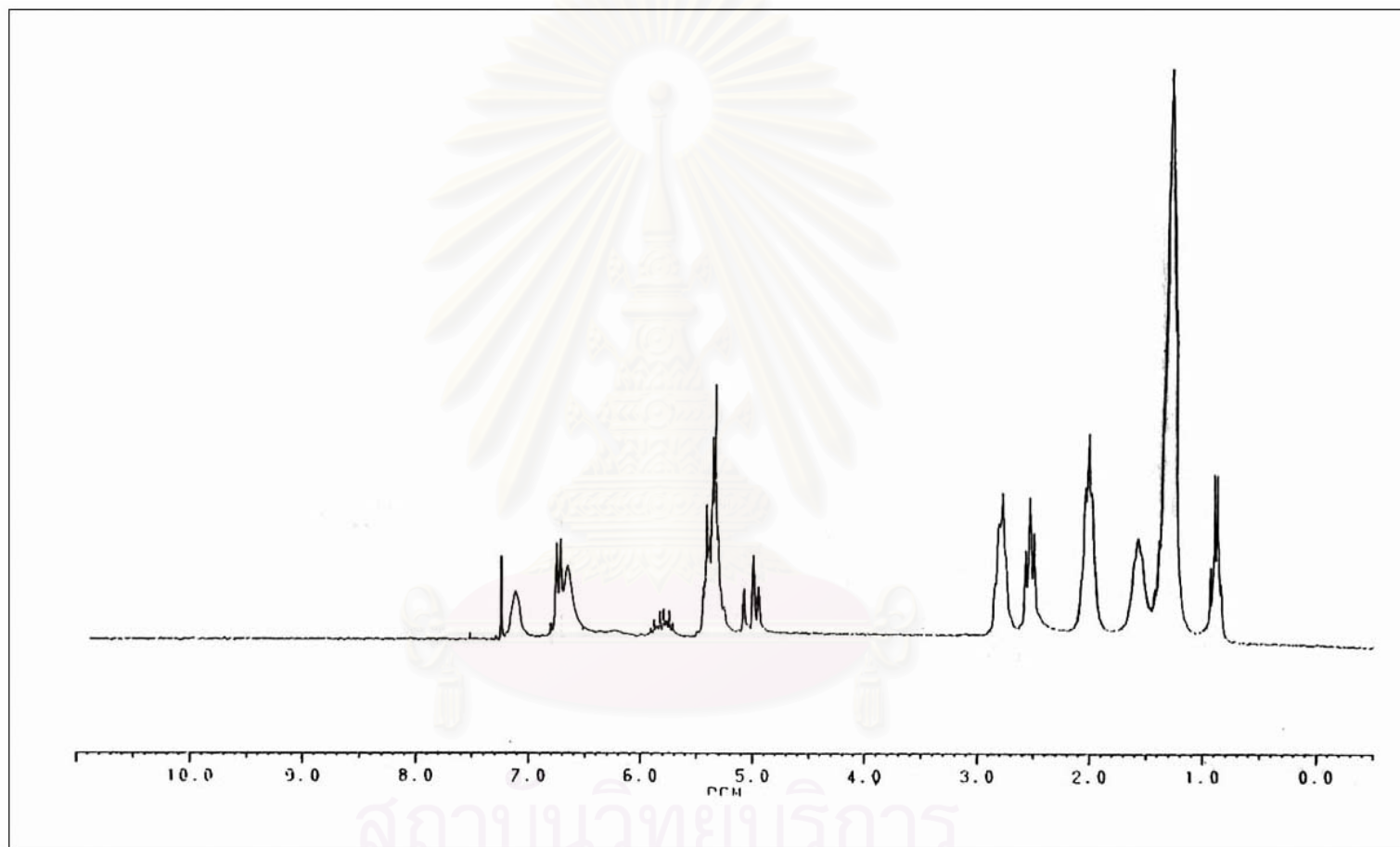


Figure A.3 $^1\text{H-NMR}$ spectrum of cardanol in CDCl_3 .

