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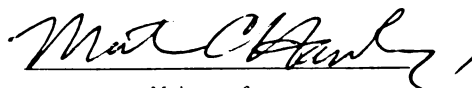
Chemical, Physical, and Thermodynamic Properties
of Neat and Polymer Modified Asphalt Binders

presented by

Lawrence Michael France

has been accepted towards fulfillment
of the requirements for

Master of Science Chemical Engineering
_____ degree in _____



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**Chemical, Physical, and Thermodynamic Properties of Neat and Polymer
Modified Asphalt Binders**

by

Lawrence M. France

A THESIS

Submitted to

Michigan State University

in partial fulfillment of the requirements for the degree of

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1997

ABSTRACT

Chemical, Physical, and Thermodynamic Properties of Neat and Polymer Modified Asphalt Binders

by

Lawrence M. France

Asphalt was modified with four different polymers to investigate the benefits of polymer modification. The modifiers studied were styrene-butadiene rubber, Elvaloy AM, recycled crumb rubber, and ethylene vinyl acetate. A mixing procedure was developed for each modifier based on improvement in the rheological properties of the blend. A number of physical properties were investigated to determine the benefit of polymer modification. Polymer modification improved high temperature properties and did not affect low temperature properties.

Fourier Transform Infrared Spectroscopy and Gel-Permeation Chromatography were used to fingerprint the modified binders. Phenomenological models were developed for SBR and CRM rheological properties. The properties of SBR are a combination of two phenomena: percolation and network formation. The properties of CRM are a result of simple two-phase dispersed mixing. Laser scanning and environmental scanning electron microscopy were used to verify the models. The applicability of the SHRP performance based specifications for modified asphalts was investigated.

DEDICATION

This work is dedicated to my parents, Larry and Cheri, without whom this work would not have been possible. Their support, both financial and emotional, has been invaluable.

Thank you for everything and God bless you.

and

In Loving Memory of A. L. "Van" VanTassel

February 8, 1926 - January 26, 1997

May the Lord bless you and keep you.

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Chapter One

Scope

The performance of asphalt pavements depends on traffic loads, material properties, environmental factors, and construction practices. Pavement deteriorates over time due to the increasing number of load repetitions and the cycling through temperature extremes in summer and winter. This deterioration manifests itself in a number of ways. Common distresses include rutting, fatigue cracking, thermal cracking, reflective cracking, aging, raveling, and stripping¹⁻³. Conventional asphalts may resist one type of distress but are susceptible to others. For example, hard asphalts are resistant to rutting but are susceptible to thermal and fatigue cracking. Soft asphalts, on the other hand, are resistant to thermal and fatigue cracking but suffer from serious rutting problems. It is therefore desirable to modify the binder to extend the temperature range of acceptable performance. The most common method is the addition of polymer modifiers to the asphalt. Much work has been done to show that polymer modification can improve pavement performance⁴⁻⁶. The majority of the studies that have been done have been rather limited in either modifiers or properties tested. There is a great need for a systematic study of polymer modified asphalts.

Michigan State University, in conjunction with the Michigan Department of Transportation, is currently conducting a comprehensive study of modified asphalts. The study is divided into three sections: the fundamental physical, chemical, and thermodynamic properties of asphalts, modifiers, and blends; the basic morphology and microstructure of modified asphalt-aggregate mixtures; and the engineering and structural

properties of modified asphalt-aggregate mixtures. The focus of this thesis is the physical, chemical, and thermodynamic properties of asphalt binders.

The main objective of this study is to evaluate the use of polymer modified asphalts as a method of improving pavement performance. To do this, the interaction between polymer and asphalt was characterized. Possible theoretical models were investigated, as well as the relationship between the chemical and physical properties of the neat binders.

A second objective of this research was the development of a comprehensive database of physical and chemical properties of neat and modified binders. This database leads to many secondary deliverables of the study, including: determination of optimum polymer content for each modifier; modifications to the fingerprinting protocol developed earlier in the study ⁷; and a review of the SHRP and MDOT binder specifications with suggested revision for use with polymer modifications.

The four most common asphalt grades used in Michigan roads (AC-2.5, AC-5, AC-10, and AC-20) were selected for this study. They are viscosity graded asphalts supplied by Amoco. They are graded from low viscosity (AC-2.5) to high viscosity (AC-20). The polymers studied were styrene-butadiene rubber (SBR) supplied in latex form by Ultrapave, Elvaloy® AM (EAM) supplied in pellet form by DuPont, crumb rubber particles supplied by Rouse Rubber, and ethylene vinyl acetate (EVA) supplied in powder form by Exxon.

The following experiments were conducted to determine binder properties:

- Dynamic Mechanical Analysis
- Rotational Viscometry

- High Performance Gel Permeation Chromatography
- Fourier Transform Infrared Spectroscopy
- Thermal Mechanical Analysis
- Differential Scanning Calorimetry
- and, Bending Beam Rheometry

Chapter Two contains relevant background information. It includes a discussion of asphalt behavior and fatigue methods, a discussion of polymer modification research found in the recent literature, and a summary of the work conducted earlier in the MSU/MDOT project by Jeffrey Shull which was concerned with styrene-butadiene-styrene (SBS) and styrene-ethylene-butylene-styrene (SEBS) modification.

