

Performance modification of Saudi-asphalt binders using SABIC polymers

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Civil Engineering

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Abstract

Asphalt binder is a thermoplastic liquid, which behaves as elastic solid at low service temperatures or during rapid loading. At high temperature or slow loading, it behaves as a viscous liquid. This classical dichotomy creates a need to improve the performance of the asphalt binder to minimize the cracking stresses that occur at low temperatures and plastic deformations at high temperatures. The use of polymer-modified asphalt binder is one of the solutions to meet the required performance standards for the pavements. It appears to be logical, practical, and economical approach.

In the Kingdom, most of the used asphalt-polymers are imported from abroad, which led to increase in the total construction cost. The main objective of this search is to modify locally produced asphalt using polymers produced by Saudi Basic Industries Company (SABIC). The study covered the asphalt binders produced by the Riyadh and Ras Tanura refineries. Ten polymers were identified as potential asphalt modifiers based on their physical properties and chemical composition. These polymers were screened into four types which were used to modify the asphalt. The results indicated that the rheological properties of the modified binders were improved significantly with sufficient polymer content (3%). The aging properties of the modified binders were found to be dependent on the type of the polymer. The fatigue life and resistance to permanent deformation were significantly improved due to the improvement in the rheological properties of the binders. In general, the research has shown the effectiveness of SABIC polymers in modifying local asphalts.

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Performance Modification of Saudi-Asphalt Binders Using SABIC Polymers

BY

ISAM ABAKER MOHAMMOD

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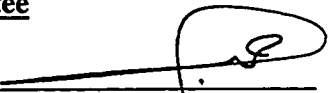
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THESIS ABSTRACT

Name : Isam Abaker Mohammad
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Asphalt binder is a thermoplastic liquid, which behaves as elastic solid at low service temperatures or during rapid loading. At high temperature or slow loading, it behaves as a viscous liquid. This classical dichotomy creates a need to improve the performance of the asphalt binder to minimize the cracking stresses that occur at low temperatures and plastic deformations at high temperatures. The use of polymer-modified asphalt binder is one of the solutions to meet the required performance standards for the pavements. It appears to be logical, practical, and economical approach.

In the Kingdom, most of the used asphalt-polymers are imported from abroad, which led to increase in the total construction cost. The main objective of this research is to modify locally produced asphalt using polymers produced by Saudi Basic Industries Company (SABIC). The study covered the asphalt binders produced by the Riyadh and Ras Tanura refineries. Ten polymers were identified as potential asphalt modifiers based on their physical properties and chemical composition. These polymers were screened into four types which were used to modify the asphalt. The results indicated that the rheological properties of the modified binders were improved significantly with sufficient polymer content (3%). The aging properties of the modified binders were found to be dependent on the type of the polymer. The fatigue life and resistance to permanent deformation were significantly improved due to the improvement in the rheological properties of the binders. In general, the research has shown the effectiveness of SABIC polymers in modifying local asphalts.

**MASTER OF SCIENCE DEGREE
KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
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خلاصة الرسالة

الإسم : عصام ابكر محمود

عنوان الدراسة : تحسين أداء الاسفلت السعودى بإضافة لدائن سابك

التخصص : هندسة مدنية – هندسة نقل

تاريخ الشهادة : نوفمبر 2002م

يعتبر الأسفلت من المواد المتغيرة بالحرارة فعند درجة الحرارة المنخفضة يكون سلوكه أشبه بالمواد الصلبة المرنة بينما يكون أشبه بالموانع اللزجة عند درجة الحرارة العالية وهذه الخاصية المزوجة جعلت من الأسفلت مادة غير متزنة حرارياً مما يؤدي الى بعض المشاكل المصاحبة لإستخدامه في رصف الطرق مثل التشققات عند درجة الحرارة المنخفضة والتخدد عند درجة الحرارة العالية مما تطلب الحاجة لتحسين خواص الأسفلت للتقليل من أثر تلك المشاكل ومن أحدى الطرق المستخدمة لتحسين خواص الأسفلت هي معالجته بإضافة اللدائن وقد وجد انها طريقة إقتصادية وعملية لتحسين الأسفلت.

تستخدم المملكة اللدائن المستوردة لتحسين خواص الاسفلت مما يزيد من التكلفة الكلية فى انشاء الطرق لذلك كان الهدف الأساسى لهذا البحث هو معالجة الأسفلت بإستخدام اللدائن المحلية فقد تم فى هذا البحث دراسة إمكانية إستخدام اللدائن المصنعة بواسطة الشركة السعودية للصناعات الأساسية (سابك) فى تحسين خواص الأسفلت حيث شملت الدراسة عشرة أنواع من وقد أظهرت الإختبارات المعملية وفقاً لمواصفات الخلطات المتميزة الأداء ان اربعة أنواع من هذه اللدائن يمكن إستخدامها وقد وجد ان اضافة اللدائن للاسفلت بنسبة كافيته (3%) تؤدي الى تحسين خواص التدفق والتشكل للخليط كما وجد ان معدل تصدق الاسفلت المحسن مع الزمن يعتمد على نوع اللدائن المضافة كما أظهرت النتائج أن مقاومة الخلطات المحسنة باللدائن ضد تشققات الكلال والتخدد قد تحسنت بصورة كبيرة كما و كما أظهرت الدراسة إمكانية استخدام لدائن سابك لتحسين خواص الأسفلت بالمملكة العربية السعودية.

درجة الماجستير فى العلوم الهندسية

جامعة الملك فهد للبترول والمعادن

الظهران، المملكة العربية السعودية

نوفمبر 2002م

Chapter 1

INTRODUCTION

1.1. PROLOGUE

Conventionally, hot mix asphalt concrete (HMAC) is composed of two materials: aggregate and asphalt binder. About 94 to 96% by weight of the mix consists of the aggregate, and the remaining 4 to 6 percentage by weight of the mix consists of the asphalt binder. Although the percentage of the asphalt binder is relatively small, the asphalt binders greatly influence pavement performance more than the aggregate because environmental factors, such as heat and sun radiation, affect the asphalt binder more than the aggregate.

The quality and quantity of the asphalt binder play significant role in the performance of the entire pavement structure. Specifications set forth by road agencies require asphalt binders to have a minimal damage effect by specifying and controlling some of their important physical properties. This was done to

minimize the inferior performance of pavement structures in the field and explains why researchers and engineers are focusing their attention on improving asphalt binder characteristics by using additives, modifiers, and modification processes.

The use of polymer-modified asphalt (PMA) to achieve better asphalt pavement performance has been observed for a long time. The improved functional properties include permanent deformation, fatigue, low temperature cracking, stripping, and aging. Most of the literatures showed that the properties of PMA are dependent on the polymer characteristics and content and bitumen nature as well as the blending process. Despite the large number of polymeric products, there are relatively few types which are suitable for bitumen modification. When used as bitumen modifiers, selected polymers should be compatible with bitumen, be capable of being processed by conventional mixing and laying equipment, and be able to maintain their premium properties during mixing, storage and application in service. The use of a modifier should also be cost-effective.

Two classes of polymers are typically used in asphalt modification: elastomers and plastomers. The relative usefulness of these polymers can vary widely. The main objective of this research is to modify and characterize the fundamental properties of bitumens supplied by both Riyadh (RY) and Ras Tanura (RT) refineries, by adding different thermoplastic polymers produced by SABIC. The factors affecting modification were also evaluated.

1.2. PROBLEM STATEMENT

Over the past 25 years, Kingdom of Saudi Arabia has invested more than SR 135 billions in road construction that were built to the best international standards. However, these roads have shown early signs of distresses due to the harsh environment and high traffic loads. The environmental variations, especially between summer and winter, and between day and night, are greatly affecting the durability of pavement's asphalt. The high pavement temperature in summer which may reach 73°C reduces the stiffness of paving mixture and consequently results in permanent deformation (Al-Abdul Wahhab et al., 1996). On the other hand, low pavement temperature in winter which may reach -10°C reduces the flexibility of the paving mixture; thus, thermal crack is likely to develop.

In addition, severe weather in some parts of the Kingdom has widely affected pavement performance and has resulted in pavement surface stripping. Moreover, stress on asphalt pavement due to the high growth rate in trucks weight, traffic volume, and tire pressure leads to an increased demand to modify asphalt binders by adding additives, such as polymers, fibers, and hydrocarbons. Although there have been previous works performed on the modification of local asphalt with polymer, all polymers used to modify local mixes were imported and expensive (\approx 7500 SR/ton). No attempt was made to explore cheaper, indigenous

polymers produced by SABIC. In this research, the suitability of using local polymers in asphalt modification was investigated. In addition, the possible improvement on asphalt mixes was defined. The modification effectiveness was judged through the degree of improvement in resistance to temperature effect, and load distress including fatigue and rutting. Use of local polymers is expected to reduce considerably construction and maintenance costs of local highways.

1.3. OBJECTIVES

The objective of this study is to modify locally produced asphalt from both RY and RT refineries using local polymer produced by SABIC. This required specific steps to study the potential of using locally produced polymer to improve the performance grade of local asphalts as follow:

1. To select potential polymers produced by SABIC and screen them for the best four polymers to be used for asphalt modification.
2. To modify asphalt from RY and RT refineries with the selected polymers and identify the optimum polymer content and required blending time.
3. To determine performance grading and evaluate storage stability of the modified asphalts.

4. To evaluate suitability of improvement through the evaluation of indirect tensile strength, permanent deformation, and fatigue life of laboratory samples prepared according to the Ministry of Communications (MOC) mix specifications.
5. To provide modification procedure including optimum polymer content, mixing time and temperature.

Chapter 2

LITERATURE REVIEW

2.1. INTRODUCTION

The concept of modifying asphalt binders and mixtures is not new. Many researchers have studied the effects of mineral fillers on the behavior of asphalt (Al-Abdul Wahhab and Al-Amri, 1991; Bouldin et al., 1991 Sartori et al., 1996). The main reason for using these fillers and some other types of modifiers is to improve the performance of paving mixture in order to meet the requirements under the prevailing conditions.

Recently, a major work was carried out to adapt SHRP binder performance specifications for the Gulf Countries (GCs) environment (Al-Abdul Wahhab et al., 1996). In this work, the GCs were divided into different temperature zones and the required asphalt performance grade (PG) for each zone was specified. They

concluded that the asphalt cement as used locally is only suitable for about 40 percent of the GCs area. They found that the asphalt binder PG, required to meet the local environmental conditions, ranged between PG 64-10 and PG 76-10. Different modification procedures (ranging from air blowing to polymer modification) for the different asphalt binders produced in the GCs need to be performed in order that these asphalt binders are suitable for the areas of use (Al-Abdul Wahhab et al., 1996).

2.2. PERFORMANCE BASED BINDER SPECIFICATIONS

From October 1987 through March 1993, the Strategic Highway Research Program (SHRP) conducted a \$50 million research and developed performance-based specifications for binder that were intended to succeed the present penetration and viscosity grade asphalt specifications. These new specifications have taken the industry to a new level in the ability to characterize binders based on their relation to pavement performance. The new tests rank binders based on performance and improve the ability to select binders that will optimize cost effectiveness for the location, climate, traffic, and structure of the pavement. A PG 70 will perform far better in rut resistance than a PG 64. A PG 64-34 will be far less likely to crack than a PG 64-28 (D'Angelo and Fee, 2000). Thus, a precise

grade may be selected to accommodate for the need to control low temperature cracking, rutting or both in a particular construction project. In addition, it will address certain aspects of fatigue cracking. For a given type of asphalt cement to satisfy performance criteria for a given temperature zone, it must satisfy the SHRP performance tests which have to be conducted at certain designated temperatures. Details about the SHRP binder specifications and testing are given in elsewhere (Harrigan et al., 1994).

2.3. PERFORMANCE OF PMA

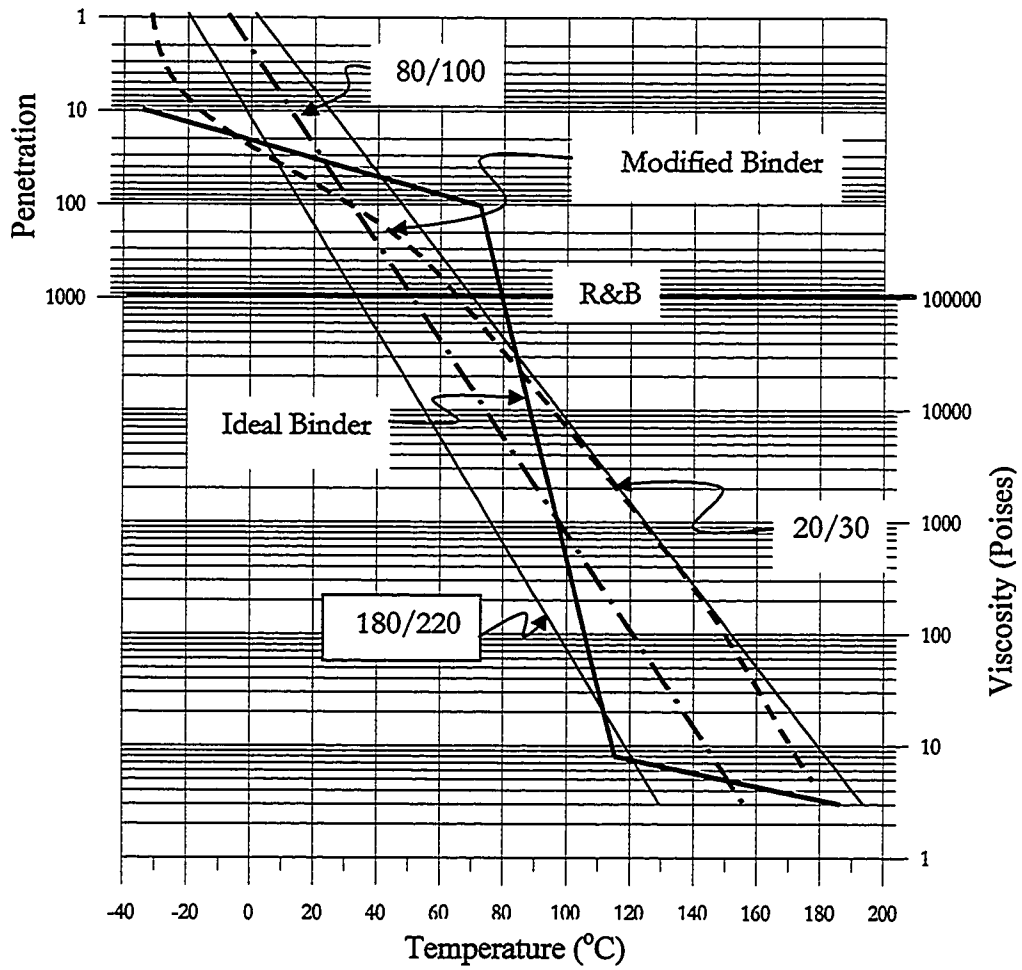
For the past two decades, significant research was conducted on PMA mixtures. It was found that polymers can successfully improve the performance of asphalt pavements at low, moderate, and high temperatures by increasing mixture resistance to fatigue, thermal cracking, and permanent deformation. In addition, it was found that the rheological and engineering properties of PMA mixtures largely depend on the polymer type and its content. The improvement in fatigue life and resistance to permanent deformation is related mainly to the improvement in the rheological properties of the binders (Khattak and Baladi, 2001). On the other hand, Airey and Brown (1998) stated that the rheological changes associated with Styrene Butadiene Styrene (SBS) modified asphalt can be linked to the

change in the molecular weight. When an asphalt binder is subjected to cyclic load or stress, the material response to tension and compression consists of three major components: elastic, viscoelastic and plastic. The plastic behavior, i.e. permanent strain or deformation, is responsible for the permanent deformation and consequently results in pavement rutting. On the other hand, a perfectly elastic material will never fail in fatigue. Polymer modification increases the elastic responses and dynamic modulus of bitumens at intermediate and high temperatures, and influences complex and stiffness moduli at low temperature (Isacsson and Lu, 1999). It also reduces the temperature susceptibility and glass transition and limits the stiffness temperatures of the bitumens. The degree of the improvement generally increases with polymer content, but varies with bitumen source and polymer type. Field tests performed by Joseph and Kennepohl (1996) showed that PMA has improved the rutting resistance of asphaltic concrete mix. Al-Dubabe et al. (1998) studied the possibility of using polymer to modify the Arab asphalt, and concluded that the change in the rheological properties due to modification is satisfying the performance requirement of the GCs. Bahia et al. (2001) concluded that PMA provides an added value to the asphalt's contribution to pavement performance. The majority of USA state highway agencies are planning on greater use of the modified asphalt to improve pavement performance.

Figure 2.1 shows schematically the consistency versus temperature for some models of bituminous materials (Diani et al., 1987). The temperature range has been divided into two parts, taking into account the service and processing conditions, respectively. The solid line shows the general shape of the consistency curve of an ideal material; consistency is slightly changed over the service range and suddenly drops in the processing temperatures. The behavior of real neat bitumen is quite different; its consistency decreases almost linearly when the temperature increases. Such a material is easy to process but shows too high thermal sensitivity at service conditions. However, for polymer-modified bitumen, the consistency-temperature curve closely approaches the ideal material behavior, combining satisfactory processability with quite constant performance at service conditions. In fact, the rheological behavior of the modified bitumen is completely different from that of neat bitumen and closely reflects the behavior of the material used for modification.

2.4. MICROSTRUCTURE OF PMA

In most cases, it has been found that the structure of the pure modified binder is completely different from the structure of the polymer in the asphalt-aggregate mixture (Wegan and Brule, 1999). While a continuous network of the



**Figure 2.1: Schematic rheological behavior of bitumen materials
(Diani et al; 1987)**

polymer phase could be detected in the binder, no continuous network of the polymer phase could be detected in the asphalt-aggregate mixture. This is the case with 7% Ethylene Vinyl Acetate (EVA) or SBS modified binder. However, for low polymer content (3%), the same structure of the polymer phase in the binder and in the asphalt-aggregate mixtures was reported. EVA seems to have an affinity for the surfaces of the aggregates. The EVA phase, swollen by a part of the maltenes, has a higher solubility parameter compared to the asphalt phase, and at equilibrium, surrounds the aggregate which has many polar groups.

In general, the morphology of the PMA can be demonstrated by using any magnification procedure. Brule et al. (1988) have suggested that optical microscopy is sufficient. McBee et al. (1981) used the scanning electron microscopy. Bouldin et al. (1991) used scanning transmission electron microscopy and fluorescence microscopy. Price and Burati (1990) studied the molecular distribution of the mixture using high-pressure gel permeation chromatography (GPC). Asi et al. (1997) studied the composition and molecular distribution of Arabian asphalt by using GPC. They characterized asphalts by separating them into generic fraction. The separation was based on separating hydrocarbon molecules by groups depending on their boiling ranges and molecular shapes. The separated materials were then purified and identified through physical and chemical methods.

2.5. FACTORS AFFECTING PMA PROPERTIES

Collins and Bouldin (1992) stated that the handling properties of the polymer-modified asphalt depend on the following factors:

- Asphalt type
- Polymer type and content
- Methods of modification

The effect of each factor is discussed in the following sections:-

2.5.1. ASPHALT

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 that occur in nature or are obtained in petroleum processing. The generic name “bitumen” refers to mixtures of hydrocarbons derived from natural or heterogeneous origins, or combinations of both, and which are completely soluble in carbon disulfide.

Asphalts are classified as either natural asphalts, which include native, rock, and lake asphalts, or artificial asphalts. Artificial asphalts include petroleum asphalts, which in contrast to native asphalts, are mostly organic with only trace

amounts of inorganic materials. Petroleum asphalts derive their characteristics from the nature of their crude origins, with some variation in composition and properties made possible by choice of manufacturing process.

Determination of the components of asphalts has always presented a challenge because of the complexity of the mixture, in which many different types of chemical species are present. For this reason, the composition of asphalts is usually investigated by analytical methods that separate the components into generic groups, such as by liquid chromatography, GPC, or ion exchange.

The structure of asphalt is viewed as a dispersion of highly associated, high molecular weight, polar aromatic hydrocarbons and heteroaromatics called “asphaltenes”, dispersed in a continuous oily phase medium called “maltenes” (ASTM D 8-91). The asphaltenes are not soluble in oils but are dispersed or peptized in the medium by lower molecular weight resins found in the maltenes.

Asphalt contains molecules with about 24 to 150 carbons. Some of the useful known chemical properties of asphalt, summarized by Goodrich and Dimpfi (1986), are as follows:

- Asphalt has significant heteroatom content. This includes nitrogen, oxygen, sulfur, vanadium, nickel, and iron.
- Heteroatoms play an important role in the physical properties of an asphalt.

The polar heteroatom-containing compounds are capable of intermolecular

associations that affect such physical properties as boiling point, solubility, and viscosity. These polar compounds tend to be concentrated in the asphalt fraction of a crude oil.

- The molecular weight of asphalt compounds ranges from about 300 to 2000. Yet, as a result of molecular associations, asphalt behaves as if it has a much higher molecular weight.
- Aging of an asphalt is associated with oxidation. An increase in the polar fractions on aging, among other things, results in increased asphalt viscosity.
- The composition, rheology, and durability of an asphalt are unique to the crude blend from which the asphalt was refined. Yet, asphalts from many sources perform well in roads.

Thus, one of the important factors affecting the behavior of the asphalt molecules between each other and with surfaces and/or molecules from other materials such as aggregate is the presence of heteroatoms, which are referred to as functional or polar groups. Thus, polarity is due to an imbalance of electrochemical forces within the molecule, which produces a dipole. The dipole molecule has both electropositive and electronegative characteristics like a magnet having both north and south poles. This dipole tends to cause molecules to organize themselves into preferred structural orientations. This structure is held

together by electrostatic and other short-range forces, which are weak, compared to covalent chemical bonds. Short-range (non-covalent) forces range from about 1 to 10 kcal/mole, while covalent bonds between two carbon atoms are more than 80 kcal/mole and between carbon and hydrogen are ~100 kcal/mole (Branthaver et al., 1993). It follows then that the organized structure may be subject to rearrangement or may be scrambled either from physical stress or by increased temperature. This will not be associated with chemical changes while as the molecular species remain the same, although it will affect the physical properties. Therefore, the more randomized the structure of the molecules of the asphalt, the weaker will be the bonds and the lower will be the viscosity of the asphalt.