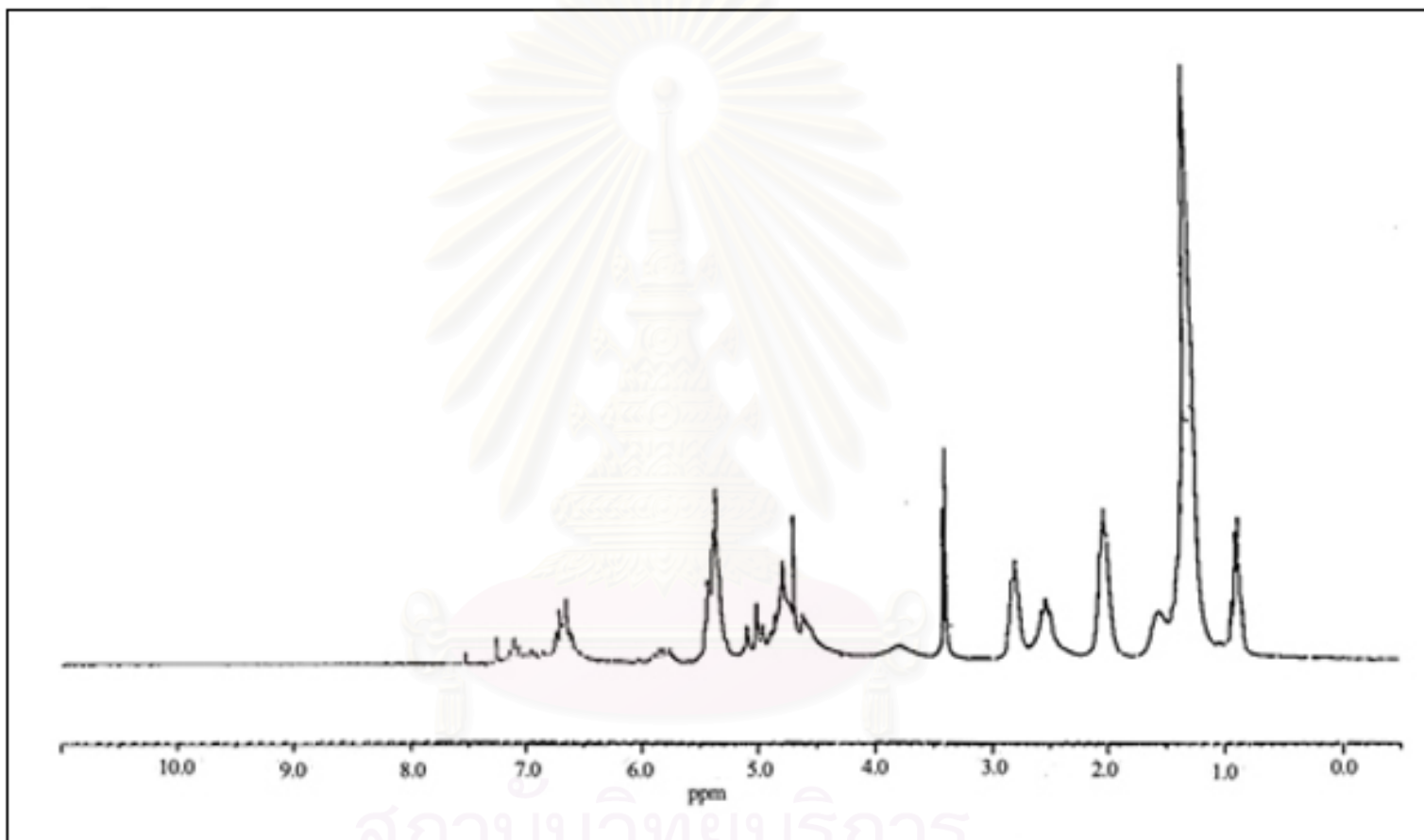
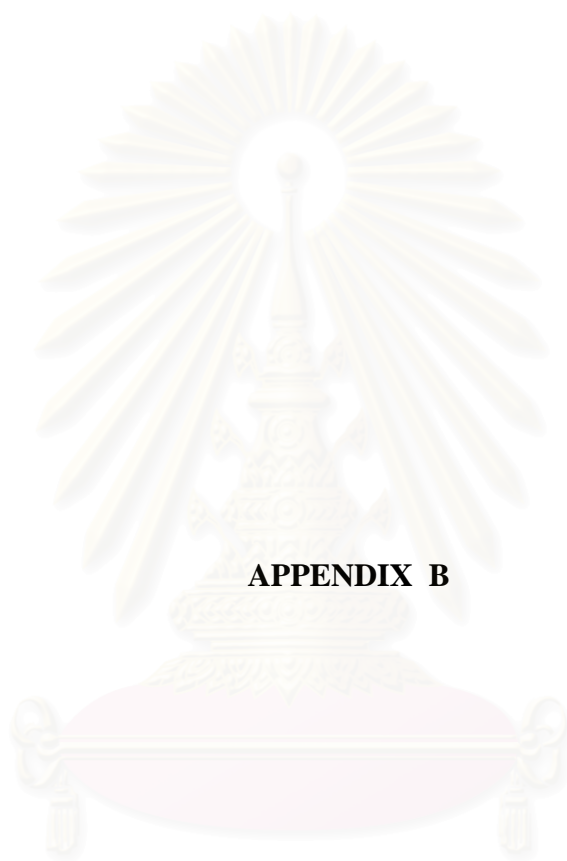