Depending on the polarity of asphalt molecules, asphalt can be defined as a collection of polar and non-polar molecules. The polar molecules tend to associate strongly to form organized structures throughout the continuous phase of the non-polar materials. On the other hand, the non-polar phase has the ability to disassociate the organized structure, which varies from one asphalt to another (Branthaver et al., 1993). The oxidation of asphalt leads to increases in both the amount of polarity and the number of polar sites present among asphalt molecules. Plancher et al. (1977) used the model of polarity of asphalt molecules to explain the bonding between asphalt and aggregate. This model suggests that some of the polar heads of the organic components find themselves near the aggregate surface

and bind to it, allowing their less polar tails to extend into the asphalt matrix.

Due to the large number of molecules in the asphalt with different chemical structures, chemists haven't attempted to separate and identify all the different molecules present in the asphalt. All efforts have been focused on trying to separate or characterize asphalt by determining different groupings or generic fractions based on polarity, reactivity, and/or the molecular size of the various molecular types present in the asphalt.

In addition, asphalts can be classified as gel or sol types. Gel asphalt contains relatively large quantities of asphaltenes (20 to 35%), which are not well peptized and which associate to form an extensive network. This network is responsible for the asphalt's non-Newtonian behavior. Sol-type asphalt contains a lower amount of well-dispersed asphaltenes (5 to 10%) and exhibits Newtonian flow (Little et al., 1986).

A road paved with a gel-type asphalt is more resistant to high temperature deformation (rutting) than a road paved with a sol-type asphalt, but at low temperatures it can be more brittle and less resistant to cracking (Sustic, 1993).

2.5.2. Polymers

Polymers can possess a wide variety of properties depending on the monomers, the way the molecules are linked, and the chemical process used in

their manufacture. Some are much stronger than steel, others can be made into very lightweight foams. The word polymer is a combination of two Greek words “polys” and “meros”. “Polys” means numerous, and “meros” means part; therefore, polymer is a compound of numerous parts. Actually, a polymer is a large molecule which consists of one or more repeating units linked together by covalent bonds. Table 2.1 shows a typical polymer’s chain.

Most of the well-known polymers available in today’s market have been categorized as follows (Button, 1992):

- Styrene Butadiene Rubber (SBR)
- Block Copolymers
 - Tailback Styrene-Butadiene-Styrene (TSBS)
 - Radial block Styrene-Butadiene-Styrene (RSBS)
- Styrene-Butadiene-Vulcanized (SBV)
 - Styrene-Isoprene-Styrene (SIS)
 - Styrene-Ethylene-Butylenes-Styrene (SEBS)
 - Styrene-Ethylene-Propylene-Styrene (SEPS)
- Polyethylene
- Ethylene Vinyl Acetate (EVA)
- Polypropylene
- Crumb Tire Rubber

Table 2. 1: The repeating units within the polymer.

Polymer	Monomer	Repeating unit
Polyethylene	$CH_2 = CH_2$	$-CH_2 - CH_2 -$
Polyisobutylene	$\begin{array}{c} CH_3 \\ \\ CH_2 = C \\ \\ CH_3 \end{array}$	$\begin{array}{c} CH_3 \\ \\ CH_2 - C - \\ \\ CH_3 \end{array}$
Polyacrylonitrile	$CH_2 = CH - CN$	$\begin{array}{c} - CH_2 - C - \\ \\ CN \end{array}$
Polyvinyl chloride	$CH_2 = CH - Cl$	$\begin{array}{c} - CH_2 - C - \\ \\ Cl \end{array}$
Polystyrene	$CH_2 = CH - C_6H_5$	$\begin{array}{c} - CH_2 - CH \\ \\ C_6H_5 \end{array}$
Poly(methyl methacrylate)	$\begin{array}{c} CH_3 \\ \\ CH_2 = C \\ \\ CO_2 - CH_3 \end{array}$	$\begin{array}{c} CH_3 \\ \\ CH_2 - C - \\ \\ CO_2 - CH_3 \end{array}$
Polyvinyl acetate	$CH_2 = CH - OCOCH_3$	$\begin{array}{c} - CH_2 - CH \\ \\ OCOCH_3 \end{array}$
Polytetrafluoroethylene	$\begin{array}{cc} F & F \\ & \\ C = & C \\ & \\ F & F \end{array}$	$\begin{array}{cc} F & F \\ & \\ -C - & C- \\ & \\ F & F \end{array}$
Polyformaldehyde (acetal)	$CH_2 = O$	$-CH - O -$
Polyisoprene	$\begin{array}{cc} CH_2 & CH_2 \\ & \\ C - & CH \\ & \\ CH_3 & \end{array}$	$\begin{array}{cc} -CH_2 & -CH_2 \\ & \\ C = & CH \\ & \\ CH_3 & \end{array}$

- Polychloroprene latex
- Polychloroprene solids
- Natural Polyisoprene
- Synthetic Polyisoprene
- Ethylene Polyene-Diene-Monomer (EPDM)

Some of these products are used routinely in bituminous paving mixtures; others are still in the experimental stage.

Brule et al. (1988) indicated that blocks polymers of butadiene and styrene are the most effective materials for converting asphalt binder into a rubber-like material. At ambient temperature, a blend of asphalt binder with a 10 to 14 percentage by weight of butadiene-styrene block copolymer exhibits a multi-phase morphology. The first is a polymer swelled with some of the lower molecular weight constituents of the asphalt (oils and resins), and the second is an asphalt phase enriched in asphaltenes. Within the polymer-rich phase, there are two phases. This is due to the increase in the polymer concentration. The first is swollen polybutadiene, and the second is pure polystyrene domains. If the polymer-rich micro-phase dominates, then the system will act like rubber and show rubber-like elasticity and almost complete recovery of deformation. However, at low polymer concentrations, the polymer-rich phase will result in

disunited particles, and the system will behave like asphalt with enhanced consistency and elastic properties.

Al-Abdul Wahhab et al. (1996) have studied several commercial polymers for their ability to improve Arab asphalts to meet the Gulf specific environmental conditions. They concluded that PMA properties depend not only on asphalt type but also on polymer type. They found that for asphalt from Riyadh refinery, the use of SBS at 3% by weight gives satisfactory results, while the required amount of crumb rubber tires (CRT) was found to be 10% by weight when used with Ras Tanura asphalt; only 5% was required when asphalt from Al-Ahmedi refinery was used.

2.5.3. Polymer Content

Since a modified binder consists of two distinct phases, two cases must be considered (Brule, 1996):

Case 1: The polymer content is low. In this case, the bitumen is the continuous phase of the system, and the polymer phase is dispersed through it. With its lower oil content, the bitumen phase has correlatively higher asphaltene content; its cohesion and elasticity are both enhanced as a result. At high service temperatures (around 60°C), the stiffness modulus of the polymer phase is higher than that of the matrix. These reinforcing properties of the polymer phase enhance the

mechanical performance of the binder. At low temperatures, the stiffness modulus of the dispersed phase is lower than that of the matrix, which reduces its brittleness. It can therefore be seen that the dispersed polymer phase enhances the properties of the binder both at high service and low temperatures. In this case, the choice of bitumen is the determining factor.

Case II: The polymer content is sufficiently high. In general, if the bitumen and polymer are correctly chosen, the polymer phase will be the matrix of the system. This is, in fact, not bitumen but a polymer plasticized by the oils in the bitumen in which the heavier fractions of the initial asphalt cement are dispersed. The properties of such a system are fundamentally different from those of bitumen and depend essentially on the properties of the polymer. One should speak not of a polymer-modified bitumen but of a thermoplastic adhesive.

2.5.4. Methods of Modification

The modification of asphalts by various additives, such as high molecular weight compounds, requires the recognition of critical phenomena like the miscibility of the composition's components (Zielinski, 1994). One must also recognize how to obtain specific properties based on such modification. Methods whose purpose is to contribute suitably beneficial properties are defined as either chemical or physical methods.

2.5.4.1. Chemical Methods

Chemical methods rely upon the action of molecules or chemical compounds with the constituents of asphalt, which bring about changes in the asphalt's chemical composition. These include reaction with oxygen, sulfur, sulfur dioxide, and chlorine. Various properties are thus obtained from such a treatment. These methods, especially oxidation, have been applied in industry for many years to obtain oxidized asphalts from petroleum residues. A separate problem is the chemical modification of asphalt based on the direct acquisition of polymers in an asphalt environment. Several types of polymer reaction are listed below (Zielinski, 1994).

Radical polymerization: in the early past, scientists used experiments dedicated to the polymerization of styrene in an asphalt environment as a basis. He promoted the idea of inhibiting the reaction using asphaltenes.

Polymerization via an ionic approach: obtaining an asphalt-polybutadiene composition in the presence of an alkali metal catalyst.

Polycondensation: reactions with phenol-type compounds found in tars produced from the alkylations of propylene with benzene; direct reactions with formalin in asphalt tedium.

Polyaddition: experiments performed on an asphalt-polyurethane

composition, obtained by an addition reaction in a molten asphalt environment. It was found that the reaction for the formation of polyurethane in asphalt occurs without difficulty and with high yields when run at 145°C for 2–6 hours.

Copolymerization: experiments performed by irradiating an aqueous dispersion of vinyl monomer in direct contact with road asphalt, or methacrylate, with visible light of a chosen wavelength.

2.5.4.2. Physical Methods

Physical methods are based on mixing asphalt with inert chemical additives but changing the composition's properties. For example, bitumen can be modified with inorganic substances, primarily of mineral origin, such as talc or chalk (used as fillers), as well as organic materials like oil based plasticizers, antioxidants, and polymers (Zielinski, 1994).

Among the various physical methods, two different paths to asphalt modification by polymers can be distinguished. In the first path, no further modification can be made when the polymer content is in the range of 10–20 %. Most of the applications of these materials are as adhesives in highway engineering. The second path involves obtaining mixtures of composite materials, which contain asphalt, polymers, fillers, plasticizers, and other components. Materials of this type are not dominated by the contents of one of the components

and find applications in the construction industry and in motorization as well as in other specific disciplines. Another related path is modifying polymers through the addition of petroleum asphalts (e.g., filling and plasticizing). The range of investigations in this last area is not large; applications are similar to those that have already been discussed.

2.6. COMPATIBILITY

Compatibility can be defined as the state of dispersion between two dissimilar components. The compatibility of polymer-modified asphalt (PMA) was shown to be largely dependent on polymer content and influenced by the characteristics of base bitumens and polymers. Brule (1996) found that if, without taking any special precautions, a road bitumen and a given thermoplastic polymer are mixed hot, one of the following three results occurs:

1. The mix is heterogeneous: This is most likely the result (i.e., where the polymer and the bitumen prove to be incompatible). In this case, the constituents in the mix separate and the mix has none of the characteristics of a road binder.
2. The mix is totally homogenous, including at the molecular level: This is the infrequent case of perfect compatibility. In this case, the oils in the bitumen

dissolve the polymer perfectly and destroy any intermacro molecular interaction. The binder is extremely stable, but the modification of service qualities with respect to those of the initial bitumen is very slight. Only its viscosity increases; this is, therefore, not the desired result.

3. The mix is micro-heterogeneous and is made up of two distinct finely interlocked phases: This is the compatibility sought and gives the bitumen genuinely modified properties. In such a system, the compatible polymer swells by absorbing some of the oily fractions of the bitumen to form a polymer phase distinct from the residual bitumen phase comprising the heavy fractions of the binder (the rest of the oils plus the resins and asphaltenes).

Isacsson and Lu (1999) used fluorescence microscopy to study the morphology and compatibility of polymer-modified binders. The modified binder was illuminated using a blue light for excitation. The fluorescent yellow light re-emitted by the swollen polymer phase was observed using one optical microscope.

2.7. STORAGE STABILITY

Isacsson and Lu (1999) stated that the PMA may separate into polymer-rich and asphaltene-rich phases during hot storage. Storage stability decreases with increasing polymer contents. For modified binder with low polymer content (3%),

almost no phase separation was observed. Storage stability was determined for SEBS, SBS, and EVA. Better storage stability was observed with lower vinyl acetate (VA) content in the EVA copolymer.

Since many PMAs display phase separation, some agitation is recommended during the storage of hot blends but it may lead to oxidative degradation of the polymer. Wegan and Brule (1999) recommended that for optimal performance at elevated temperatures, the selected polymer should be able to form a continuous elastic network when dispersed in bitumen. The rheological changes are consistent with the degradation of polymers and oxidation of bitumen. An increasing content of functional groups may change bitumen polarity and molecular association. As a result, compatibility (microstructure) between the polymer and bitumen is changed. On the other hand, the breakdown of the polymer reduces the number of large polymer molecules, and consequently, the effectiveness of the polymer in modifying bitumen rheology is reduced. The rheological changes in aged modified binders are dependent on a combined effect of bitumen oxidation and polymer degradation, which varies with types of bitumen and polymer as well as polymer contents. The chemical interaction and structural buildup of the polymer phase in a PMA are influenced by several factors. It is well known that mechanical treatment and mixing temperature affect the quality of the polymer-modified asphalt (PMA). In addition, the cooling rate influences how the

polymer structures in the binder during placement and compaction of the final asphalt pavement. Moreover, oxidation and degradation during mixing, storage and transportation of the hot mix asphalt greatly affect the stability state of the PMA. The chemical interaction of the polymer phase and the surface of the mineral aggregates also greatly affect the structure of the PMA and finally the performance of the asphalt mixture. It is impossible to predict this effect by only looking at the structure of the pure polymer-modified binder.

Bahia et al. (2001) recommended the Laboratory Asphalt Stability Test (LAST) to evaluate the storage stability of the modified asphalt. This test depends on the rheological properties before and after conditioning at temperature and agitation conditions that simulate field conditions. They recommended that the frequently sweep tests at high and intermediate temperatures should be determined.

2.8. BLENDING

2.8.1. BLENDING MECHANISM

Blending of asphalt binders with high molecular weight materials, such as polymers, is not a steady and easy operation since two heterogeneous materials are

forced together to form a two-phase system. The polymer is required to disperse and not to dissolve in the base asphalt binder. Therefore, it is recommended that the blender be capable of providing high shear rate (Al-Dubabe et al., 1998). The configuration of the blender head (i.e. blade) and the speed of blending define the level of shear rate that the blender induces into the asphalt binder. To ensure that high shear blending is obtained, the recommended speed should not be less than 3000 rpm. However, some polymers, such as SBS, do not require high shear blenders although blending time can be reduced by their use. For each modifier, the method of mixing and handling is known either from experience or from supplier's recommendations (Terrel and Epps, 1989).

Collins and Bouldin (1992) blended the polymer with asphalt by blending the highest polymer concentration with the asphalt binder. This way, they developed a master batch; then lower concentrations were obtained by diluting part of the master batch with neat asphalt under low shear mixing for 1.5 to 2 hours at 180°C. Stirring speed was adjusted, between 600 and 2500 rpm, during blending to provide good and consistent agitation without undue entrapment of air.

Al-Abdul Wahhab et al. (1996) assembled a special blender comprising of a high shear blade, a heated oil bath, and a DC motor capable of producing up to 2500 rpm. Each polymer type was blended with 800 gm of asphalt binder to produce the polymer-modified asphalt binder.

2.8.2. BLENDING TIME

The blending time, which depends greatly on the blending shear rate and blending temperature, shall be kept to the minimum since economical, practical and technical issues could be affected by unnecessary long blending time. It was found that prolonged blending time besides being uneconomical is detrimental to the rheological properties of the modified binder (Brule et al., 1988).

Since blending time is dependent on the blender configuration and polymer type, Al-Abdul Wahhab et al. (1996) recommended that identification of the optimum blending time for a specific polymer type, blender head configuration, and speed can be done by monitoring the increase in the consistency such as softening point of PMA. They measured the softening point at uniform time intervals during the blending process (20 minutes). The blending process was ceased once the softening point stabilized and did not show significant increase with time. A plot of the blending time and softening point, such as that shown in Figure 2.2, was generated from which the optimum blending time was determined.

2.8.3. BLENDING TEMPERATURE

The blending temperature greatly depends on the molecular weight of the polymer. Generally, higher molecular weight polymers, require higher temperature

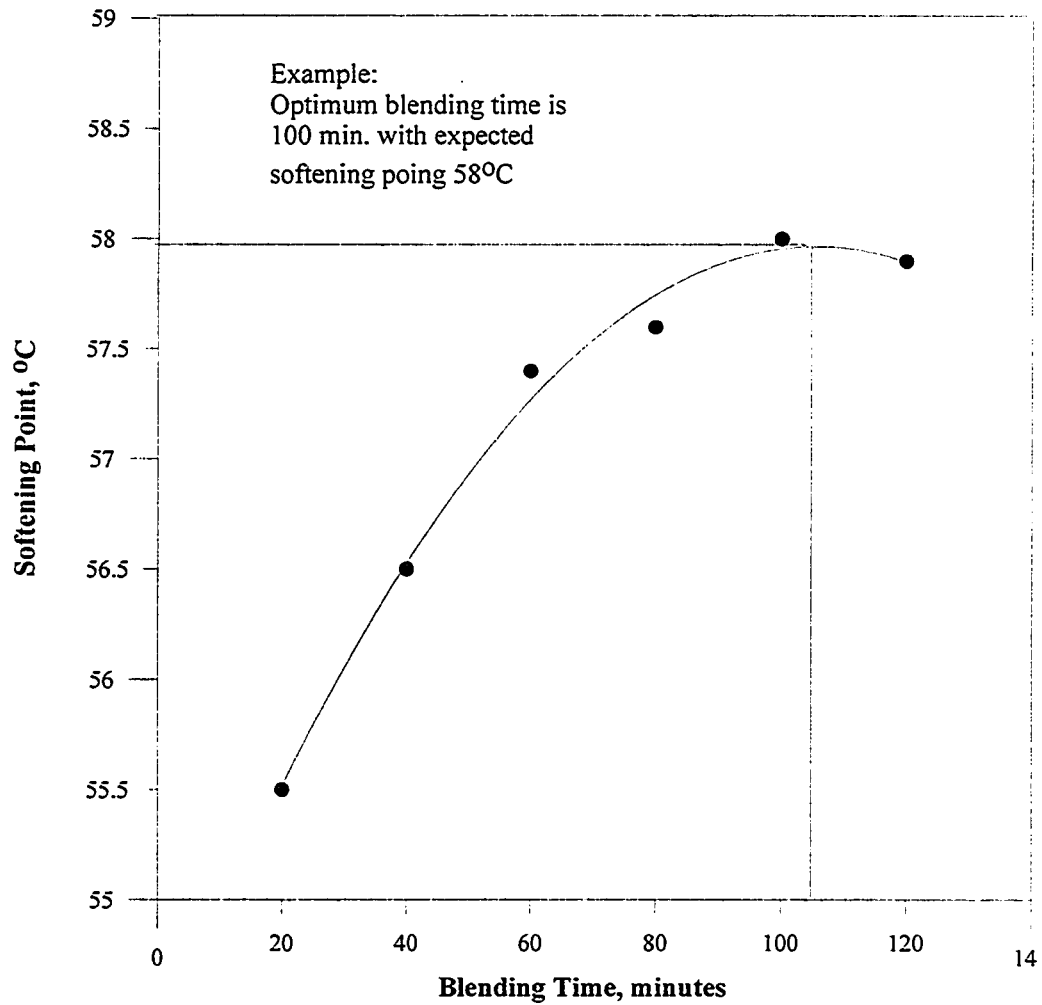


Figure 2. 2: Determation of the optimum blending time of typical asphalt using the softening point (Al-Abdul Wahhab et al., 1996).

than lower molecular weight polymers. Collins and Bouldin (1992) reported that no significant changes in the mean molecular weight of SBS polymers were observed during the blending process. However, temperature must be controlled to avoid excessive heating that might lead to degradation.

2.9. COMMON TYPES OF POLYMER-MODIFIED ASPHALT

2.9.1. Epoxy-Asphalt

Epoxies react with curing agents or hardeners to cross-link. They offer a unique combination of properties and characteristics, such as low curing shrinkage, no by-products of cure, chemical and environmental resistance, very good adhesion to many substrates, and excellent mechanical properties.

Epoxies contain a highly reactive ring called an “oxirane” or “epoxide” group (O dian, 1991). There are many types of epoxies, e.g., biphenyl alepichlorohydrin resin (aromatic), epoxy novalac resin, aliphatic epoxy, cycloaliphatic epoxy, highly functional resin, and high molecular weight linear epoxy resin. Aliphatic polyamines and their derivatives cure epoxies at room temperature. Examples are diethylenetriamine (DETA) and polyamides. Acid anhydrides, e.g., hexahydro-phthalic anhydride, are the second most commonly used curing agents. Aromatic epoxies are compatible and make asphalt rigid.

2.9.2. Polyurethane-Asphalt

Polyurethanes are formed by condensation of an isocyanate and a polyol (Saunders, 1973). The commonly used isocyanates are toluene diisocyanate (TDI), methylene biphenyl isocyanate (MDI), and polymeric diisocyanate (PMDI5). Polyols used with isocyanate are polymeric glycols based on polyesters, polyether, or hydroxylated acrylic. Polyesters, e.g., polyethylene adipate or phthalate, have free hydroxyl groups that can react with isocyanate. Polyethers are low molecular weight glycols usually based on polyalkylene oxides. Acrylics are usually low molecular weight resins containing a hydroxylated monomer, e.g., hydroxypropyl methacrylates. Tin compounds, e.g., dihydroxytin dilaurate, added to polyols catalyze the formation of urethane linkages as well as cross-link allophanate and biuret linkages for added rigidity.

2.9.3. Polysulfide-Asphalt

The highly reactive terminal mercaptans of liquid polysulfide polymers are converted into high molecular weight products at ambient temperature by oxidation or by reaction with other active polymers (Akmal and Usami, 1994). Polysulfides have excellent solvent resistance, predictable cure, good low temperature performance, good weathering, and excellent adhesion to many

substrates.

Polysulfide sealants have found wide acceptance in construction, aircraft, automotive, marine, and insulating glass applications. A typical liquid polysulfide, such as Thiokol LP-2 or LP-3, can be cured by 3% activated manganese dioxide. Asphalt and liquid polysulfide can be compounded with filler. The curative consists of MnO_2 plus cure modifiers.