Figure A.4 $^1\text{H-NMR}$ spectrum of cardanol-formaldehyde resin in CDCl_3 .



APPENDIX B

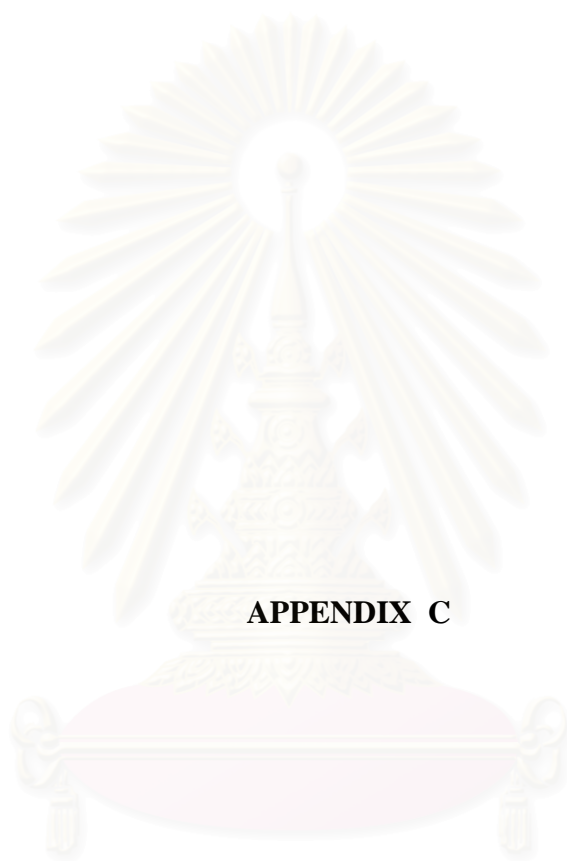
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Table B.2 Physical properties of maleic anhydride modified asphalt.

ITEM No.	PROPERTIES	UNIT	-SP 408/2536		MA (%)						
			MIN.	MAX.	0.5	1	2	4	6	8	10
1	Penetration 25 °C (100 g, 5 sec)	0.1mm	60	70	54	52	49	45	40	39	36
2	Softening point , Ring and Ball	°C	70	-	48	49	49.5	51	52	53.2	55
3	Penetration Index	-	+3	-	-1.51	-1.48	-1.3	-1.16	-1.17	-0.95	-0.73
4	Ductility at 13 °C. , 5cm/ mm	cm	55	-	123	97	64	47.9	25.6	13.4	5
5	Ductility at 25 °C. , 5cm/ mm	cm	100	-	>150	>150	>150	136	124.5	98	93
6	- Toughness at 25 °C	Kg cm	200	-	80.93	92.34	105	119.1	147.9	150.9	152.5
	- Tenacity at 25 °C	Kg cm	100	-	25.75	26.56	27.38	34.79	37.91	39.89	47.22
7	Brookfield viscosity at 135 °C	cp	1,100	-	455	478.5	502.5	534.5	550	574	598.5
	Brookfield viscosity at 165 °C	cp	300	-	142.5	145	146	147.5	149	155	177
8	Flash point (Cleveland Open Cup)	°C	220	-	332	335	335	336	340	341	346
TEST ON RESIDUE FROM THIN FILM OVEN TEST											
9	Weight loss	% wt	-	0.5	0.07	0.06	0	0.03	0.06	0.14	0.21
10	Retained penetration at 25 °C	%	70	-	89.5	87.5	86.3	81	77.8	59.8	50.9
11	Variation in softening point	°C	-4	+6	3	2	2.5	1.5	1	0.5	-1
12	Ductility of residue at 13 °C, 5cm/ mm	cm	40	-	77.6	54.2	41.6	23.7	12	3.2	1.2
13	Ductility of residue at 25 °C, 5cm/ mm	cm	50	-	>150	>150	>150	132.5	117	91.2	83.4

Table B.3 Physical properties of maleic resin modified asphalt.

ITEM No.	PROPERTIES	UNIT	-SP 408/2536		MR (%)						
			MIN.	MAX.	0.5	1	2	4	6	8	10
1	Penetration 25 °C (100 g, 5 sec)	0.1mm	60	70	60	54	50	47	45	44	41
2	Softening point , Ring and Ball	°C	70	-	47.2	48.2	49	50	50.5	52	53.5
3	Penetration Index	-	+3	-	-1.48	-1.46	-1.42	-1.31	-1.28	-0.97	-0.78
4	Ductility at 13 °C , 5cm/ mm	cm	55	-	137	123	94	72	38.2	15	14
5	Ductility at 25 °C , 5cm/ mm	cm	100	-	>150	>150	>150	>150	143	127	124
6	- Toughness at 25 °C	Kg cm	200	-	79.1	87.96	115.3	124.4	126.4	137.2	144.8
	- Tenacity at 25 °C	Kg cm	100		29.9	33.5	34.2	36.75	38.12	41	44.7
7	Brookfield viscosity at 135 °C	cp	1,100	-	427.5	455	485	521	525	550	557.5
	Brookfield viscosity at 165 °C	cp	300		135	137.5	139	140	142	142.5	154
8	Flash point (Cleveland Open Cup)	°C	220	-	332	334	335	335	337	339	342
TEST ON RESIDUE FROM THIN FILM OVEN TEST											
9	Weight loss	% wt	-	0.5	0.01	0.01	0.02	0.05	0.08	0.09	0.17
10	Retained penetration at 25 °C	%	70	-	79.6	78.8	75.6	74	60.9	47	36
11	Variation in softening point	°C	-4	+6	2	-2	0	2	1.5	1.5	2
12	Ductility of residue at 13 °C, 5cm/ mm	cm	40	-	79.6	42.3	28.2	25.4	11.8	7	6.2
13	Ductility of residue at 25 °C, 5cm/ mm	cm	50	-	>150	>150	>150	>150	140.5	119	115.4



APPENDIX C

สถาบันวิทยบริการ
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Table C.1 Complex shear modulus (G^*), Phase angle (δ), $G^*/\sin \delta$ and $G^*\sin \delta$ of Asphalt Cement.

Temp. °C	G^* (Pa)	Phase angle ; δ (degree)	$G^*/\sin \delta$	$G^*\sin \delta$
25	4.30E+05	77.478	4.40E+05	4.19E+05
30	1.87E+05	81.562	1.89E+05	1.85E+05
35	55696	83.745	5.60E+04	5.54E+04
40	26667	86.131	2.67E+04	2.66E+04
46	12969	88.781	1.30E+04	1.30E+04
52	2779.7	89.842	2.78E+03	2.78E+03
58	1378.5	90.727	1.38E+03	1.38E+03
64	586.67	91.049	5.87E+02	5.87E+02
70	258.78	91.015	2.59E+02	2.59E+02

Table C.2 Complex shear modulus (G^*), Phase angle (δ), $G^*/\sin \delta$ and $G^*\sin \delta$ of Polymer modified asphalt.

Temp. °C	G^* (Pa)	Phase angle ; δ (degree)	$G^*/\sin \delta$	$G^*\sin \delta$
25	6.60E+05	69.4	7.05E+05	6.18E+05
30	2.81E+05	70.65	2.98E+05	2.65E+05
35	1.17E+05	70.08	1.24E+05	1.10E+05
40	5.20E+04	68.2	5.60E+04	4.83E+04
46	1.65E+04	66.8	1.80E+04	1.52E+04
52	7.80E+03	65.15	8.60E+03	7.08E+03
58	4.00E+03	63.5	4.47E+03	3.58E+03
64	2.39E+03	61.9	2.70E+03	2.10E+03
70	1.35E+03	59.27	1.57E+03	1.16E+03

Table C.3 Complex shear modulus (G^*) of cardanol formaldehyde resin modified asphalt.