2.9.4. Unsaturated Polyester-Asphalt

The usual unsaturated polyester resins result from the condensation of an aliphatic diol with an unsaturated dibasic acid or acid anhydride (Payne, 1984), specifically maleic anhydride. The unsaturated polyesters are generally solutions in a monomer that serves to cross-link the resin chains during the curing reaction. The most commonly reactive monomer is styrene, which is usually present in amounts ranging from 25 to 45%. Since all the styrene is consumed in the curing reaction, the unsaturated polyester resin is a 100% solid coating.

Free radical initiators, e.g., organic peroxides or hydro peroxides, are useful catalysts in curing unsaturated polyesters. A 60% solution of methyl ethyl ketone peroxide in dim ethyl phthalate produces room temperature cure. Cobalt naphthenate is an accelerator in curing.

Modification of asphalt with unsaturated polyester should be aimed at

developing coatings. Room temperature and elevated temperature curing coatings can result from unsaturated polyester modification of asphalt.

2.9.5. Phenolic-Asphalt

Phenolics result from condensation of phenol and formaldehyde and have many outstanding properties, e.g., chemical resistance and durability. Phenolics are used as molding compounds and as bonding agents in plywood, laminated sheets, foundry sand bonding, grinding wheel and friction brake elements, and coatings. Phenolics have been used successfully to bond bagasse and clay to produce roofing and building materials (Usmani and Salyer, 1982).

A phenolic powder resin can be slurried into molten asphalt and then allowed to convert to the desired form. Fillers, e.g., clays, calcium carbonate and sand, can be useful in molding and coating applications.

2.9.6. Polyester-Asphalt

Polyesters are condensation polymers obtained by reacting a polyol and a dibasic acid (Seymour and Carraher, 1992). Polyacrylates are aromatic polyesters of phthalic acids and bisphenols. Polybutylene terephthalate (PBT) is obtained by condensation of dimethyl terephthalate and 1, 4-butane-diol. PBT is highly

crystalline with a melting point of 440°F. Polyethylene terephthalate (PET) is widely used as fiber and film. Polyesters can be slurried into molten asphalt.

2.9.7. Rubber-Asphalt

Rubber modification of asphalt has been known for more than 100 years. The early interest was in caulking compositions and sealants. Current interest in this system is for paving and roofing (Usmani and Salyer, 1982).

Almost any type of rubber can be used, including ground rubber, vulcanized tire stocks, reclaimed (crumb) rubber, natural rubber, and various synthetic elastomers, e.g., SBS. The type of asphalt, type of rubber, method of rubber blending, and processing parameters determine the properties of rubberized asphalt. Rubber modification of asphalt usually produces softening point increase, hardness increase, reduction of cold flow properties, and improvement in low temperature brittleness.

Rubber can be added to asphalt in many ways. The easiest form of addition is as rubber latex. Latex is added to molten asphalt above the boiling point of water. Controlling foaming is essential. With a heavy-duty mixer, rubber can be directly added, although it is better to break down the rubber. Thermoplastic elastomers (TPEs) are appearing on the market now. Although they are more expensive now, the potential for obtaining improved products is good.

Synthetic and crumb rubbers are used as binders for paving. The presence of rubber improves resistance to compaction under heavy traffic, eliminates rutting and results in less “shoving” in areas that have stop-and-start traffic. Nitric rubberized asphalt can be developed for building paved areas with jet fuel resistance in airports. In a similar vein, a host of industrial products can be developed using asphalt as a filler.

2.9.8. Thermoplastic Olefinic (TPO)-Asphalt

TPOs are unique in that they are processed as thermoplastics yet produce properties similar to those of thermo sets. Recently, other researchers have introduced TPOs that could potentially modify asphalt. At present, they are more expensive than polypropylene. Also, these TPOs have high molecular weight. For asphalt modification, the molecular weight of TPOs must be lowered substantially. Roofing companies should work with manufacturers so that several grades of TPOs suitable for asphalt modification become available. Ultimately, TPOs will dominate asphalt modification (Usmani and Salyer, 1982).

Chapter 3

EXPERIMENTAL PROGRAM

3.1. INTRODUCTION

The work was divided into three phases; the first phase comprised of collection of asphalt from local refineries (Riyadh and Ras Tanura), and potential polymers from SABIC. In the second phase, the use of local polymers to modify the asphalt was evaluated based on Superpave binder performance specifications. In the third phase, polymer-modified asphalt was used to prepare hot asphalt concrete mixture (HACM) based on MOC mix specifications. The HACM was tested for fatigue, permanent deformation and environmental effect by using Lottman test. The flow chart in Figure 3.1 shows the sequence of the experimental program. The following paragraphs describe the steps in details.

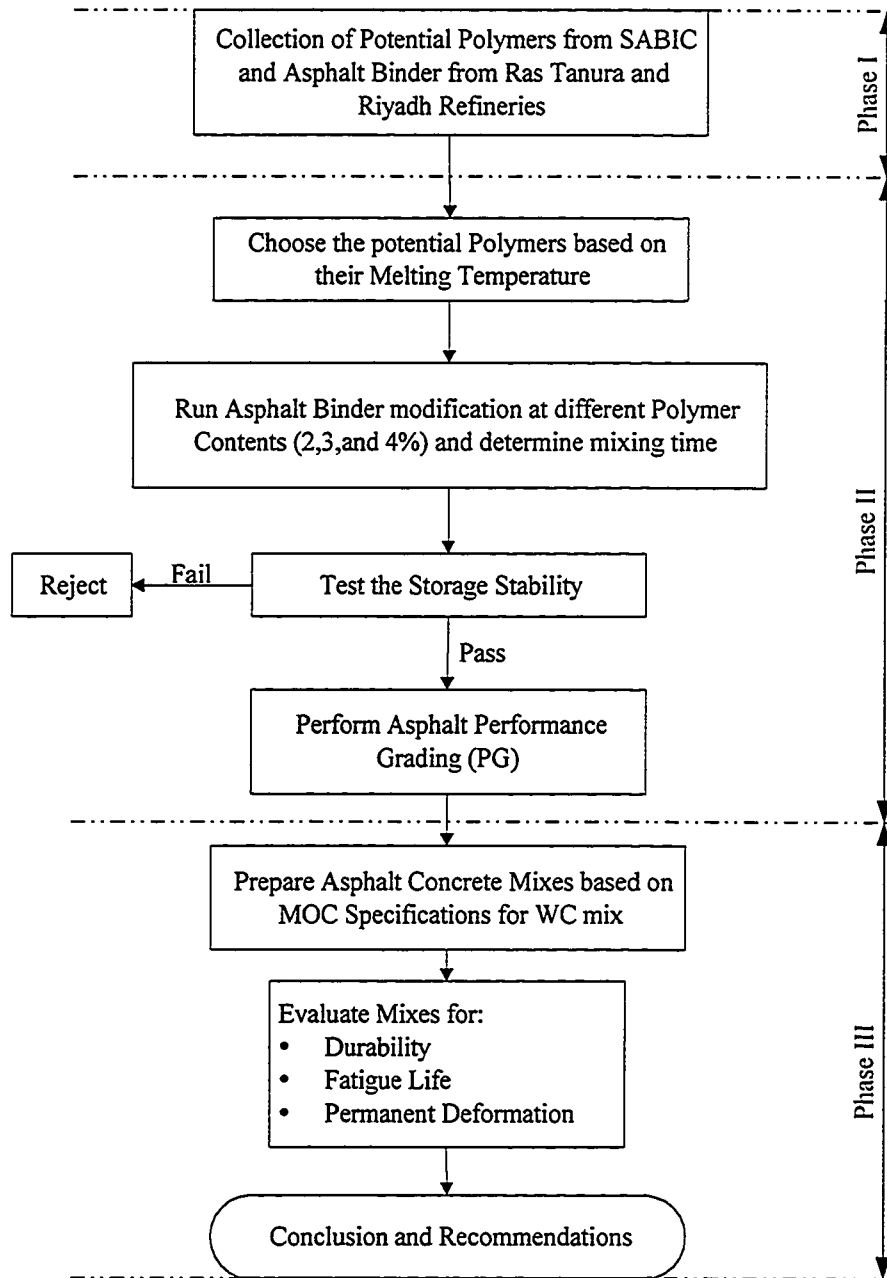


Figure 3. 1: Schematic work flow chart.

3.2. MATERIALS

Ten different grades of potential polymers were used in this study. These polymers were selected in cooperation with SABIC Research Group. They can be grouped into six main groups: linear low density polyethylene, high density polyethylene, low density polyethylene, medium density polyethylene, polypropylene and styrenic heavy waste. Table 3.1 shows the list of the selected polymers according to their grade.

A survey of the existing refineries in the Kingdom indicated that there are only two refineries that produce asphalt binder, namely: Riyadh and Ras Tanura refineries. Therefore, asphalt binder was collected from these refineries.

The coarse and fine aggregates used in the asphalt mixture were obtained from Abuhadryah, Eastern Province of Saudi Arabia.

3.3. ASPHALT MODIFICATION (BLENDING)

The suitability of the different polymers was determined based on their ability to improve the rheological properties of the virgin asphalt, which was collected from Riyadh and Ras Tanura refineries. In the initial stage, the required blending time was decided based on the relation between rutting parameter-

Table 3. 1: List of the selected polymers

SN	Commercial Name	M.I.* (g/10min.)	Density (g/cm ³)	Grade Code
1	Linear Low Density Polyethylene (LLDPE)	1	0.918	118N
2	" "	20	0.924	M200024
3	" "	50	0.926	M500026
4	High Density Polyethylene (HDPE)	0.05	0.952	F00952
5	" "	8	0.964	M80064
6	" "	20	0.956	M200056
7	Low Density Polyethylene (LDPE)	4	0.922	HP4023W
8	Medium Density Polyethylene (MDPE)	5	0.935	R50035
9	Polypropylene (PP)	3	--	500U
10	Styrenic Heavy Waste (SHW)	--	--	---

*M.I. = Melt Index

($G^*/\sin \delta$) at 76°C and blending time; testing at 76°C was selected since it represents the maximum asphalt performance grade temperature in the GCs (Al-Abdul Wahhab et al., 1996).

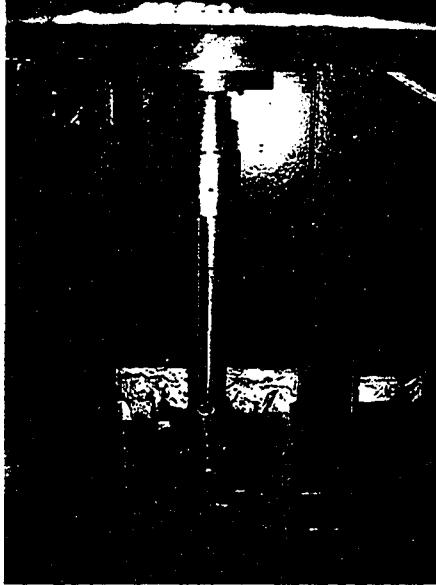
The blending temperature was determined based on the melting temperature of the polymers. The selected blending temperature was made equal to the melting temperature plus 5°C in order to ensure good dispersion of polymers. A special blender composed of high shear blade was used to blend the polymer with the asphalt; the blending speed was controlled with a Direct Current motor capable of producing up to 3000 rpm. The temperature was controlled through a heating oil bath, Figures 3.2 and 3.3 show the blending machine and its components. The PG of both neat and modified asphalt was also determined.

The optimum polymer content was selected based on the evaluation of different percentages of the polymer-asphalt binder blends through their improvements in the Superpave binder performance grade.

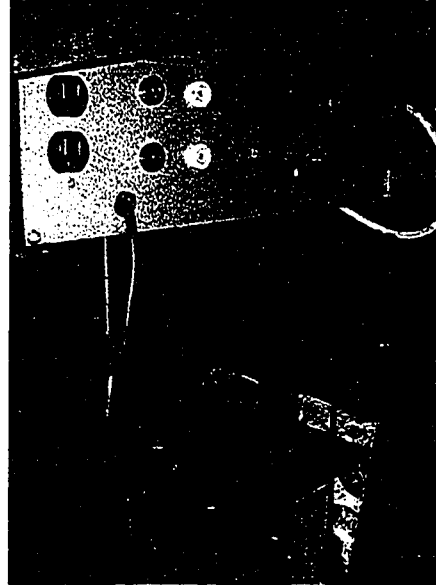
The third parameter which had been determined was the storage stability of the blends. Two major factors were evaluated in this test which includes:

- The effect of extended storage at high temperature in the range of 160 to 180°C
- The effect of mechanical agitation of the modified binders.

The test procedure was conducted at 160°C for 72 hours. The agitation speed was



The Blender



Blending machine

Figure 3. 2: Blending machine and its components.

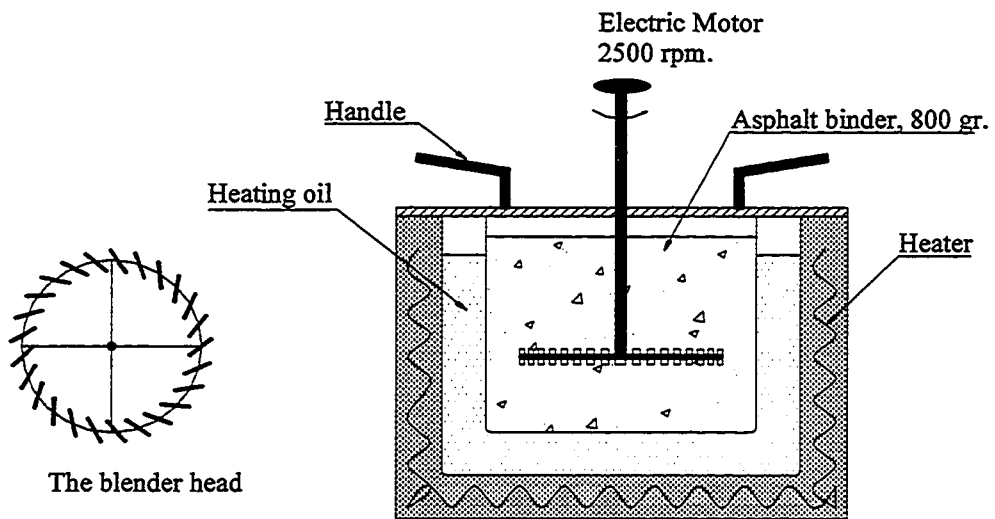


Figure 3. 3: Schematic diagram for the blending machine.

fixed to be 500 rpm. The criterion for determining the storage stability is based on conducting Dynamic Shear Rheometer (DSR) at high temperature of pavement design as recommended by Bahia et al. (2001). In addition, Rotational Viscosity (RV) was added as a new measurement for storage stability to ensure adequate pumpability of the binder after the storage time. The ratio of separation under agitation condition was calculated. The binder is considered stable if the percent loss in RV and $G^*/\sin \delta$ is less than 20%.

Using the information gathered from the field (actual tanks sizes, agitation speeds, and storage temperature), a typical vertical tank was scaled down, Figures 3.4 and 3.5. Its temperature was controlled by using an oil bath heater. The dimensions are such that a sample of 800 ml is used and sampling is done periodically using a pipette from the top and bottom of the container without stopping the conditioning. The storage stability of the modified asphalt binders was evaluated according to the Laboratory Asphalt Stability Test (LAST) procedure (Bahia et al., 2001). The rheological properties before and after conditioning at temperature and agitation conditions that simulate field conditions were measured. Then, the ratio of separation and gradations was calculated. Bahia, 2001, stated that its acceptable limits are from 0.8 to 1.2. Table 3.2 shows the experimental design for binder testing.

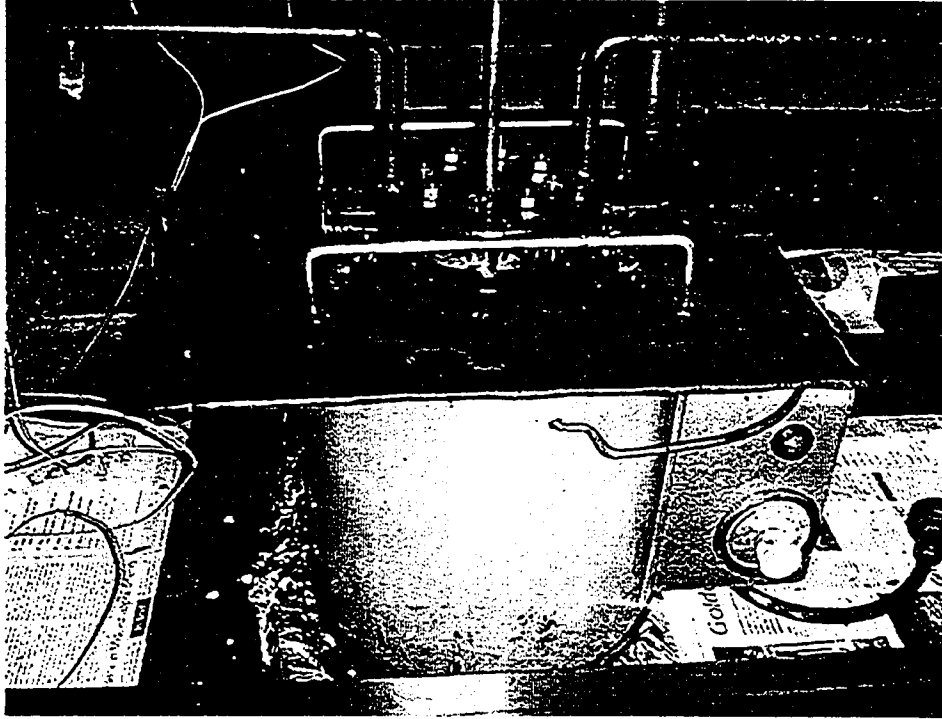


Figure 3. 4: The storage stability machine.

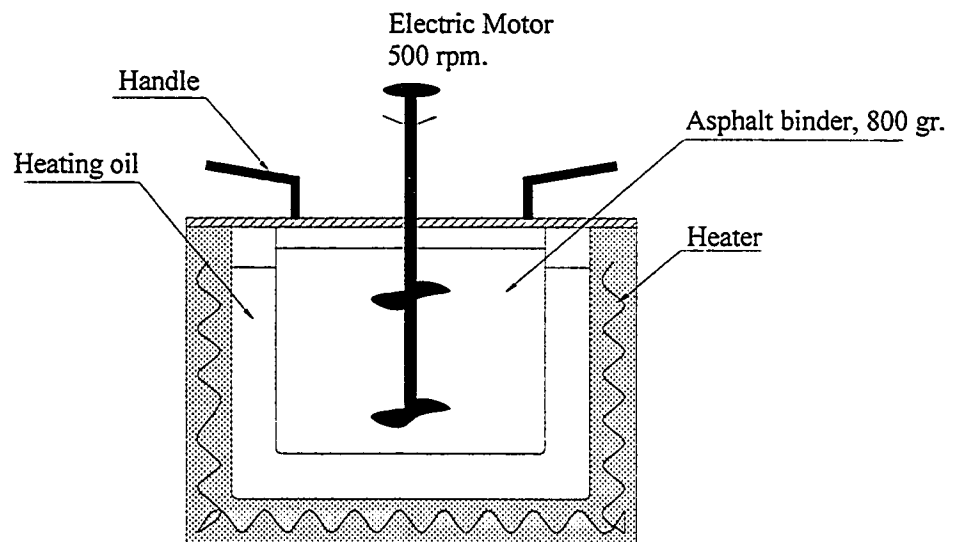


Figure 3. 5: Schematic diagram for the storage stability test machine.

Table 3. 2: Experimental design for binder testing.

Binder type	Polymer type	Polymer content	Blending (DSR @ 30 minutes intervals @ 76°C)	Storage stability				DSR after RTFO	DSR after PAV	Creep test (BBR)		PG Grading
				DSR @ 76°C						S-value	m-value	
				Top	Bottom	Top	Bottom					
RY	P0	0%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		2%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		3%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
	P1	4%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		2%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		3%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
	P2	4%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		2%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		3%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
	P3	4%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		2%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		3%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
P4	4%	✓	✓	✓	✓	✓	✓	✓	✓	✓		
	2%	✓	✓	✓	✓	✓	✓	✓	✓	✓		
	3%	✓	✓	✓	✓	✓	✓	✓	✓	✓		
RT	P0	0%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		2%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		3%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
	P1	4%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		2%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		3%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
	P2	4%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		2%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		3%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
	P3	4%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		2%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
		3%	✓	✓	✓	✓	✓	✓	✓	✓	✓	
P4	4%	✓	✓	✓	✓	✓	✓	✓	✓	✓		
	2%	✓	✓	✓	✓	✓	✓	✓	✓	✓		
	3%	✓	✓	✓	✓	✓	✓	✓	✓	✓		

3.4. PREPARATIONS AND TESTING OF ASPHALT CONCRETE MIXES

3.4.1. Introduction

To evaluate the effectiveness of polymer modification, asphalt concrete mixes were prepared according to the Ministry of Communications (MOC) specifications for asphalt mix design. The following tests were carried out in order to fully evaluate the polymer-modified mixes and to compare it with control mix:

1. Lottman test for durability (AASHTO T-283-89),
2. Resilient modulus test (ASTM D 4123),
3. Fatigue test, and
4. Permanent deformation (rutting test).

3.4.2. Mix design

Asphalt concrete mix has been designed following Marshall Mix design as per MOC specifications.

The optimum asphalt content obtained through Marshall mix design for wearing course is used for preparing control mix and polymer-modified asphalt concrete specimens. Table 3.3 shows the required number of specimens per test.

Table 3. 3: Required number of specimens per test.

Binder type	Polymer type	Required Number of Specimens				Total number of specimens
		MR @ 25 and 50°C	Fatigue and Rutting @ 25 and 50°C	Lottman Test	Marshall Stability	
RY	P0	18*	18	6	6	30
	P1	18*	18	6	6	30
	P2	18*	18	6	6	30
	P3	18*	18	6	6	30
	P4	18*	18	6	6	30
RT	P0	18*	18	6	6	30
	P1	18*	18	6	6	30
	P2	18*	18	6	6	30
	P3	18*	18	6	6	30
	P4	18*	18	6	6	30
Total						300

*The same specimen was used in fatigue and rutting tests.

Appendix B shows the mix design results. The standard Marshall specimens of 100 mm × 62.5 mm were prepared separately for each polymer and control mix.