Temp (°C)	G^* (Pa)						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	8.87E+05	9.50E+05	9.96E+05	1.18E+06	1.26E+06	1.66E+06	2.01E+06
30	2.11E+05	2.37E+05	2.72E+05	3.29E+05	5.08E+05	6.69E+05	7.89E+05
35	57620	59876	62474	1.06E+05	1.40E+05	1.84E+05	2.20E+05
40	27065	29631	35381	46105	49998	62670	70737
46	15844	17658	24710	25799	29007	31051	33392
52	4475.6	4517.7	6009.5	7139.9	8120	8248.1	8540.2
58	1538.7	1575.2	1958.3	2047.2	2423.4	2462.2	3096.8
64	661.45	677.24	796.33	842.72	844.79	929.05	1094
70	272.85	295.27	328.17	335.14	336.14	388.93	394.64

Table C.4 Phase angle (δ) of cardanol formaldehyde resin modified asphalt.

Temp. °C	Phase angle; δ (degree)						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	75.856	75.736	74.628	74.112	74.396	73.434	72.437
30	79.675	79.439	78.982	78.443	78.492	77.668	76.419
35	82.426	83.017	83.41	82.505	82.296	81.618	80.398
40	84.848	85.385	85.742	84.665	85.205	84.56	83.594
46	88.121	87.725	87.379	87.524	87.211	87.065	86.116
52	89.888	89.883	89.427	89.478	89.481	89.085	88.426
58	90.851	90.788	90.725	90.775	90.539	90.488	89.772
64	91.021	90.869	90.965	90.93	90.868	91.041	90.267
70	91.194	91.087	91.104	91.066	90.971	91.171	90.747

Table C.5 $G^*/\sin \delta$ of cardanol formaldehyde resin modified asphalt.

Temp. °C	$G^*/\sin \delta$						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	9.14E+05	9.80E+05	1.03E+06	1.22E+06	1.31E+06	1.73E+06	1.31E+06
30	2.14E+05	2.41E+05	2.77E+05	3.35E+05	5.18E+05	6.85E+05	5.18E+05
35	5.81E+04	6.03E+04	6.29E+04	1.07E+05	1.42E+05	1.86E+05	1.42E+05
40	2.72E+04	2.97E+04	3.55E+04	4.63E+04	5.02E+04	6.30E+04	5.02E+04
46	2.08E+04	2.23E+04	2.56E+04	3.32E+04	3.62E+04	3.73E+04	3.94E+04
52	3.98E+03	4.42E+03	6.25E+03	6.27E+03	5.95E+03	6.90E+03	8.25E+03
58	1.40E+03	1.61E+03	1.96E+03	2.10E+03	2.16E+03	2.23E+03	2.79E+03
64	6.78E+02	6.99E+02	7.08E+02	8.96E+02	9.01E+02	9.53E+02	1.05E+03
70	2.77E+02	3.39E+02	3.43E+02	3.57E+02	3.70E+02	4.20E+02	4.29E+02

Table C.6 $G^* \sin \delta$ of cardanol formaldehyde resin modified asphalt.

Temp. °C	$G^* \sin \delta$						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	6.65E+05	7.58E+05	1.02E+06	1.07E+06	1.16E+06	1.26E+06	1.35E+06
30	2.86E+05	3.06E+05	4.53E+05	4.62E+05	4.64E+05	4.69E+05	5.12E+05
35	9.06E+04	9.67E+04	1.22E+05	1.38E+05	1.40E+05	1.55E+05	1.65E+05
40	3.46E+04	3.78E+04	5.56E+04	5.59E+04	5.75E+04	5.87E+04	6.09E+04
46	1.58E+04	1.76E+04	2.47E+04	2.58E+04	2.90E+04	3.10E+04	3.34E+04
52	4.48E+03	4.52E+03	6.01E+03	7.14E+03	8.12E+03	8.25E+03	8.54E+03
58	1.54E+03	1.58E+03	1.96E+03	2.05E+03	2.42E+03	2.46E+03	3.10E+03
64	6.61E+02	6.77E+02	7.96E+02	8.43E+02	8.45E+02	9.29E+02	1.09E+03
70	2.73E+02	2.95E+02	3.28E+02	3.35E+02	3.36E+02	3.89E+02	3.95E+02

Table C.7 Complex shear modulus (G^*) of maleic anhydride modified asphalt.