3.4.3. Water sensitivity test (Lottman Test AASHTO T-283-89)

This test is used to test asphalt concrete mixtures to determine the potential for moisture damage utilizing Indirect Tensile Strength (ITS). The degree for susceptibility to moisture damage is determined by preparing a set of laboratory-compacted specimens. The set is divided into two subsets of approximately equal void content. One subset is maintained dry (Initial), while the other subset is partially saturated with water and moisture conditioned (Final). The tensile strength of each subset is determined by the tensile splitting test. The potential for moisture damage is indicated by the difference in the tensile strength of the wet subset to that of the dry subset.

3.4.4. Resilient modulus test, M_R (ASTM D 4123)

The resilient modulus of pavement materials is an important input item for design of flexible pavement structures. It is the measure of pavement response in terms of dynamic stresses and corresponding strains. It is measured by applying a vertical load along the diameter of a specimen and measuring the resulting elastic

horizontal deformation as shown in figure 3.6. The value of resilient modulus is used to evaluate the relative quality of materials as well as to generate input for pavement design or pavement evaluation and analysis.

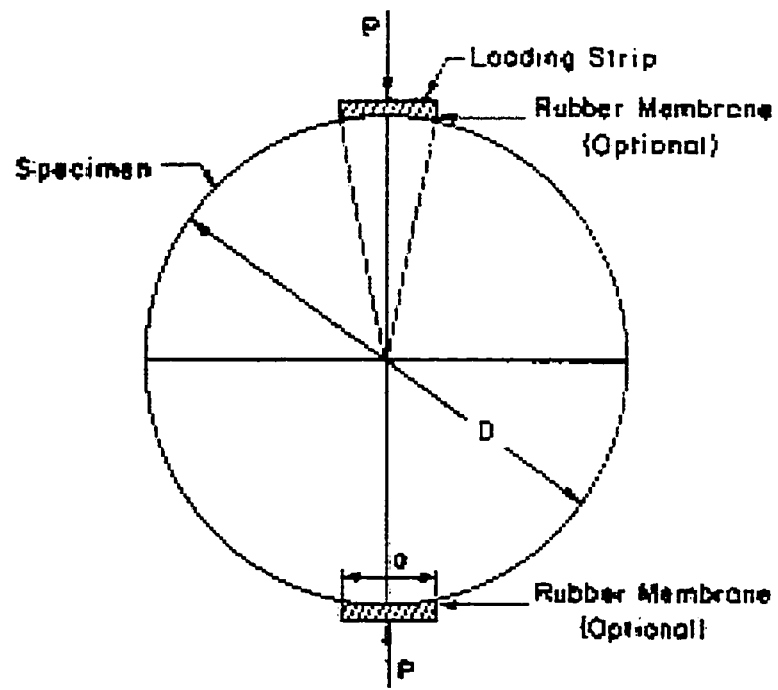


Figure 3.6: Indirect tension loading.

Chapter 4

RESULTS AND DISCUSSION

4.1. INTRODUCTION

This chapter provides detailed laboratory testing, analysis, and discussion of the test results performed in this research. In addition, it contains a through discussion about the performance requirements.

4.2. IDENTIFICATION OF POTENTIAL POLYMERS

4.2.1. Blending Temperature

The melting temperature of the polymer was determined in order to specify the blending temperature. The first five polymers which have the lowest melting temperature have been chosen to be used in the asphalt blends. Table 4.1 shows the five selected polymers based on their melting temperatures.

Table 4. 1: Selected types of polymer based on melting temperatures.

SN	Commercial Name	M.I.* (g/10min.)	Density (g/cm³)	Grade Name	Code Name
1	Linear Low Density Polyethylene (LLDPE)	50	0.926	M200026	P5
2	Medium Density Polyethylene (MDPE)	5	0.935	R50035	P6
3	Linear Low Density Polyethylene (LLDPE)	20	0.924	M200024	P7
4	High Density Polyethylene (HDPE)	20	0.956	M200056	P8
5	High Density Polyethylene (HDPE)	8	0.964	M80064	P9

*M.I. = Melt Index

4.2.2. Blending Time

Dynamic shear modulus ($G^*/\sin \delta$) at 76°C was used as a measure to monitor the consistency of asphalt-polymer blend during blending (Appendix A shows the test procedure). The shear modulus at 76°C was selected since it represents the highest PG temperature required in the GCs. The shear modulus was monitored during the blending at intervals of 30 minutes. The $G^*/\sin \delta$ at 76°C versus time of blending for each asphalt-polymer blend is graphically presented in Figures 4.1 to 4.4 for RY asphalt, and in Figures 4.5 to 4.8 for RT asphalt. It was reorganized that the $G^*/\sin \delta$ at 76°C exhibits an increase as the asphalt binder molecular association due to polymer addition increases. Once a uniform dispersion of the polymer within the body of the asphalt is achieved, the $G^*/\sin \delta$ stabilizes and becomes steady. Examining Figure 4.1 (Eg. P5-3%), it can be seen that after about 30 minutes of blending time, the $G^*/\sin \delta$ curve reaches a constant value. This means that the minimum blending time for polymer P5 at concentration of 3% is 30 minutes. This concept was used to identify the minimum blending times for all of the asphalt polymer blends.

Moreover, the minimum polymer content can be determined from the graphs of concentration versus $G^*/\sin \delta$ (Figures 4.9 and 4.10). The target $G^*/\sin \delta$ is 1 kPa.

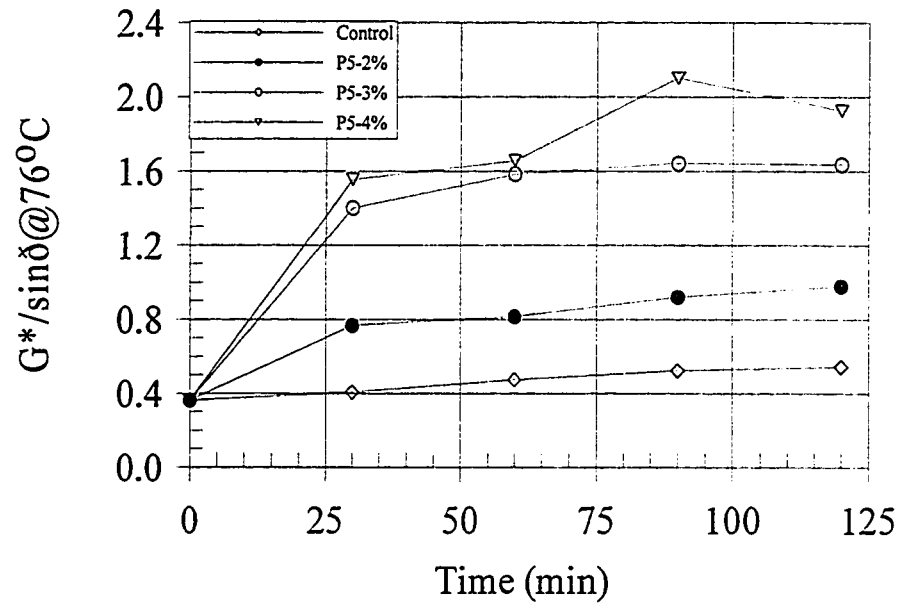


Figure 4. 1: The effects of blending time on $G^*/\sin \delta$ (P5-RY).

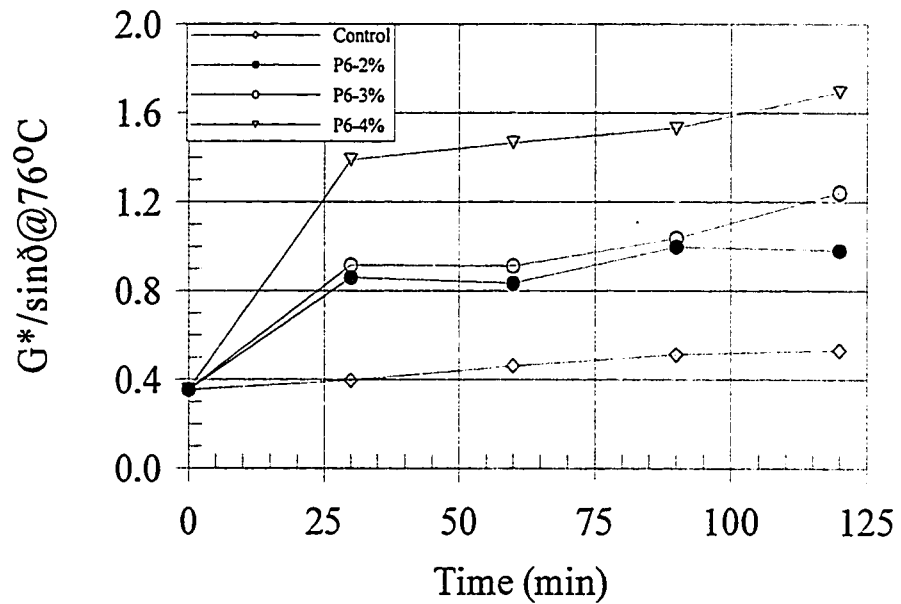


Figure 4. 2: The effects of blending time on $G^*/\sin \delta$ (P6-RY).

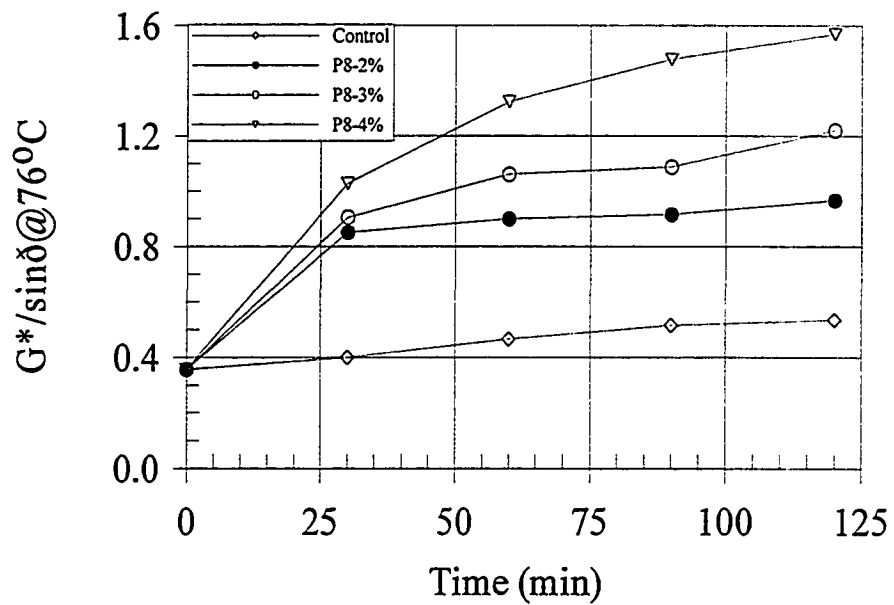


Figure 4. 3: The effects of blending time on $G^*/\sin \delta$ (P8-RY).

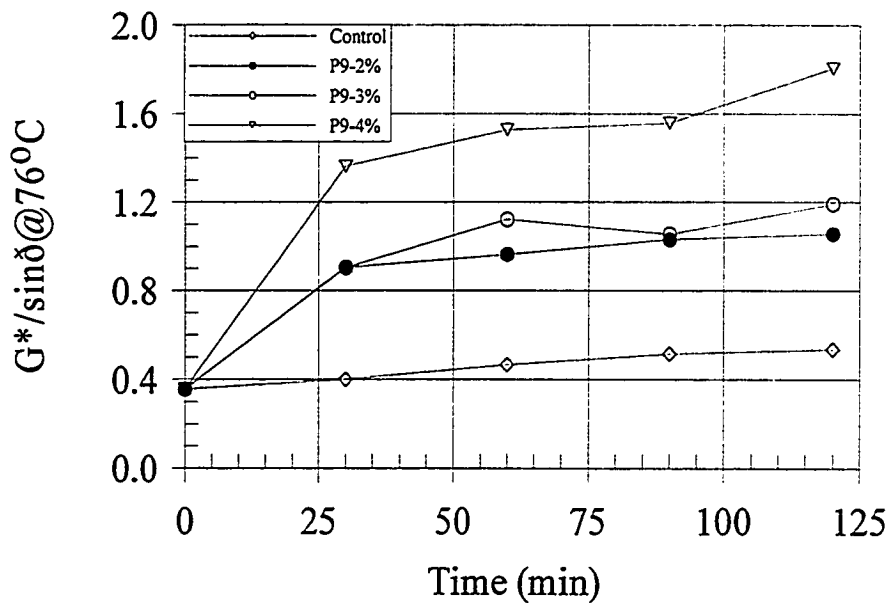


Figure 4. 4: The effects of blending time on $G^*/\sin \delta$ (P9-RY).

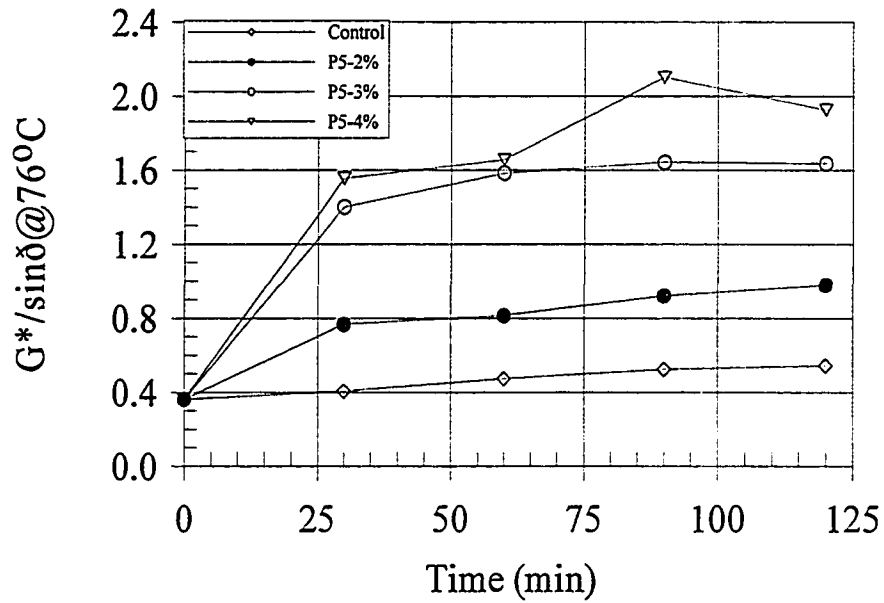


Figure 4. 5: The effects of blending time on $G^*/\sin \delta$ (P5-RT).

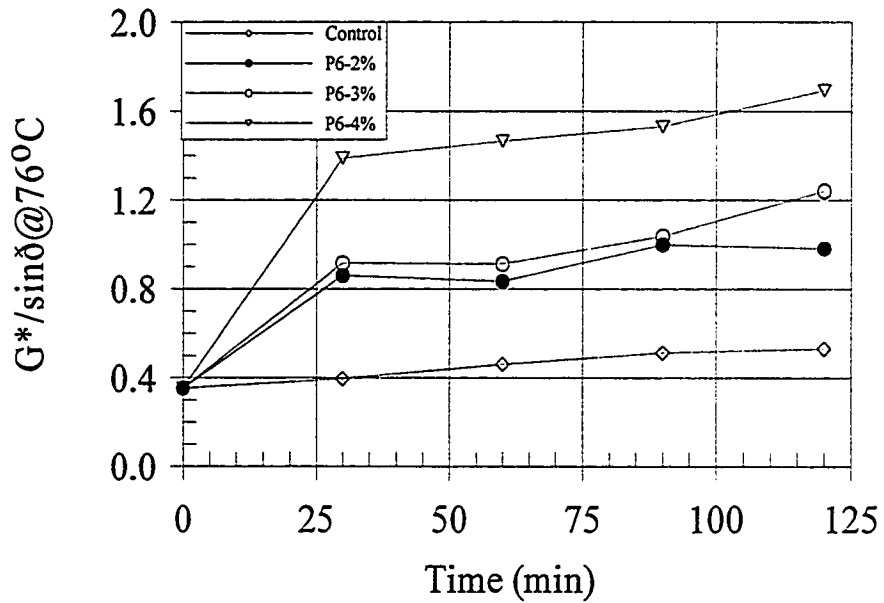


Figure 4. 6: The effects of blending time on $G^*/\sin \delta$ (P6-RT).

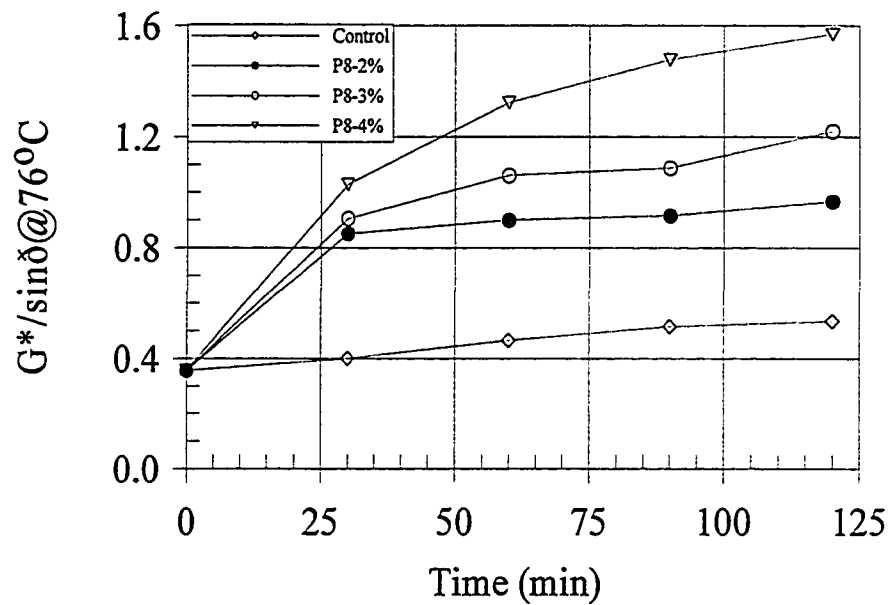


Figure 4. 7: The effects of blending time on $G^*/\sin \delta$ (P8-RT).

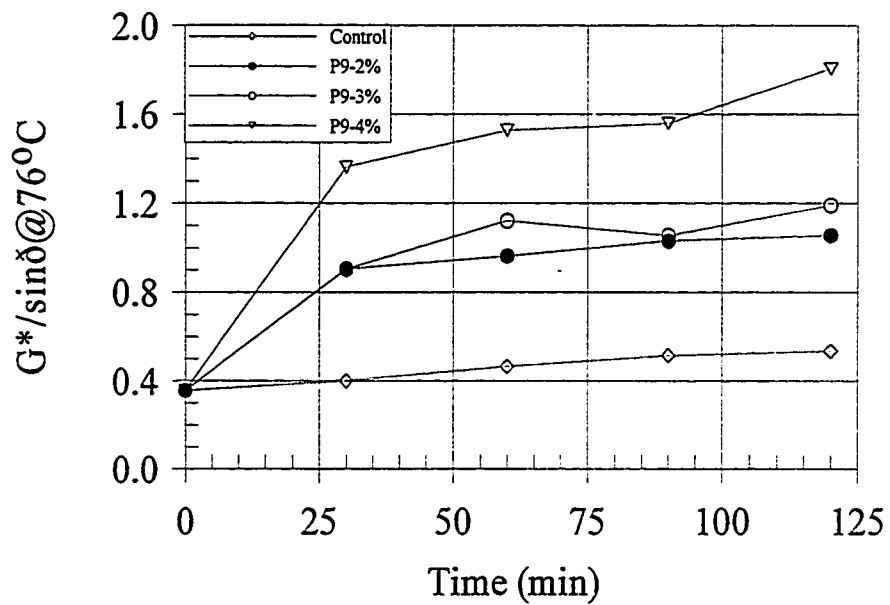


Figure 4. 8: The effects of blending time on $G^*/\sin \delta$ (P9-RT).

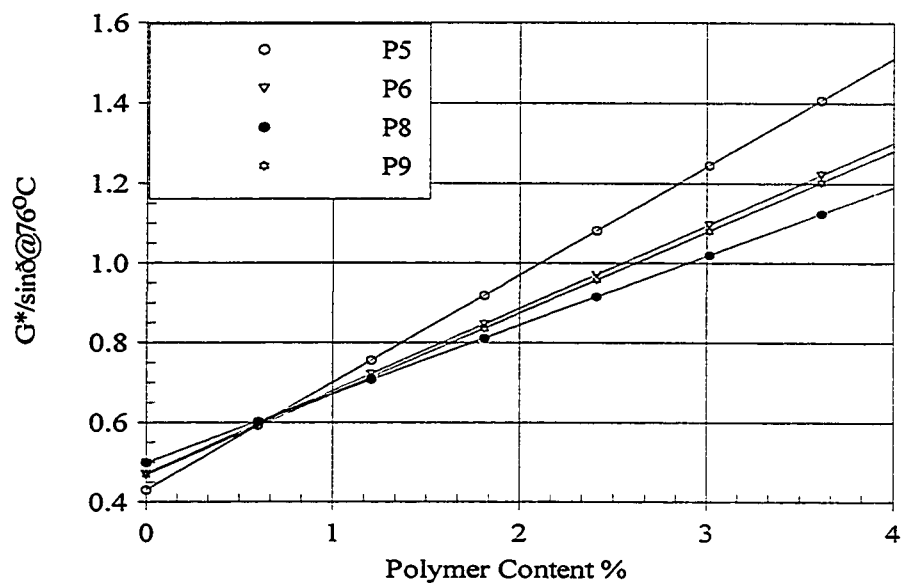


Figure 4. 9: The effects of the polymer content on $G^*/\sin \delta$ (RY).

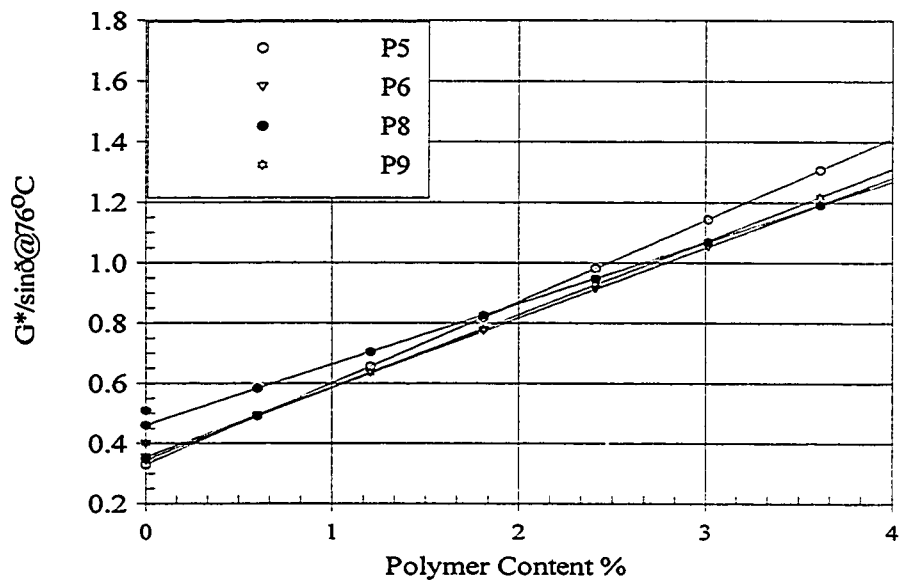


Figure 4. 10: The effects of the polymer content on $G^*/\sin \delta$ (RT).

The results showed that the required P8 content, for example, should be 1.7% with RY asphalt while it should be 2.5% with RT asphalt in order to achieve the target $G^*/\sin \delta$ at 76°C. However, additional amount may be required to achieve the other specifications.

4.2.3. Storage Stability

The modified asphalt was stored in hot storage condition to find the effect of modification on the required storage and handling properties of the end product. The storing temperature was 160°C similar to the storing condition in the field. Continuous stirring was applied during the storage time. Two samples were taken from the upper and lower points of the storage container. The storage stability was measured based on the difference in $(G^*/\sin \delta)$ of the upper and lower samples. The polymer content was fixed to be 3% for all mixtures because it was estimated, from Figures 4.9 and 4.10, that the 3% polymer content is satisfactory to improve the RT asphalts' grade to PG 76-10 while 2.0 is required to rise RY grade to PG 76-10.

Table 4.2 shows the storage stability results. The results are also graphically presented in Figures 4.11 to 4.12. The results show that P7 has higher separation potential; therefore, it is rejected to be used in the blend.

Table 4. 2: Storage stability results.

Asphalt Type		RY			RT		
Polymer Type	Time (hr)	G*/sin δ kPa		Loss %	G*/sin δ kPa		Loss %
		Top	Bottom		Top	Bottom	
P5-3%	0	1.635	1.635	0.000	1.425	1.425	0.000
	24	1.896	2.016	5.952	1.623	1.803	9.980
	48	2.543	2.896	12.189	2.171	2.236	2.900
	72	3.177	3.786	16.086	2.526	2.674	5.510
	RV after 72 hours	2436	2596	6.163	2037	2062	1.210
P6-3%	0	1.241	1.241	0.000	1.108	1.108	1.108
	24	1.203	1.256	4.220	1.101	1.139	3.370
	48	1.288	1.378	6.531	1.212	1.292	6.650
	72	1.639	1.811	9.498	1.547	1.635	5.360
	RV after 72 hours	2768	2808	1.425	2237	2250	0.580
P7-3%	0	1.381	1.381	0.000	1.337	1.337	0.000
	24	1.750	2.011	14.914	2.942	3.024	2.720
	48	4.490	7.626	69.844	3.154	19.229	83.600
	72	8.109	13.776	69.885	5.648	21.331	73.520
	RV after 72 hours	3202	5732	79.013	3737	6062	38.350
P8-3%	0	1.219	1.219	0.000	1.081	1.081	0.000
	24	1.550	1.568	1.148	1.123	1.155	2.780
	48	2.455	2.517	2.463	2.235	2.271	1.550
	72	3.678	3.987	7.750	4.477	4.742	5.590
	RV after 72 hours	2635	2799	5.859	2485	2490	0.200
P9-3%	0	1.191	1.191	0.000	1.056	1.056	0.000
	24	1.973	2.011	1.890	1.602	1.861	13.930
	48	2.513	2.713	7.372	2.713	2.927	7.290
	72	3.149	3.500	10.029	3.164	3.497	9.530
	RV after 72 hours	3210	3350	4.179	2795	2850	1.930

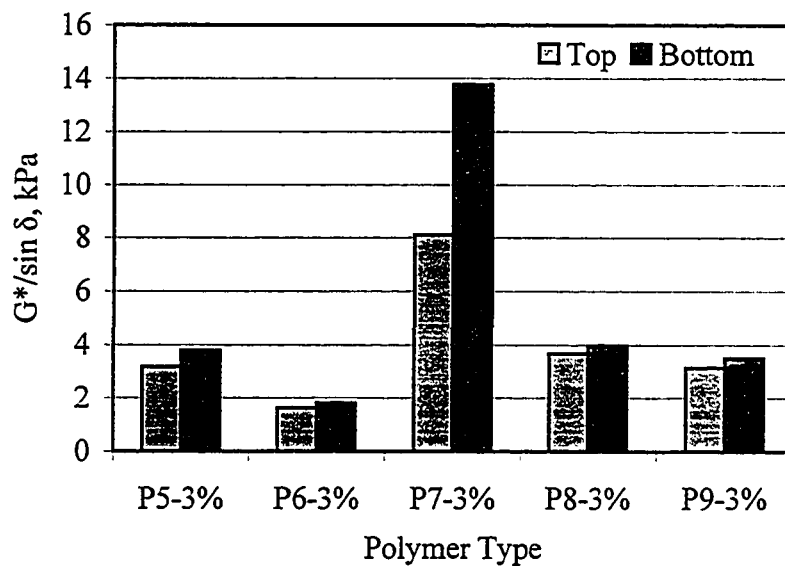


Figure 4. 11: Measured storage stability through the DSR properties after 72 hours storing time (RY).

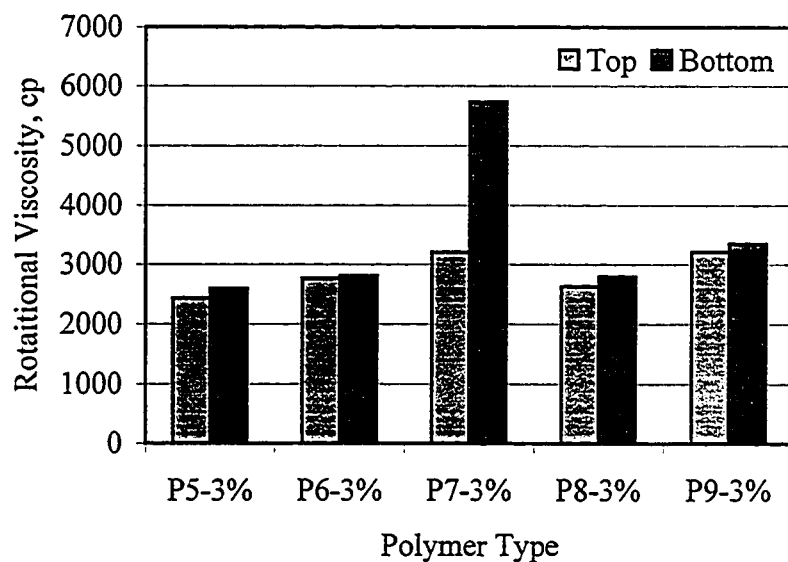


Figure 4. 12: Measured storage stability through the RV properties after 72 hours storing time (RY).

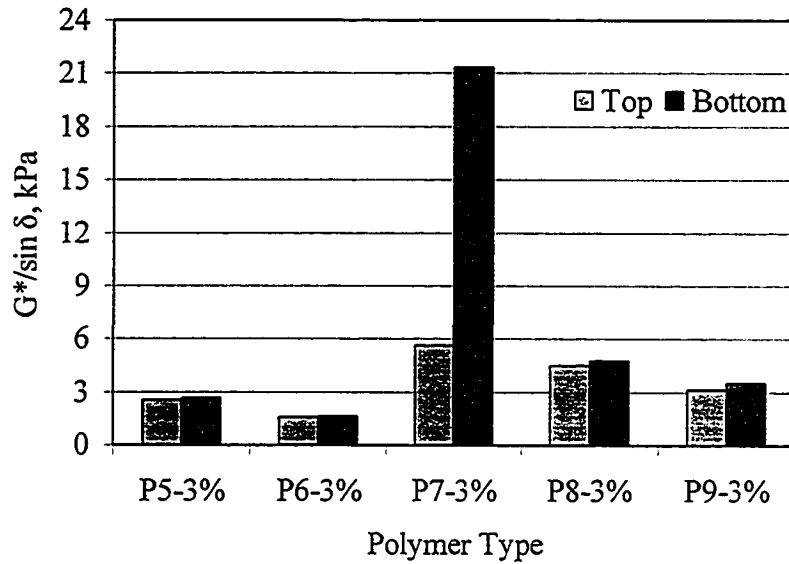


Figure 4. 13: Measured storage stability through the DSR properties after 72 hours storing time (RT).

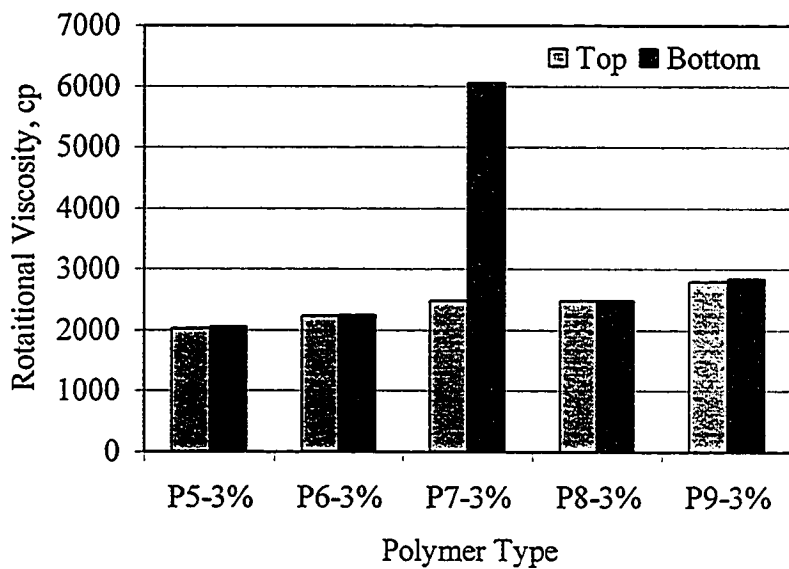


Figure 4. 14: Measured storage stability through the RV properties after 72 hours storing time (RT).

4.2.4. PG and Rheological Properties

The SHRP binder specification was implemented to find out which polymer is satisfying the specifications. The PG system considers asphalt binder as a linear viscoelastic material whose properties change with temperatures and loading times. The SHRP binder characterization test procedures include Dynamic Shear Rheometer (DSR), Bending Beam Rheometer (BBR), and Direct Tension Test (DTT). The parameters obtained from DSR test are as follows:

- Complex shear modulus, $G^* = \text{peak stress/peak strain}$
- Phase angle, δ (defined as the phase difference between stress and strain)
- Shear storage modulus, $G' = G^* \cos \delta$
- Shear loss modulus, $G'' = G^* \sin \delta$
- $G^*/\sin \delta$

The output of BBR, which evaluate the low temperature creep stiffness properties of the asphalt binders, are the creep stiffness (S) and the creep rate (m -value). The creep rate is the slope of log stiffness versus log loading time at 60-second time. These parameters (S and m) were measured on the aged, RTFO aged, and the PAV aged binder. In addition, the rotation viscosity test was performed on the fresh binder at 135°C. Table 4.3 shows typical PG process for RY-P5-2%.

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Table 4. 3: Riyadh asphalt + 2% P5 @ 180°C blending temperature.

Grade	Original	RTFO	RTFO+PAV					
	Flash Point: Vis@135 1212	Loss						
	Dynamic Shear 10rad/s	Dynamic Shear 10rad/s	Dynamic Shear 10rad/s		Flexural Creep			DT
	$G^*/\sin\delta$ >1.0kPa	$G^*/\sin\delta$ >2.2kPa	Temp. °C	$G^*\sin\delta$ <5MPa	Temp. °C	Stiffness <300MPa	Slope >0.3	Strain >1.0%
PG 58			25		-6			
			22		-12			
			19		-18			
			16		-24			
			13		-30			
PG 64			28		-6			
			25		-12			
			22		-18			
			19		-24			
			16		-30			
PG 70	<i>1.213</i>	<i>4.235</i>	34		0			
			31	<i>3.3071</i>	-6			
			28	<i>3.9218</i>	-12	<i>87350</i>	<i>0.313</i>	
			25	<i>4.5560</i>	-18	<i>108653</i>	<i>0.283</i>	
			22	<i>5.2130</i>	-24			
PG 76	<i>0.814</i>		37		0			
			34		-6			
			31		-12			
			28		-18			
PG 82			40		0			
			37		-6			
			34		-12			
			31		-18			

The final PG for all samples is shown in Table 4.4. The results show that polymer types P5, P6, P8 and P9 are satisfying the performance requirements based on PG with percentage of 3%, 2%, 2% and 2% respectively when blended with RY asphalt, while they are satisfying the PG with percentage of 3% when blended with RT asphalt.

It is noticeable that an increase in polymer content caused an increase in creep stiffness and a decrease in m -value. It appears that higher polymer content reduced the resistance against low temperature cracking.

4.3. PREPARATIONS AND TESTING OF ASPHALT CONCRETE MIXES

4.3.1. Introduction

Asphalt concrete mix has been designed following Marshall Mix design as per MOC specifications. The optimum asphalt content obtained through Marshall Mix design for wearing course is used for preparing control mix and polymer-modified asphalt concrete specimens. The standard Marshall specimens of 100 mm × 62.5 mm were prepared separately for each polymer and control mix. The prepared specimens were tested for resilient modulus at two different temperatures and three strain levels; also, resistance to fatigue and rutting was evaluated.

Table 4. 4: PG-Grading for RY and RT blends.

Asphalt Type		RY	RT
Polymer type	Polymer Content (%)	PG	PG
P5	0	PG 70-10	PG 64-22
	2	PG 70-22	PG 70-22
	3	PG 76-16	PG 76-10
	4	PG 82-10	PG 76-10
P6	0	PG 70-10	PG 64-22
	2	PG 76-22	PG 70-22
	3	PG 76-16	PG 76-16
	4	PG 76-10	PG 76-10
P8	0	PG 70-10	PG 64-22
	2	PG 76-22	PG 70-22
	3	PG 76-22	PG 76-10
	4	PG 82-16	PG 76-10
P9	0	PG 70-10	PG 64-22
	2	PG 76-16	PG 70-22
	3	PG 76-10	PG 76-10
	4	NA	PG 76-10

4.3.2. Water Sensitivity Test (Lottman Test AASHTO T-283-89)

This test was carried out in order to find the water susceptibility (stripping resistance) of modified and control mixes utilizing Indirect Tensile Strength (ITS). The results obtained indicated that the average percent loss in strength due to water damage was effectively reduced when P8 modified asphalt concrete mix was used. The percent loss in P5, P6, and P9 were less than the percent loss in the control mix but still they were higher than the recommended limit based on Superpave specification (20%). Table 4.5 and Figure 4.15 show the percent loss in the indirect tensile strength after Lottman conditioning of the samples. The results indicate significant improvement of stripping resistance of local mixes when P8 is used to modify the asphalt.

Generally, the ITS results of both RY and RT asphalt seem to be the same except when polymer type P9 is used. The percent loss in ITS of P9-RY is almost 50% of the percent loss of P9-RT. This indicates that P9 is somehow more effective when used with RY asphalt.

Table 4. 5: Indirect Tensile Strength test results.

Asphalt Type	Polymer Type	Condition	Sample No.			Average	Loss%	
			1	2	3			
RY	Control	Initial I.T.S	11.1	10.42	9.23	10.25	48.8	
		Final I.T.S	5.51	4.98	5.26	5.25		
	P5-3%	Initial I.T.S	15.51	16.2	15.28	15.66	28.6	
		Final I.T.S	9.75	10.35	13.45	11.18		
	P6-3%	Initial I.T.S	16	15.6	14.2	15.27	32.7	
		Final I.T.S	11.2	10.45	9.16	10.27		
	P8-3%	Initial I.T.S	13.52	12.65	12.68	12.95	16.3	
		Final I.T.S	10.31	11.42	10.8	10.84		
	P9-3%	Initial I.T.S	13.56	14.17	13.21	13.65	39.9	
		Final I.T.S	8.52	7.77	8.32	8.2		
	RT	Control	Initial I.T.S	10	9.12	8.37	9.16	56.17
			Final I.T.S	3.23	4.05	4.77	4.02	
P5-3%		Initial I.T.S	18.51	18.01	15.28	17.27	39.15	
		Final I.T.S	8.72	9.35	13.45	10.51		
P6-3%		Initial I.T.S	14.99	14.76	13.16	14.3	37.31	
		Final I.T.S	8.26	10.45	8.19	8.97		
P8-3%		Initial I.T.S	13.28	11.65	12.31	12.41	25.89	
		Final I.T.S	8.31	11.42	7.87	9.2		
P9-3%		Initial I.T.S	13.56	15.17	14.16	14.3	65.12	
		Final I.T.S	5.81	4.87	4.28	4.99		

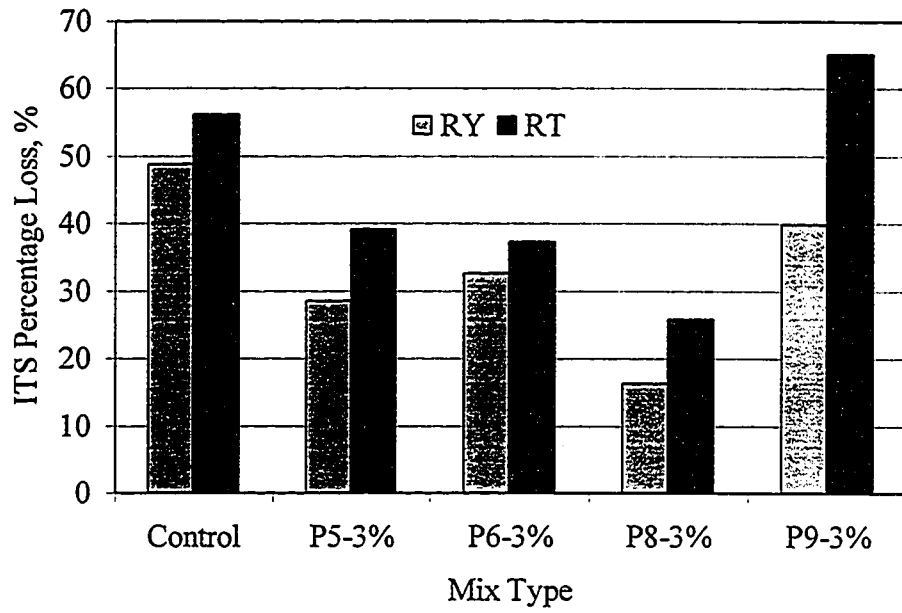


Figure 4. 15: Lottman test results.

4.3.3. Resilient Modulus Test, M_R (ASTM D 4123)

Resilient modulus is the most important variable to mechanistic design approaches for pavement structures. It is the measure of pavement response in terms of dynamic stresses and corresponding strains. It is measured by applying a vertical load along the diameter of a specimen and measuring the resulting elastic horizontal deformation. Polymer-modified mixes have improved the diametral resilient modulus of modified mixes as compared to the control mix for both asphalt types. The average resilient modulus at 25°C was found to be 547.3 ksi for the control RY mix; this value increased to 799.8 ksi for P8 blend. The average resilient modulus at 50°C increased from 85.0 ksi for the control RY mix to 369.3 ksi for P8. The other obtained results are shown in Table 4.6 along with Figures 4.16 and 4.17. Although control RT mix has low M_R compared to control RY mix, its blends with P5, P6, and P8 showed higher M_R values compared to RY blends. This phenomenon may be linked to the way that polymers are dispersed in the asphalt and the cross-linking between polymer molecules and asphalt molecules.

Table 4. 6: Resilient modulus (ksi).

Polymer Type \ Asphalt Type	RY		RT	
	Temperature		Temperature	
	50°C	25°C	50°C	25°C
Control	85	547.3	76.5	497.3
P5 – 3%	171.9	576.4	335.2	850.1
P6 – 3%	293.6	654.2	258.5	780.8
P8 – 3%	369.3	799.8	344.6	1005.3
P9 – 3%	305.6	671.7	305.6	447.5

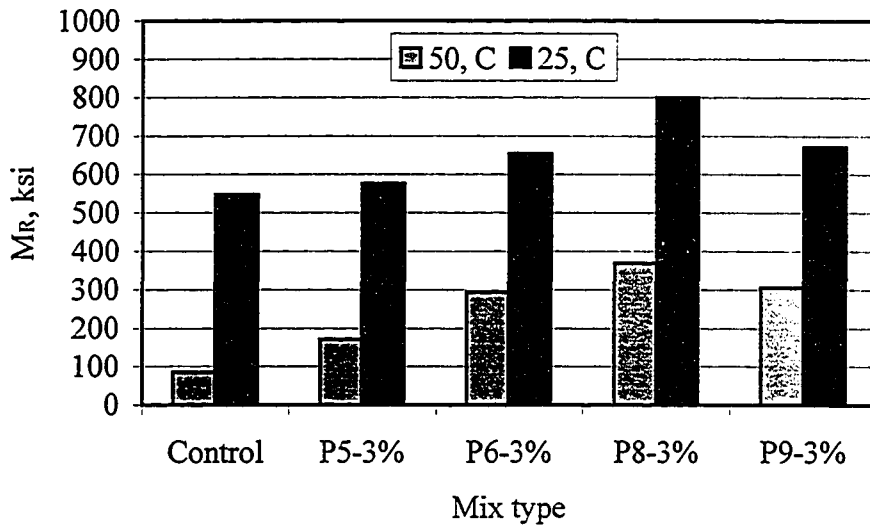


Figure 4. 16: Comparison of M_R (ksi) at 50°C and 25°C for RY.