Temp (°C)	G^* (Pa)						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	9.43E+05	1.08E+06	1.16E+06	1.20E+06	1.27E+06	1.32E+06	1.49E+06
30	2.82E+05	3.62E+05	4.32E+05	4.98E+05	5.33E+05	5.59E+05	6.16E+05
35	67964	8.23E+04	1.09E+05	1.41E+05	1.73E+05	1.85E+05	1.91E+05
40	33327	38419	54485	66322	71861	77296	80446
46	15405	16326	22336	24932	25661	28270	30273
52	4556.3	5044.4	6359.6	7246.2	7603.8	8604.7	9062.4
58	1640.4	1802.1	2091.5	2572.2	2923.1	2993.4	3371.3
64	724.59	751.55	947.08	1056.9	1158.6	1197.4	1225
70	296.83	319.04	403.29	468.34	507.2	527.77	543.46

Table C.8 Phase angle (δ) of maleic anhydride modified asphalt.

Temp. °C	Phase angle; δ (degree)						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	74.312	73.672	70.826	69.586	69.245	69.693	68.102
30	77.726	76.897	76.024	73.094	73.117	73.597	73.225
35	81.701	81.633	80.229	77.423	77.458	77.764	77.58
40	84.414	84.074	82.882	80.446	80.407	80.335	80.216
46	87.194	87.027	85.882	83.912	84.06	83.859	83.687
52	89.181	88.933	88.298	86.756	86.712	86.406	86.38
58	90.15	90.073	89.695	88.308	88.541	87.942	88.044
64	90.612	90.74	90.378	89.452	89.473	89.016	88.967
70	90.956	90.861	90.729	89.821	89.86	89.533	89.36

Table C.9 $G^*/\sin \delta$ of maleic anhydride modified asphalt.

Temp. °C	$G^*/\sin \delta$						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	9.79E+05	1.12E+06	1.23E+06	1.28E+06	1.36E+06	1.41E+06	1.61E+06
30	2.89E+05	3.72E+05	4.45E+05	5.20E+05	5.57E+05	5.83E+05	6.43E+05
35	6.87E+04	8.32E+04	1.11E+05	1.45E+05	1.77E+05	1.90E+05	1.95E+05
40	3.35E+04	3.86E+04	5.49E+04	6.73E+04	7.29E+04	7.84E+04	8.16E+04
46	2.08E+04	2.23E+04	2.56E+04	3.32E+04	3.62E+04	3.73E+04	3.94E+04
52	3.98E+03	4.42E+03	6.25E+03	6.27E+03	5.95E+03	6.90E+03	8.25E+03
58	1.40E+03	1.61E+03	1.96E+03	2.10E+03	2.16E+03	2.23E+03	2.79E+03
64	6.78E+02	6.99E+02	7.08E+02	8.96E+02	9.01E+02	9.53E+02	1.05E+03
70	2.77E+02	3.39E+02	3.43E+02	3.57E+02	3.70E+02	4.20E+02	4.29E+02

Table C.10 $G^* \sin \delta$ of maleic anhydride modified asphalt.

Temp. °C	$G^* \sin \delta$						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	6.65E+05	7.58E+05	1.02E+06	1.07E+06	1.16E+06	1.26E+06	1.35E+06
30	2.86E+05	3.06E+05	4.53E+05	4.62E+05	4.64E+05	4.69E+05	5.12E+05
35	9.06E+04	9.67E+04	1.22E+05	1.38E+05	1.40E+05	1.55E+05	1.65E+05
40	3.46E+04	3.78E+04	5.56E+04	5.59E+04	5.75E+04	5.87E+04	6.09E+04
46	1.54E+04	1.63E+04	2.23E+04	2.48E+04	2.55E+04	2.81E+04	3.01E+04
52	4.56E+03	5.04E+03	6.36E+03	7.23E+03	7.59E+03	8.59E+03	9.04E+03
58	1.64E+03	1.80E+03	2.09E+03	2.57E+03	2.92E+03	2.99E+03	3.37E+03
64	7.25E+02	7.51E+02	9.47E+02	1.06E+03	1.16E+03	1.20E+03	1.22E+03
70	2.97E+02	3.19E+02	4.03E+02	4.68E+02	5.07E+02	5.28E+02	5.43E+02

Table C.11 Complex shear modulus (G^*) of maleic resin modified asphalt.

Temp (°C)	G^* (Pa)						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	8.87E+05	9.50E+05	9.96E+05	1.18E+06	1.26E+06	1.66E+06	2.01E+06
30	2.11E+05	2.37E+05	2.72E+05	3.29E+05	5.08E+05	6.69E+05	7.89E+05
35	57620	59876	62474	1.06E+05	1.40E+05	1.84E+05	2.20E+05
40	27065	29631	35381	46105	49998	62670	70737
46	15844	17658	24710	25799	29007	31051	33392
52	4475.6	4517.7	6009.5	7139.9	8120	8248.1	8540.2
58	1538.7	1575.2	1958.3	2047.2	2423.4	2462.2	3096.8
64	661.45	677.24	796.33	842.72	844.79	929.05	1094
70	272.85	295.27	328.17	335.14	336.14	388.93	394.64

Table C.12 Phase angle (δ) of maleic resin modified asphalt.

Temp. °C	Phase angle; δ (degree)						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	75.856	75.736	74.628	74.112	74.396	73.434	72.437
30	79.675	79.439	78.982	78.443	78.492	77.668	76.419
35	82.426	83.017	83.41	82.505	82.296	81.618	80.398
40	84.848	85.385	85.742	84.665	85.205	84.56	83.594
46	88.121	87.725	87.379	87.524	87.211	87.065	86.116
52	89.888	89.883	89.427	89.478	89.481	89.085	88.426
58	90.851	90.788	90.725	90.775	90.539	90.488	89.772
64	91.021	90.869	90.965	90.93	90.868	91.041	90.267
70	91.194	91.087	91.104	91.066	90.971	91.171	90.747

Table C.13 $G^*/\sin \delta$ of maleic resin modified asphalt.

Temp. °C	$G^*/\sin \delta$						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	9.14E+05	9.80E+05	1.03E+06	1.22E+06	1.31E+06	1.73E+06	1.31E+06
30	2.14E+05	2.41E+05	2.77E+05	3.35E+05	5.18E+05	6.85E+05	5.18E+05
35	5.81E+04	6.03E+04	6.29E+04	1.07E+05	1.42E+05	1.86E+05	1.42E+05
40	2.72E+04	2.97E+04	3.55E+04	4.63E+04	5.02E+04	6.30E+04	5.02E+04
46	2.08E+04	2.23E+04	2.56E+04	3.32E+04	3.62E+04	3.73E+04	3.94E+04
52	3.98E+03	4.42E+03	6.25E+03	6.27E+03	5.95E+03	6.90E+03	8.25E+03
58	1.40E+03	1.61E+03	1.96E+03	2.10E+03	2.16E+03	2.23E+03	2.79E+03
64	6.78E+02	6.99E+02	7.08E+02	8.96E+02	9.01E+02	9.53E+02	1.05E+03
70	2.77E+02	3.39E+02	3.43E+02	3.57E+02	3.70E+02	4.20E+02	4.29E+02

Table C.14 $G^* \sin \delta$ of maleic resin modified asphalt.

Temp. °C	$G^* \sin \delta$						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	6.65E+05	7.58E+05	1.02E+06	1.07E+06	1.16E+06	1.26E+06	1.35E+06
30	2.86E+05	3.06E+05	4.53E+05	4.62E+05	4.64E+05	4.69E+05	5.12E+05
35	9.06E+04	9.67E+04	1.22E+05	1.38E+05	1.40E+05	1.55E+05	1.65E+05
40	3.46E+04	3.78E+04	5.56E+04	5.59E+04	5.75E+04	5.87E+04	6.09E+04
46	1.58E+04	1.76E+04	2.47E+04	2.58E+04	2.90E+04	3.10E+04	3.34E+04
52	4.48E+03	4.52E+03	6.01E+03	7.14E+03	8.12E+03	8.25E+03	8.54E+03
58	1.54E+03	1.58E+03	1.96E+03	2.05E+03	2.42E+03	2.46E+03	3.10E+03
64	6.61E+02	6.77E+02	7.96E+02	8.43E+02	8.45E+02	9.29E+02	1.09E+03
70	2.73E+02	2.95E+02	3.28E+02	3.35E+02	3.36E+02	3.89E+02	3.95E+02

Table C.15 Complex shear modulus (G^*) of paraformaldehyde modified asphalt.