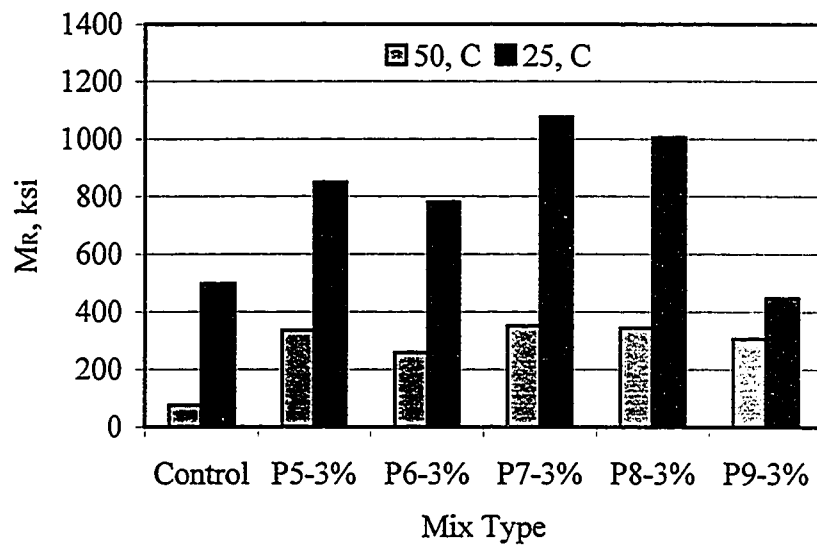


Figure 4. 17: Comparison of M_R (ksi) at 50°C and 25°C for RT.

4.3.4. Fatigue Performance

Diametral fatigue test results for wearing course mixes of the four polymer types (P5, P6, P8 and P9) mixed with RY and RT asphalts in addition to the control mix (neat RY and RT mixes) at testing temperatures of 25°C and 50°C are shown in Figures 4.18 and 4.19 for RY blends with 3% polymer, and in Figures 4.20 and 4.21 for RT blends with 3% polymer. Nine samples were tested for fatigue (3 at each strain level), regression lines were then drawn through the mean of samples at each strain level. These results show a normal linear relationship between the logarithm of applied initial tensile strain and the logarithm of fatigue life (number of applied load repetitions until failure). The fatigue data were analyzed by running a regression analysis to determine the fatigue relationship parameters in the following form:

$$\varepsilon_t = I * (N_f)^S \quad (3.1)$$

where:

- ε_t = initial tensile strain,
- N_f = number of load repetitions to failure,
- I = anti-log of the intercept of the logarithmic relationship, and
- S = slope of the logarithmic relationship.

Regression parameters for Equation (3.1) are shown in Tables 4.7 and 4.8. The results showed significant improvement in fatigue life of the specimens

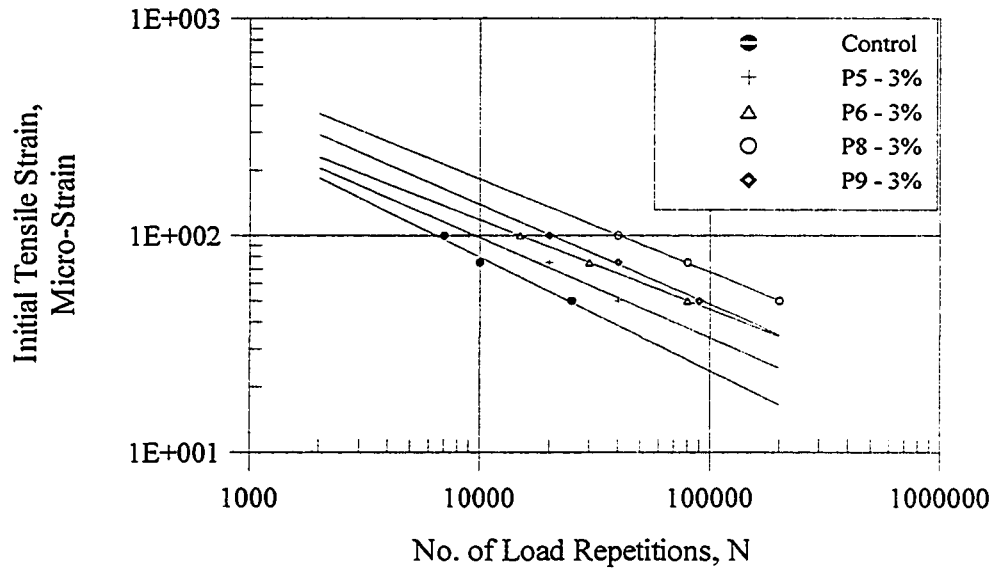


Figure 4. 18: Fatigue curves for modified wearing course mixes at 25°C (For RY asphalt).

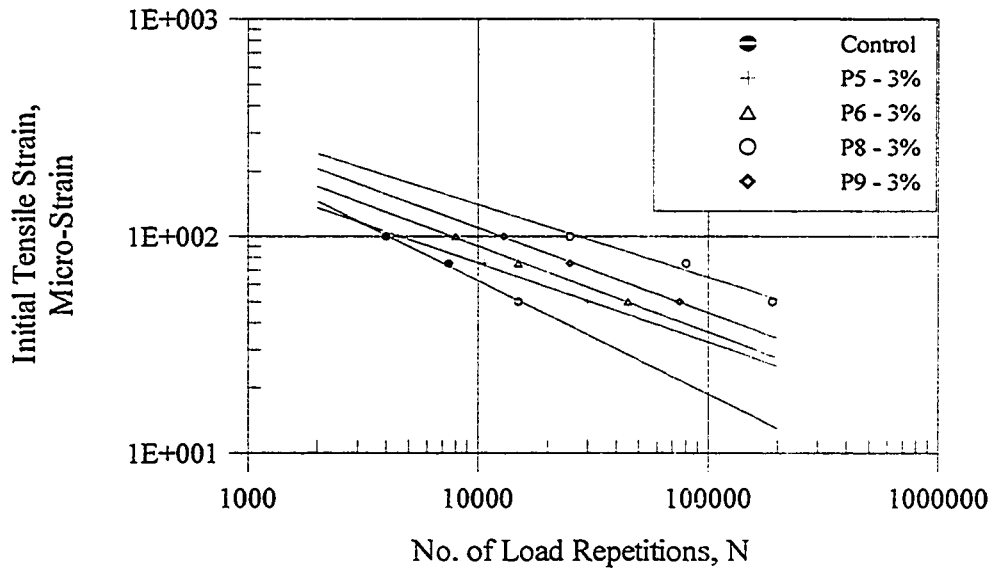
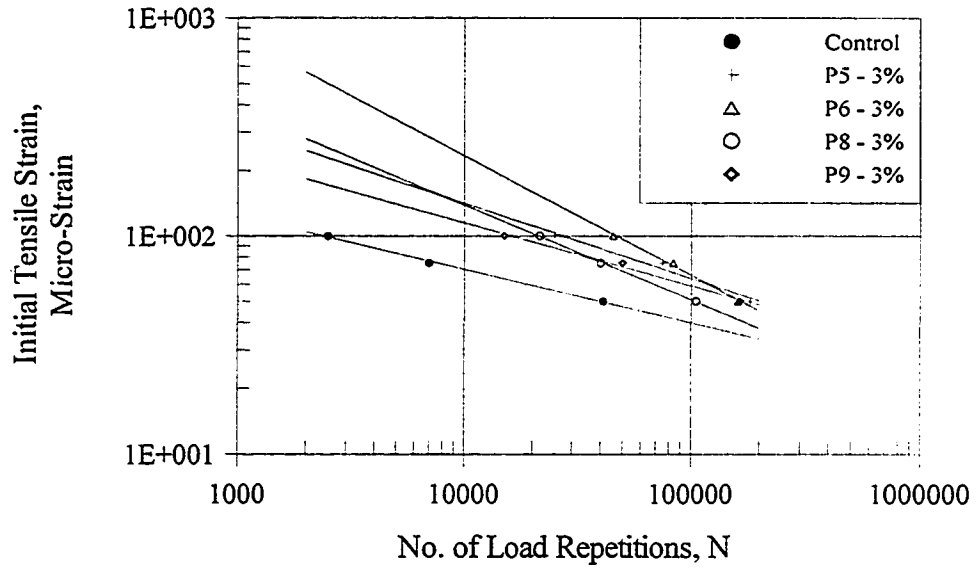
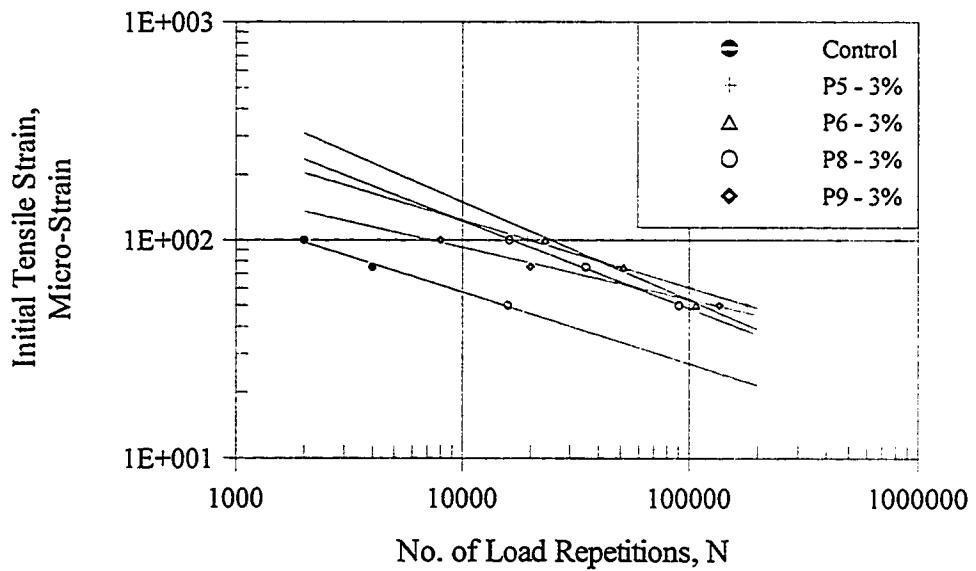


Figure 4. 19: Fatigue curves for modified wearing course mixes at 50°C (For RY asphalt).



**Figure 4. 20: Fatigue curves for modified wearing course mixes at 25°C
(For RT asphalt).**



**Figure 4. 21: Fatigue curves for modified wearing course mixes at 50°C
(For RT asphalt).**

**Table 4. 7: Regression factors for fatigue test
(For RY Asphalt).**

Mix Type	Regression Factors @ 25°C		Regression Factors @ 50°C	
	I	S	I	S
Control	9946.5	-0.5243	7924.9	-0.6255
P5	6890.9	-0.4641	3623.5	-0.4110
P6	7961.3	-0.4621	3514.0	-0.3977
P8	4384.3	-0.3645	1801.8	-0.2946
P9	9812.7	-0.4619	4079.9	-0.3928

**Table 4. 8: Regression factors for fatigue test
(For RT asphalt).**

Mix Type	Regression Factors @ 25°C		Regression Factors @ 50°C	
	I	S	I	S
Control	806.3	-0.2608	920.8	-0.2467
P5	4032.8	-0.3622	1566.3	-0.2860
P6	36590	-0.5487	9489.1	-0.4506
P8	7012.5	-0.4287	5026.0	-0.4034
P9	562.45	-0.2016	920.7	-0.2860

modified with polymer, particularly at low strain and high temperature levels. P8 has shown higher fatigue life (about 50 times higher than control mix) followed by P9, P6, and P5, respectively at high and low temperatures in both types of asphalt.

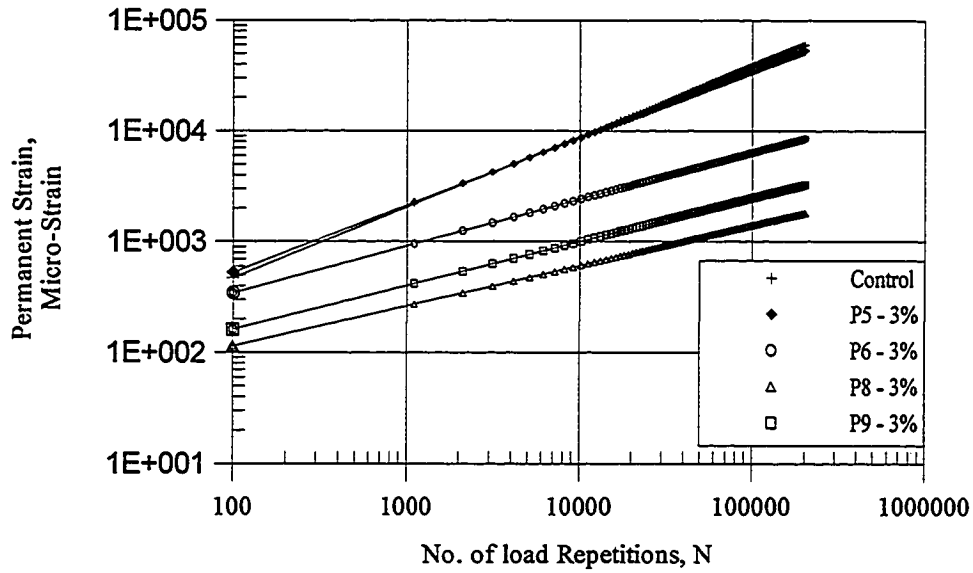
4.3.5. Permanent Deformation

Permanent deformation was simultaneously recorded while running the fatigue test, as mentioned before for all tested specimens, at testing temperatures of 25°C and 50°C. Results of permanent deformation test at initial strain level of 100 micro-strain are presented in Figures 4.22 and 4.23 for RY blends, and in Figures 4.24 and 4.25 for RT blends. Other test results are shown in Appendix C. Results indicate that a straight-line relationship exists between the logarithm of number of load repetitions and the logarithm of permanent strain. The permanent deformation properties were determined using the following form:

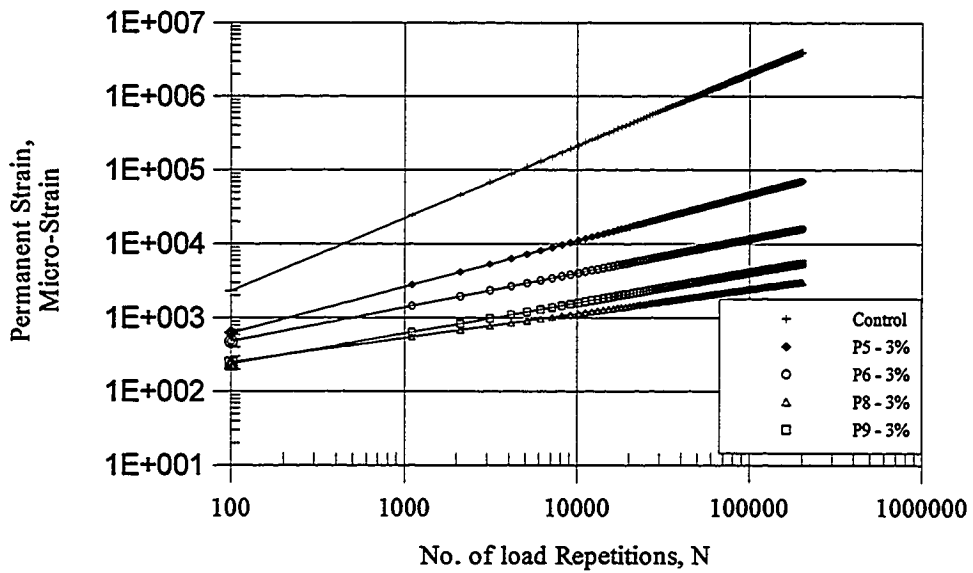
$$\varepsilon_p = I * (N)^S \quad (3.2)$$

where:

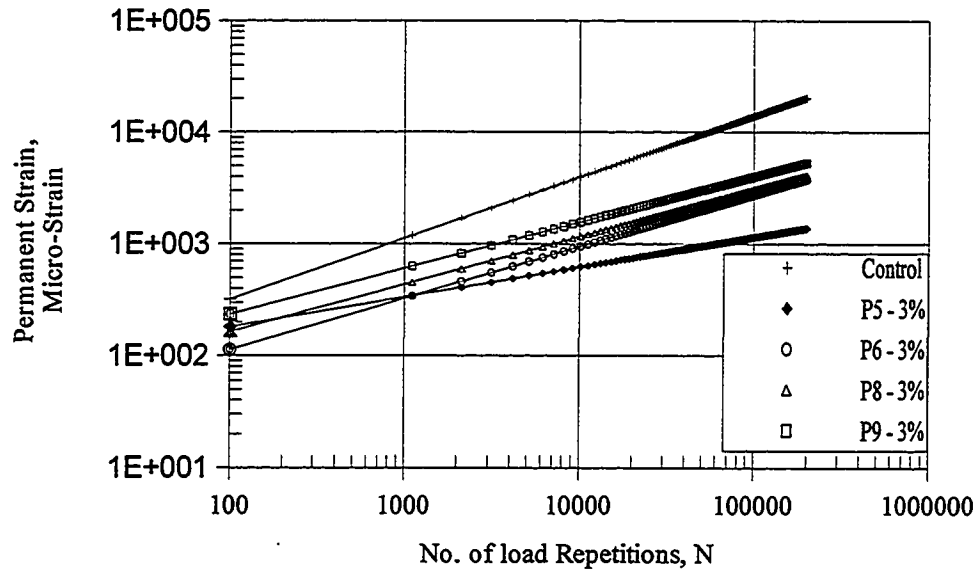
- ε_p = accumulated permanent strain,
- N = number of load repetitions,
- I = anti-log of the intercept of the logarithmic relationship, and
- S = slope of straight line.



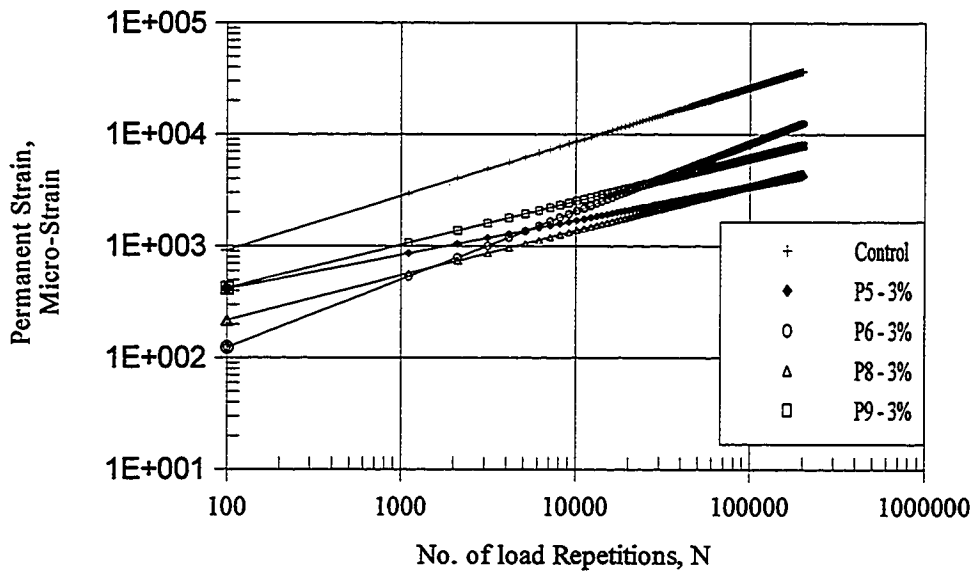
**Figure 4. 22: Rutting curve at 100-initial micro-strain @ 25°C
(For RY asphalt).**



**Figure 4. 23: Rutting curve at 100-initial micro-strain @ 50°C
(For RY asphalt).**



**Figure 4. 24: Rutting curve at 100-initial micro-strain @ 25°C
(For RT asphalt).**



**Figure 4. 25: Rutting curve at 100-initial micro-strain @ 50°C
(For RT asphalt).**

Parameters I and S in the above equation were obtained by using permanent deformation experimental data in a regression analysis.

Results indicate that polymer modification has reduced permanent deformation of asphalt mixes (by 1/5th) as compared to the control mix. The improved rutting resistance is clear at low and high temperatures. P5 has shown similar behavior as the control mix at 25°C while its behavior becomes more plastic at 50°C. P8 has shown best rutting performance followed by P9, P6, and P5, respectively.

Chapter 5

CONCLUSIONS

Based on the findings of this study, the following conclusions were drawn:

1. SABIC polymers were found to be suitable for modifying local asphalt mixtures with many advantages:
 - Polymer types P6 (MDPE, M.I.=0.935), P8 (HDPE, M.I.=0.956) and P9 (HDPE, M.I.=0.964) showed significant increase in resilient modulus at both high and low temperatures compared to the control mixture.
 - Modified asphalt mixtures varied significantly in their water susceptibility. Some mixtures were more sensitive than others and this might be referred to their composition or microstructure. The average percentage loss in strength due to water damage was reduced effectively in polymer type P8 while it was reduced in polymer types P5 (LLDPE, M.I.=0.926), P6 (MDPE, M.I.=0.935) and P9 (HDPE, M.I.=0.964) but had higher value (more than 20%), even though the reductions in the average percent loss in strength indicated that the modified mixtures

were more durable than the control mix.

- The results showed significant improvement in fatigue behavior of all the polymer type mixes compared with the control mix. P8 showed higher fatigue life (about 50 times higher than the control mix) at high and low temperatures in both types of asphalt followed by P9, P6, and P5, respectively.
 - The results indicate that polymer modification has reduced the permanent deformation of asphalt mixes (by 1/5th) as compared to the control mix. The improved rutting resistance is clear at low and high temperatures. P5 has shown similar behavior to the control mix at 25°C while its behavior becomes more elastic at 50°C. P8 has shown the best rutting performance followed by P9, P6, and P5, respectively.
2. Based on the findings of this research, the following modification procedure is recommended in order to achieve the best modification results:
- Determine the melting point of polymer in order to estimate the blending temperature. It is recommended to reject polymers which possess flow temperature higher than 180°C since the chemical properties of the asphalt may change at high temperatures.
 - Select the polymer content as recommended by the manufacturer or from previous experiences.

- Set the blending temperature to be higher than the flow temperature by 5°C in order to ensure that polymers are in liquid state. Test for DSR during the blending process at 30 minutes interval and select the optimum blending time at the highest value of $G^*/\sin \delta$ for the desired polymer content (section 4.2.2).
- Test the storage stability and determine the critical storage time as detailed in section 4.2.3.
- Determine the PG as per SHRP specifications (section 4.2.4).
- Further tests can be performed on modified asphalt concrete mixtures to formulate the best choice of the modifiers. It is noteworthy to mention that different polymers with the same PG may perform differently in their asphalt concrete mixtures. Effect of polymer characteristics should be explored in further studies.

Chapter 6

RECOMMENDATIONS

In this project, there were some areas of research that were not covered because of the limitation of time and resources. The following recommendations briefly describe the topics in which further research would be valuable:

1. It was found that polymer's melting temperature limits its use in modifying asphalt binder. High melting temperature requires high blending temperature, which may affect asphalt properties because some of its components have low boiling points and thus can possibly increase volatilization during the blending process. Moreover, it also increases the overall cost. Research on polymer's melting temperature (i.e. increasing polymer's melting index) is needed to give guidance in this area.
2. It was found that susceptibility to moisture damage greatly depends on polymer type. Some polymers have shown very good resistance to moisture damage while others are very weak although they have the same PG. More

research in this area would be valuable to determine the specific polymers' characteristics that would improve the sensitivity of mixtures to moisture damage. It is expected that blending two polymers may give good results.

3. Results of this research are based on laboratory study. It is therefore recommended that the binder mixtures be evaluated for fatigue and rutting under real temperature, traffic, and pavement structure condition to mimic field conditions during service. In this regard, test sections need to be constructed and actual pavement performance should be monitored.

APPENDICES

APPENDIX A

TESTS PROCEDURES AND SPECIMENS FABRICATION

A.1- AGING

A.1.1- RTFO

The RTFO test is used to simulate the aging that takes place during production and up to the first year of life of the pavement. The binder is poured into cylindrical bottles, placed horizontally in a convection oven and rotated at 163°C for 85 minutes. This process creates a thin film of asphalt on the inside the bottles, which ages due to heat and the injection of air into the bottle.

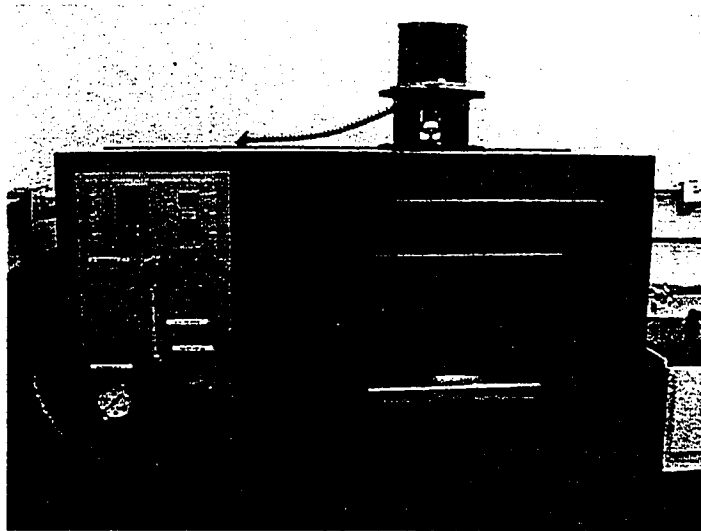


Figure A. 1: Rolling Thin Film Oven

A.1.2- PAV

The next step in the simulation of the aging process for the binder is the Pressure Aging Vessel. The RTFO aged binder is placed in shallow pans approximately 3 mm thick. The pans are placed in a pressure vessel at 2.1 MPa at 110°C for 20 hours. During the PAV process, oxygen is driven into the binder simulating long-term aging of the binder in the pavement.

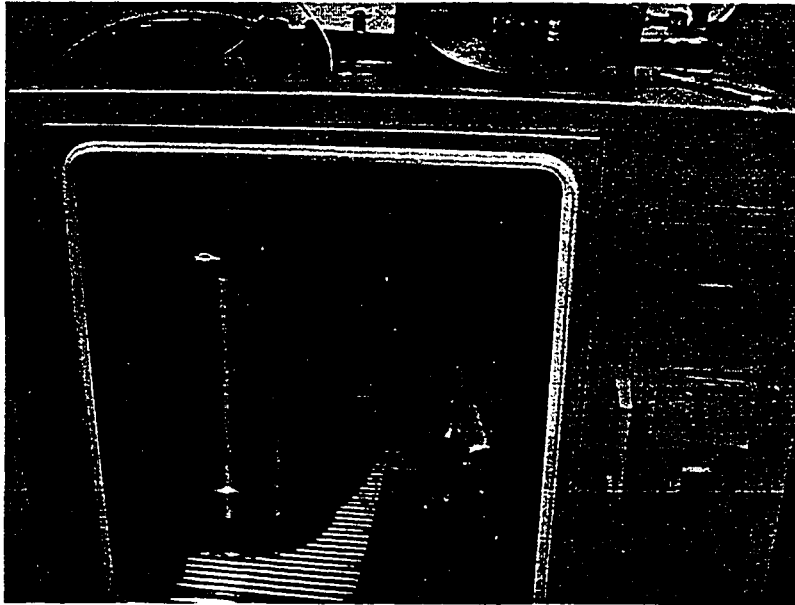


Figure A. 2: Pressure Aging Oven

A.2- Dynamic Shear Rheometer

The Dynamic Shear Rheometer (DSR) is used to measure the high temperature and intermediate temperature properties of the asphalt binder. An asphalt binder sample is placed between parallel plates and a torsional load is applied to the binder at the specified temperature (gap 2 mm for Φ 8 mm and 1 mm for Φ 25 mm). The binder response to loading is measured and the lag time to that response is determined. From these data, the complex modulus G^* and phase angle δ are determined and used to calculate the viscous and elastic properties of the binder. This is measured on the unaged, RTFO aged, and the PAV aged binder.

The current DSR high temperature specification requires $G^*/\sin \delta$ to be equal to or greater than 1 kPa for unaged binder and 2.2 kPa for RTFO aged binder at the specified pavement temperature. For high temperature, dividing the complex modulus by the sine of the phase angle is intended to account for the elastic component of the binder and give the modified systems some additional credit.

The specification of the DSR at intermediate temperature requires $G^*/\sin \delta$ to be less than 5000 kPa. For intermediate temperature, $G^*/\sin \delta$ is the viscous component of the binder and is related to dissipated energy. It was intended to relate how the binder relaxes stress at intermediate temperature to fatigue cracking.

Table A. 1: Typical DSR result for Riyadh asphalt with 2% polymer type P5.

DSR Project - SHRP Binder Test - Strain Controlled (Created by Version 2.05)	
Parameters:	
Measurement Type:	Intermediate Temperature Range
Target Temperature:	22.0 °C
Strain Amplitude:	1.00 percent
Plate Diameter:	8.0 mm
Plate Gap:	2.0 mm
Equilibration Time:	15.0 minutes
Ancillary Info:	
Operator ID:	ISAM
Sample ID:	RY-P5-2%
Sample Type:	Pressure Aging Vessel Residue
Test Number:	0003
Measurement Results:	
Completed:	6/14/01 3:04:59 PM
Modulus (G*):	9.3808E6 Pascal
Phase Angle (delta):	27.8 degrees
G*.sin(delta):	4.5560E6 Pascal
Strain Amplitude:	1.01 percent
Final Temperature:	22.0 °C
Osc. Frequency:	10.08 radians/second
Test Status:	PASSED
Operator Notes:	
RY-P5-2%-AFTER PAV	

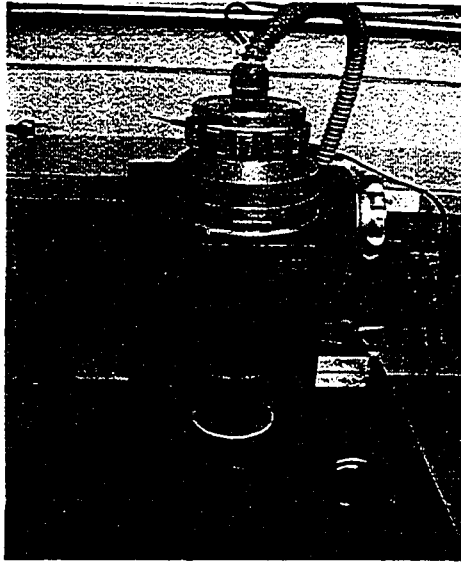


Figure A. 3: DSR test machine

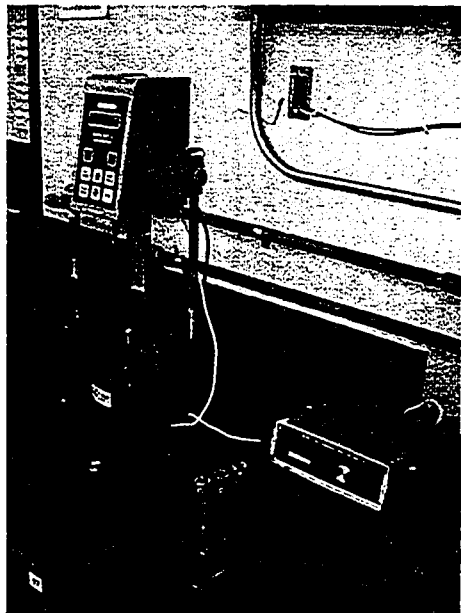


Figure A. 4: RV test machine

A.3- BENDING BEAM RHEOMETER

The Bending Beam Rheometer (BBR) is used to measure the low temperature stiffness properties of a binder. In the test, a beam of asphalt is subjected to a three-point loading in a low temperature bath at 10°C above the expected low pavement temperature. The specimen was fabricated by pouring the sample from PAV into a beam mold, trimming the excess material, conditioning the sample at room temperature for 2 hours, demolding the sample, conditioning the sample at the test temperature for 1 hour, and loading the specimen with a 100 g load for a period of 240 seconds (The beam dimensions are 125 mm long, 12.5 mm wide, 6.25 mm thick supported at a span of 100 mm). The deflection of the beam is measured with time. From this measurement, the low temperature creep compliance and slope of the creep compliance curve are determined. The low temperature stiffness of the binder is determined from the creep compliance curve measured at sixty seconds loading time. The slope of the curve or *m*-value at sixty seconds loading time is also included in the specification as an indication of the binder's ability to dissipate stress buildup during contraction of the pavement as it cools. The low temperature specification requires the BBR-measured stiffness to be ≤ 300 MPa and the *m*-value to be ≥ 0.30 at the test temperature.

TEST INFORMATION						
Project : thesis	Target Temp: 0.0 C	Conf. Test: 9.01604e+00				
Operator: isam	Actual Temp: -12.0 C	Date: 06/04/01				
Specimen: ry-p8-3%-12	Soak time : 30.0 min	Load Const: 0.243309				
Time : 14:01:32	Beam Width : 12.70 mm	Defl Const: 0.002402				
Date : 06/04/01	Thickness : 6.35 mm	Date: 06/04/01				
File : RY-P8-3.DAT						
RESULTS						
t Time (sec)	P Force (N)	d Defl (mm)	Measured Stiffness (kPa)	Estimated Stiffness (kPa)	Difference (%)	m-value
8	0.9860	.6296	135200.0	134800.0	-.3476	.282
15	0.9825	.7541	112900.0	113400.0	.4384	.287
30	0.9835	.9153	93090.0	93450.0	.3845	.292
60	0.9836	1.106	77040.0	76710.0	-.4375	.303
120	0.9837	1.353	62930.0	62730.0	-.3150	.312
240	0.9837	1.671	50970.0	51120.0	.2814	.323
Regression Coefficients						
a = 5.368 b = -.2561 c = -.008822 R^2 = 0.999875						
- CANNON BENDING BEAM RHEOMETER - V3.1 P to print - ESC to continue						

Figure A. 5: Typical BBR result for Riyadh asphalt with 2% polymer type P8.

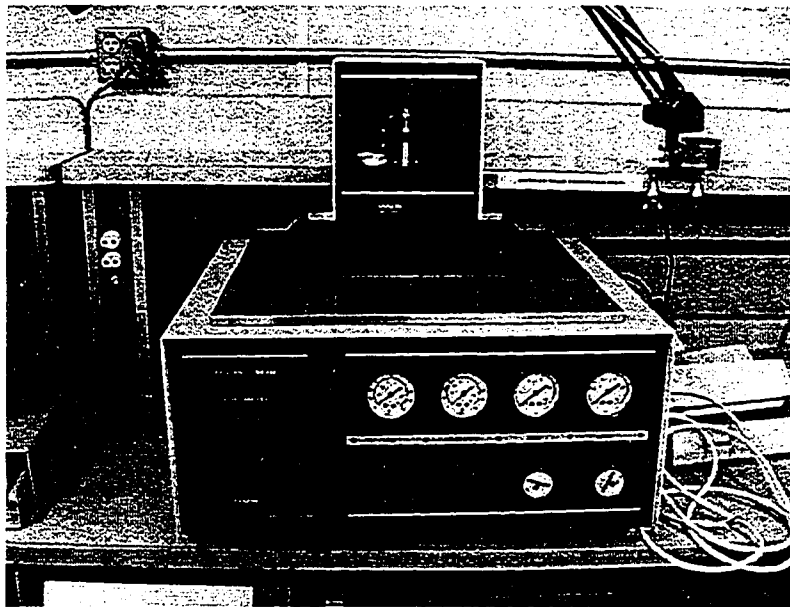


Figure A. 6: BBR test machine

Appendix B

MARSHALL MIX DESIGN

Asphalt mix design

MARSHALL METHOD

SUMMARY

Date: 13 May, 2000
Client: A.A. Dossary Trad. Ent. Dammam
Project: SABIC
Mix Code: Wearing Course (WC)
Sample Location: Aggregate & Asphalt were taken from Al-Dossary batch mix plant in Dammam.

Test Results Wearing Course

	Job Mix Formula (JMF)	Specification Limits
1. Optimum Asphalt Content, % (60/70 Pen grade asphalt)	5.3	5.3 +/- 0.3
2. Aggregate Grading: % Passing		
1"	100	100
3/4"	87	80 - 95
# 4	55	48 - 62
# 10	38	32 - 45
# 40	21	16 - 26
# 80	13	8 - 18
# 200	6	4 - 8

3. Marshall Test Results (75 blows, compaction temperature 150°C.)

Stability (Kg)	1804	800 Min.
% Air Voids. Total Mix	4.4	4.0 - 6.0
Flow (mm)	3.2	2.0 - 4.0
% Voids filled w/asphalt	74	70 - 80
Stability Loss, (%)	16.2	20 Max.
VMA	16.04	-

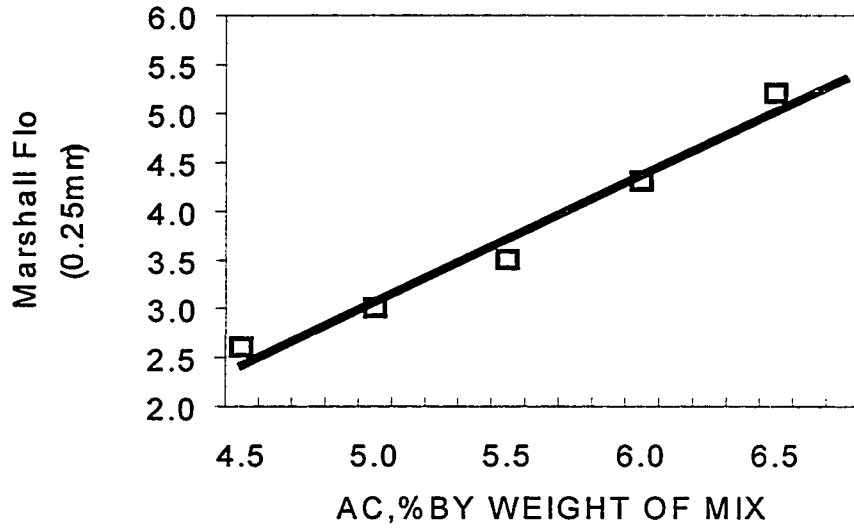


Figure B. 1: Marshall Flow vs. AC (% by weight)

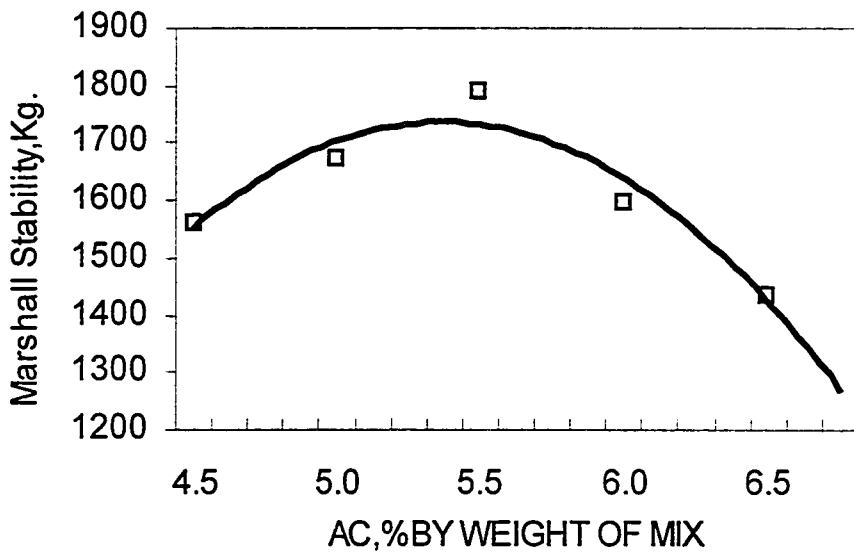


Figure B. 2: Marshall Stability vs. AC (% by weight)

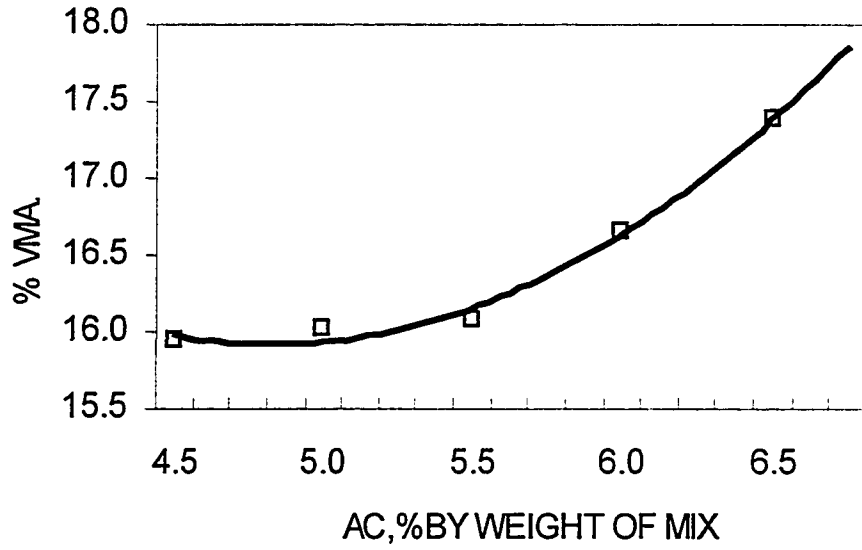


Figure B. 3: % VMA vs. AC (% by weight)

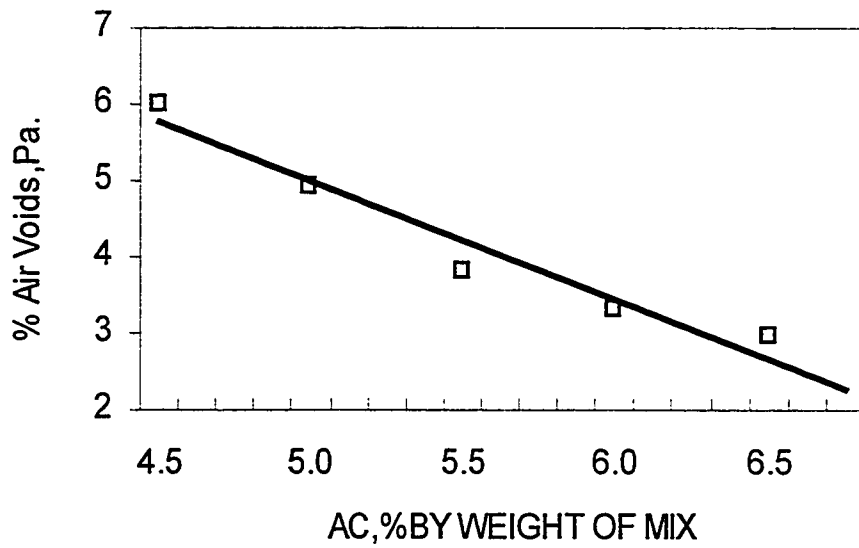


Figure B. 4: % Air Voids vs. AC (% by weight)

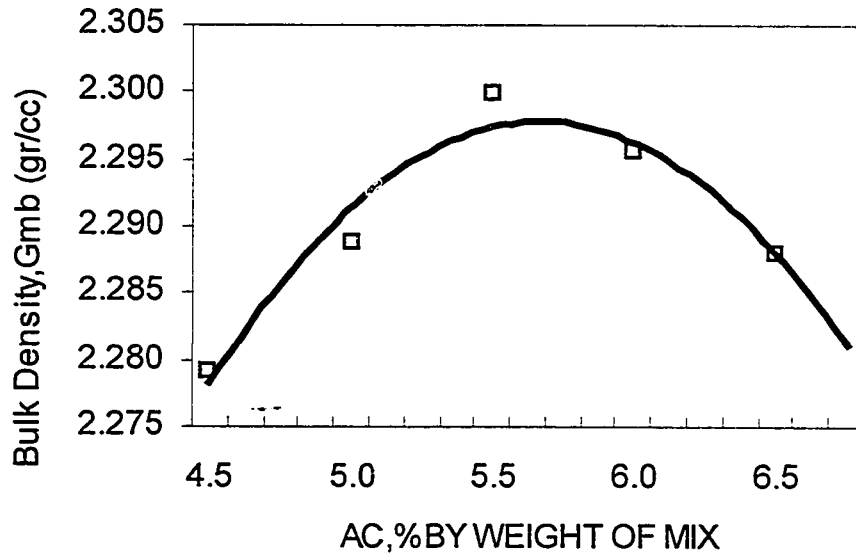


Figure B. 5: Bulk Density vs. AC (% by weight)