Temp (°C)	G^* (Pa)						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	6.85E+05	7.82E+05	1.06E+06	1.11E+06	1.21E+06	1.33E+06	1.42E+06
30	2.91E+05	3.11E+05	4.62E+05	4.73E+05	4.75E+05	4.83E+05	5.29E+05
35	91146	97310	1.23E+05	1.39E+05	1.41E+05	1.57E+05	1.67E+05
40	34661	37893	55813	56142	57799	59106	61298
46	20766	22274	25517	33121	36124	37138	39259
52	3978.3	4424.2	6252.9	6269.5	5951.4	6900.2	8246
58	1396.3	1608.2	1960.8	2098.3	2157	2229.6	2793.7
64	677.89	698.65	708.3	895.79	900.56	952.43	1054.5
70	276.52	339.27	343.29	356.67	370.28	419.6	428.57

Table C.16 Phase angle (δ) of paraformaldehyde modified asphalt.

Temp. °C	Phase angle; δ (degree)						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	76.318	75.767	73.479	73.908	73.288	71.625	71.035
30	79.998	79.672	78.405	77.616	77.428	76.387	75.608
35	83.714	83.462	82.347	81.849	81.958	80.89	80.114
40	85.798	85.603	85.168	84.517	84.491	83.686	83.268
46	87.811	87.013	86.952	86.053	85.716	85.381	85.039
52	89.781	89.643	89.071	88.831	88.935	88.945	88.541
58	90.364	90.63	90.303	90.181	90.356	90.245	89.979
64	90.859	90.745	90.838	90.733	90.744	90.779	90.669
70	91.147	90.974	90.928	90.856	90.878	90.904	90.704

Table C.17 $G^*/\sin \delta$ of paraformaldehyde modified asphalt.

Temp. °C	$G^*/\sin \delta$						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	7.05E+05	8.06E+05	1.11E+06	1.16E+06	1.26E+06	1.40E+06	1.51E+06
30	2.95E+05	3.16E+05	4.72E+05	4.85E+05	4.87E+05	4.97E+05	5.46E+05
35	9.17E+04	9.79E+04	1.25E+05	1.41E+05	1.43E+05	1.59E+05	1.70E+05
40	3.48E+04	3.80E+04	5.60E+04	5.64E+04	5.81E+04	5.95E+04	6.17E+04
46	2.08E+04	2.23E+04	2.56E+04	3.32E+04	3.62E+04	3.73E+04	3.94E+04
52	3.98E+03	4.42E+03	6.25E+03	6.27E+03	5.95E+03	6.90E+03	8.25E+03
58	1.40E+03	1.61E+03	1.96E+03	2.10E+03	2.16E+03	2.23E+03	2.79E+03
64	6.78E+02	6.99E+02	7.08E+02	8.96E+02	9.01E+02	9.53E+02	1.05E+03
70	2.77E+02	3.39E+02	3.43E+02	3.57E+02	3.70E+02	4.20E+02	4.29E+02

Table C.18 $G^* \sin \delta$ of paraformaldehyde modified asphalt.

Temp. °C	$G^* \sin \delta$						
	0.5 %	1 %	2 %	4 %	6 %	8 %	10 %
25	6.65E+05	7.58E+05	1.02E+06	1.07E+06	1.16E+06	1.26E+06	1.35E+06
30	2.86E+05	3.06E+05	4.53E+05	4.62E+05	4.64E+05	4.69E+05	5.12E+05
35	9.06E+04	9.67E+04	1.22E+05	1.38E+05	1.40E+05	1.55E+05	1.65E+05
40	3.46E+04	3.78E+04	5.56E+04	5.59E+04	5.75E+04	5.87E+04	6.09E+04
46	2.08E+04	2.22E+04	2.55E+04	3.30E+04	3.60E+04	3.70E+04	3.91E+04
52	3.98E+03	4.42E+03	6.25E+03	6.27E+03	5.95E+03	6.90E+03	8.24E+03
58	1.40E+03	1.61E+03	1.96E+03	2.10E+03	2.16E+03	2.23E+03	2.79E+03
64	6.78E+02	6.99E+02	7.08E+02	8.96E+02	9.00E+02	9.52E+02	1.05E+03
70	2.76E+02	3.39E+02	3.43E+02	3.57E+02	3.70E+02	4.20E+02	4.29E+02

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