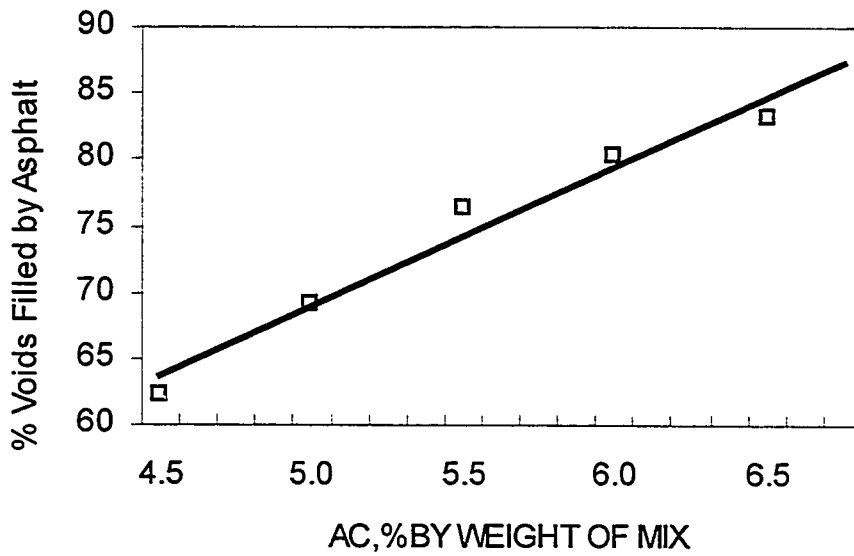


Figure B. 6: % Voids filled by asphalt vs. AC (% by weight)

Final results:

Asphalt Content At:

- | | |
|--------------------------|------|
| 1) Maximum Density | 5.5% |
| 2) Maximum Stability | 5.5% |
| 3) 5.0% of Air Voids | 5.0% |

Optimum Asphalt Content for WC = 5.3%

Field Tolerance = 5.0 to 5.6%

Appendix C

TEST RESULTS OF PERMANENT DEFORMATION TEST

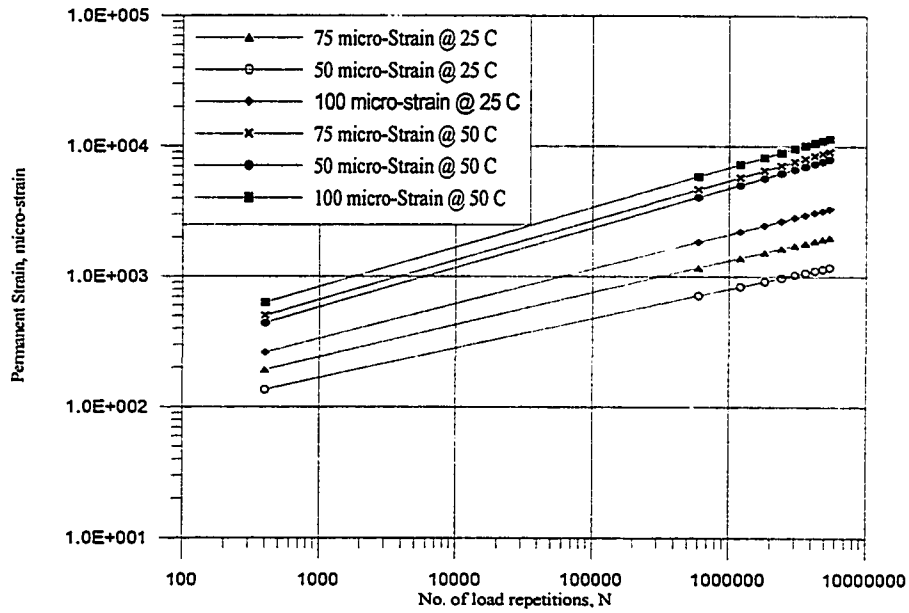


Figure C.1: Rutting curves of P5-3% with RY asphalt

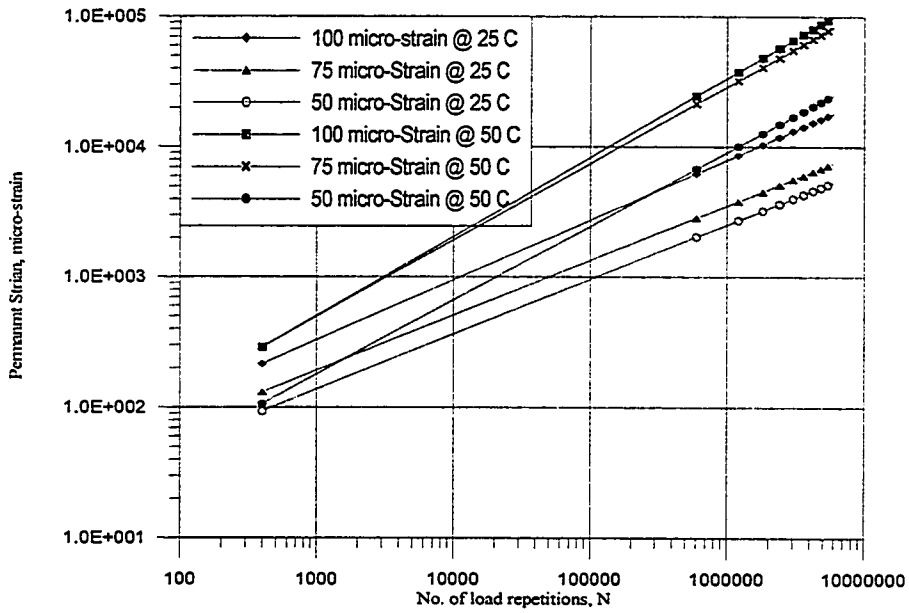


Figure C.2: Rutting curves of P6-3% with RY asphalt

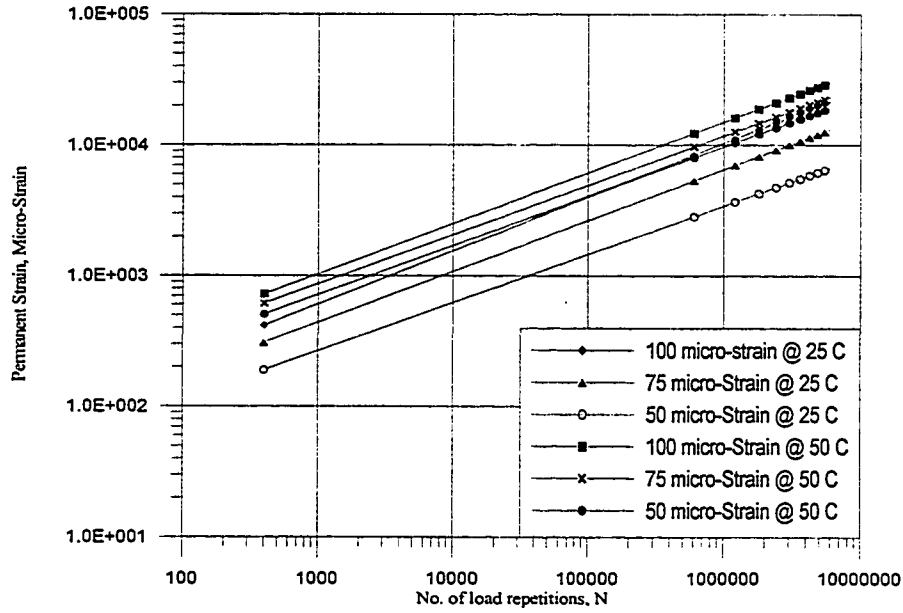


Figure C.3: Rutting curves of P8-3% with RY asphalt

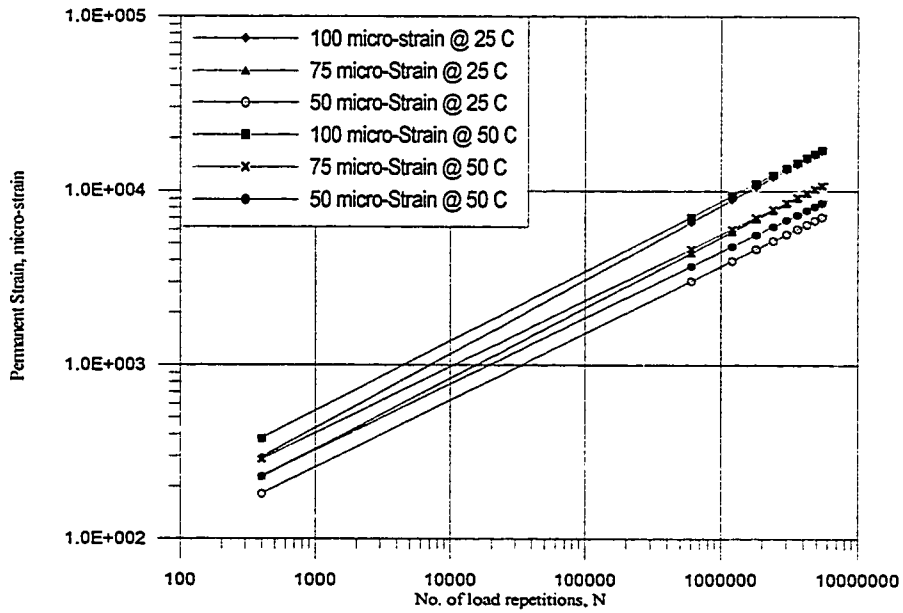


Figure C.4: Rutting curves of P9-3% with RY asphalt

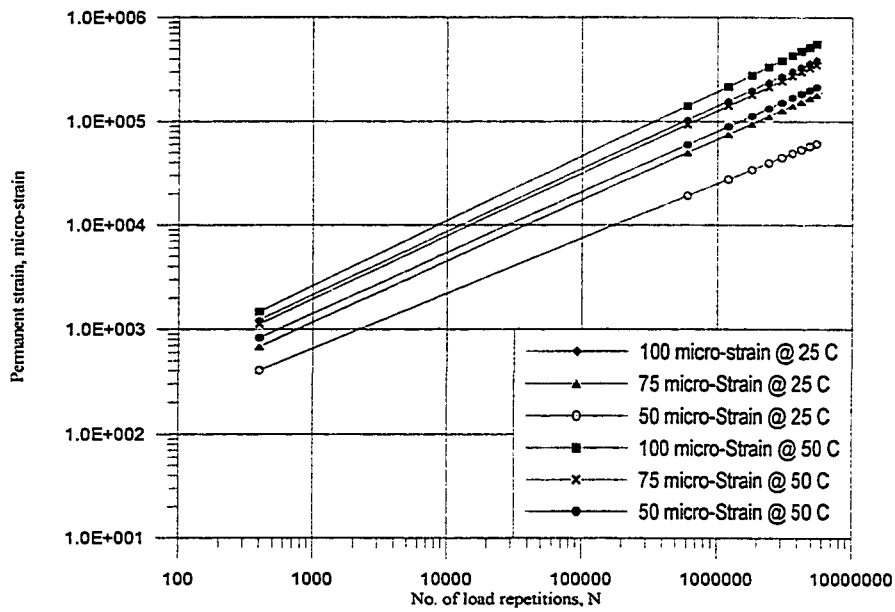


Figure C.5: Rutting curves of P5-3% with RT asphalt

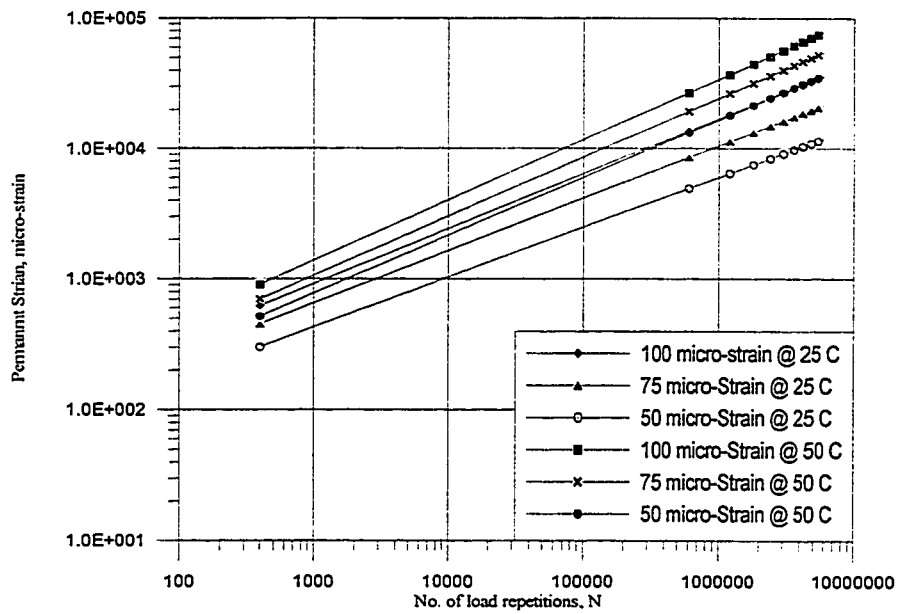


Figure C.6: Rutting curves of P6-3% with RT asphalt

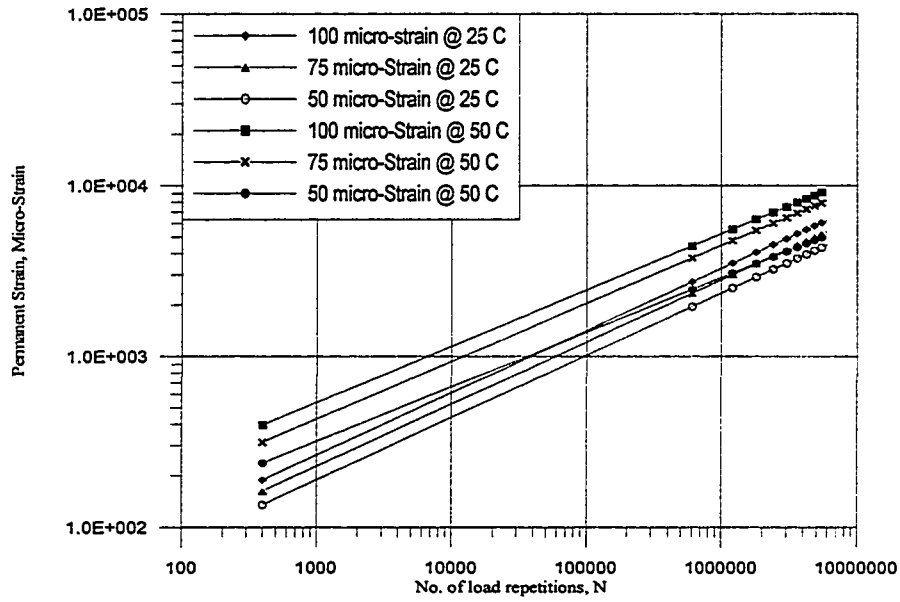


Figure C.7: Rutting curves of P8-3% with RT asphalt

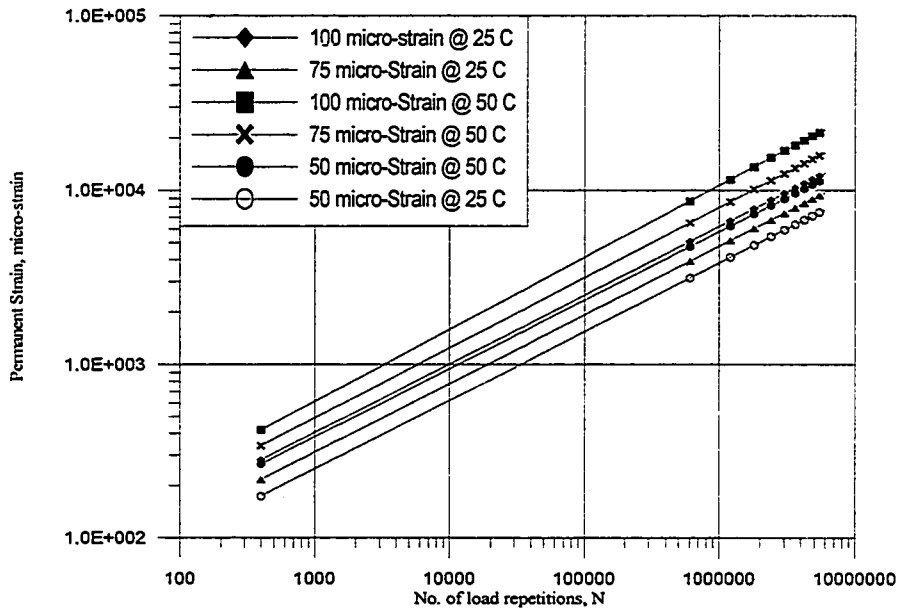


Figure C.8: Rutting curves of P9-3% with RT asphalt

REFERENCES

- Airey, G.D. and Brown, S.F. (1998), "Rheological performance of aged polymer modified bitumens", *Proc., AAPT*, Vol. 67, p. 67.
- Akmal, N. and Usmani, A.M. (1994), *Handbook of Adhesive Technology*, Dekker, New York.
- Al-Abdul Wahhab, H. and Al-Amri, G. (1991). "Laboratory evaluation of reclaimed rubber asphaltic concrete mixes", *ASCE Journal of Materials*, Vol. 3, No. 3, pp. 189-203.
- Al-Abdul Wahhab, H., Ali, F., Asi, I. and Al-Dhubeeb, I. (1996), "Adaptation of SHRP performance based asphalt specifications to the Gulf countries", Final Report, King Abdulaziz City for Science and Technology (KACST), Riyadh.
- Al-Dubabe, I.A., Al-Abdul Wahhab, H.I. and Asi, I. M. (1998), "Polymer modification of Arab asphalt", *Journal of Materials in Civil Engineering*, ASCE, p. 161.
- Asi, I.M., Al-Abdul Wahhab, H.I., Al-Dubabe, I.A. and Ali, M.F. (1997), "Performance Modeling of Arabian Asphalt Using HP-GPC", *Materials Engineering and Performance Journal*, Ohio, Vol. 6, No. 4, August, pp. 503-510.

- Bahia, H., Hanson, D. I., Zeng, M., Zhai, H., Khatri, M. and Anderson, R. (2001),
“Characterization of modified asphalt binder in Superpave mix design”,
TRB, NCHRP Report 459, National Academy Press, Washington, D. C.
- Bouldin, M.G., Collins J. H., Berker, A., (1991), “Rheology and microstructure of
polymer/asphalt blends”, *Journal of Rubber Chemistry and Tech.*, Vol. 67,
No. 4.
- Branthaver, J.F., Petersen, J.C., Robertson, R.E., Duvall, J.J., Kim, S.S.,
Harnsberger, P.M., Mill, T., Ensley, E.K., Brabour, F.A. and Schabron, J.F.
(1993), “Binder Characterization and Evaluation, Volume 2: Chemistry”,
SHRP Publication, *SHRP-A-368*, pp. 1-76.
- Brule B., Brion, Y. and Tanguy, A. (1988), “Paving asphalt polymer blends:
relationship between composition, structure and properties”, *Proc., AAPT*,
Vol. 57, pp. 41-64.
- Brule, B. (1996), “Polymer modified asphalt cements used in the road construction
industry: Basic principles”, *TRB No. 1535*, pp. 48-53.
- Button, J.W. (1992), “Summary of asphalt additive performance at selected sites”,
TRR No. 1342.
- Collins, J.H. and Bouldin, M. (1992). “Stability of straight and polymer modified
asphalts”, *TRB No. 1342*, pp. 92-100.

- D'Angelo, J.A. and Fee, F. (2000), "Superpave binder tests and specifications on how have they performed in real world", *Proc., AAPT*, Vol. 69, p. 697.
- Diani A. (1987), "Chemistry and technology of SBS modifiers", *Polymer Science and Technology*.
- Goodrich, J.L. and Dimpfi, L.H. (1986), "Performance and Supply Factors to Consider in Paving Asphalt Specifications", *Proc., AAPT*, Vol. 55.
- Harrigan, E.T. Leahy, R.B, Uyoutcheff, J.S., (Editors) (1994), "The SUPERPAVE Mix Design System Manual of Specifications, Test Methods, and Practices", *SHRP-A-379*, National Research Council, Washington, D.C.
- Isacsson, U. and Lu, X. (1999), "Laboratory investigation of polymer modified binders", *Proc. AAPT*, Vol. 68, p. 35.
- Joseph, P. and Kennepohl, G. (1996), "Polymer-modified asphalt pavements in Ontario: Performance and cost-effectiveness", *TRB No. 1545*, p. 151.
- Khattak, M.J. and Baladi, G.Y. (2001), "Paving asphalt polymer blends: Relationships between composition, structure and properties", *TRB 10, No. 01-2813*, 80th Transportation Research Board Annual Meeting, Washington D.C.
- Little, D.N., Button, J.W., Kim, Y. and Ahmed, S.J. (1986), "Hot in-plane recycling and asphalt concrete", *Synthesis of Highway Practice*, Washington National Academy Press.

- McBee, W.C. Romans, P.A, Sullivan, T.A, Uhde, R.R. (1981), "Role of Sulphur in SEA pavements", *Sulphur Research and Development*, Vol. 4.
- Odian, G. (1991), *Principles of Polymerization*, 3rd Ed., Wiley, New York.
- Payne, H.F. (1984), *Organic Coating Technology*, Vol. 1, Wiley, New York.
- Plancher, H., Dorrence, S.M. and Petersen, J.C. (1977), "Identification of Chemical Types in Asphalts Strongly Absorbed at the Asphalt-Aggregate Interface and Their Relative Displacement by Water", *Proc., AAPT*, Vol. 46, pp. 151-175.
- Price, R.P. and Burati Jr., J.L. (1990), "Prediction of laboratory results for modified asphalts using HP-GPC", *Proc., AAPT*, Vol.59.
- Sartori, F., Bonemazzi, F., Bbraga, V. and Corrieri, R. (1996), "Characteristic of polymers and polymer modified binders", *TRR No. 1535*.
- Saunders, K.J. (1973), *Organic Polymer Chemistry*, Wiley, New York.
- Seymour, R.B. and Carraher, C.E. (1992), *Polymer Chemistry*, 3rd ed., M. Dekker, New York.
- Sustic, A. (1993), "Amorphous polyalphaolefins (APAOs) as performance improvers in asphalt containing materials".
- Terrel, R.L. and Epps, J.A. (1989), "Using additives and modifiers in hot mix asphalt", *QI Series 114, NAPA*, pp. 3-10.

- Usmani, A.M. and Salyer (1982), *Use of Renewable Resources for Polymer Applications*, Plenum, New York.
- Wegan, V. and Brule, B. (1999), "The structure of polymer modified binders and corresponding asphalt mixtures", *Proc., AAPT*, Vol. 68, pp. 65-88.
- Zielinski, J. (1994), "Factors influencing compounding of constituents in bitumen-polymer compositions". *Erdol Kohle Erdgas Petrochem*, pp. 337-347.