Chapter Three contains a detailed description of the experiments used in this study. It starts with an introduction to the Strategic Highway Research Program (SHRP) findings, continues with a discussion of the SHRP performance based binder specifications and test procedures, and finishes with a discussion of additional binder tests not found in the SHRP specifications.

Chapter Four contains the physical and chemical property data for the modifiers studied. It includes, but is not limited to, rheological properties, molecular weight distributions, functional group determination, softening point, and SHRP performance grade. It also contains the mixing procedures used for each modifier, the determination of the optimum polymer content for each polymer/asphalt system, and a discussion of the effect of polymer molecular weight on SBR and EVA modification.

Chapter Five contains the physical and chemical property data for the neat binders studied. It shows the correlation between molecular weight and various physical

properties of asphalt. It also investigates correlations between asphaltene content and physical properties.

Chapter Six contains an evaluation of the applicability of the SHRP performance grading system for modified binders. Chapter Seven concludes the thesis with a summary of the findings and recommendations for future research.

Chapter Two

Introduction and Background

A large majority of roads in the United States are paved with asphalt concrete. These roads are showing signs of premature stress, especially in states like Michigan whose climate causes both high and low temperature extremes. Roadways can be designed using conventional asphalt to perform extremely well in areas with only high temperature extremes and reasonably well in areas with only low temperature extremes. Unmodified asphalts do not hold up well in areas with both extremes. There are a number of ways to modify asphalts: careful selection of crudes and refining processes can be used to give a better asphalt; asphalt constituent composition can be engineered to give improvements in certain properties; the asphalt can be aged by heating which results in better high temperature properties due to oxidation; or a modifier such as polymers or fibers can be added to improve the properties. The majority of modification being done involves polymer addition. Michigan State University, in conjunction with the Michigan Department of Transportation, is currently finishing a three year study of polymer modified asphalt. The goal of this study is to provide a systematic protocol for selecting asphalt modifiers and for establishing mixture processing conditions to provide pavements with longer service life. The focus of the research in this thesis is a greater understanding of the underlying chemical properties which govern asphalt physical properties and how modification can effect these properties.

2.1. Asphalt Composition

Asphalt is a complex mixture of organic molecules. An elemental analysis of a generic asphalt shows the following composition: 84 percent carbon, 10 percent hydrogen, 1 percent oxygen, and the remainder consisting of several trace elements including nitrogen, sulfur, vanadium, nickel, and iron ⁸. The molecular structure is much more important with regard to properties than the actual elemental components. Asphalt consists mainly of linear and organic ring structures with an average molecular weight of 500 to 5000 ⁸. Typical elemental analysis and molecular weight data for three different asphalt grades studied are presented in Table 2.1 ⁸.

Table 2.1 - Elemental analysis of several asphalts

	AC-5	AC-10	AC-20
Carbon, %	85.7	82.3	84.5
Hydrogen, %	10.6	10.6	10.4
Oxygen, %	-----	0.8	1.1
Nitrogen, %	0.54	0.54	0.55
Sulfur, %	5.4	4.7	3.4
Vanadium, PPM	163	220	87
Nickel, PPM	36	56	35
Iron, PPM	-----	16	100
Aromatic C, %	32.5	31.9	32.8
Aromatic H, %	7.24	7.12	8.66
Molecular Weight	570-890	810-930	840-1300

Asphalt components have traditionally been divided into three categories: oils, resins, and asphaltenes. Asphaltenes, which govern many of the properties of asphalts, are the heaviest molecules. They have an average molecular weight greater than 2000. They contain the trace elements such as nickel, iron, and vanadium and are soluble in carbon tetrachloride. Resins are intermediate molecular weight (800-2000) polar

molecules. Resins often contain sulfur and nitrogen and are soluble in light petroleum naphtha ⁹. Oils are low molecular weight (25-800) molecules which have a large number of side chains and few ring structures. They have a carbon/hydrogen ratio of less than 0.6 and are soluble in hexane ⁹. An typical asphalt sample has an asphaltene/resin/oil ratio of 23/27/50 with harder asphalts having a higher concentration of asphaltenes. Table 2.2 lists the ratios for three different asphalts ¹⁰.

Table 2.2 -Asphaltene/Resin/Oil ratio of three asphalts

	Asphaltene	Resin	Oil
Average Sample	23	27	50
Mexican Asphalt (170 pen, AC-20)	18.6	39.7	41.22
Mexican Asphalt (238 pen, AC-40)	28	37.7	44

This three component classification leads to a general two phase asphalt model ⁹. The model consists of an assembly phase (asphaltene and resins) dispersed in an oil phase. This can be seen in figure 2.1. The resins serve to stabilize the asphaltene in the oil phase.

The assembly phase can vary between 40 and 60 angstroms in diameter. The size of the assembly phase increases with increasing asphaltene content. This adds structure to the asphalt and makes the asphalt stiffer. This translates to better high temperature properties. The asphaltene and oil combination acts as a colloid, with the polar resins stabilizing the colloid. The asphaltene can exist as discrete particles or in a micelle structure. Depending on whether the polar groups are oriented inward or outward determines whether it is an oil-external or oil-internal micelle. The presence of these

micelles is affected by temperature, resin content, and any other modifiers present in the asphalt. These micelles greatly affect engineering properties of the asphalt.

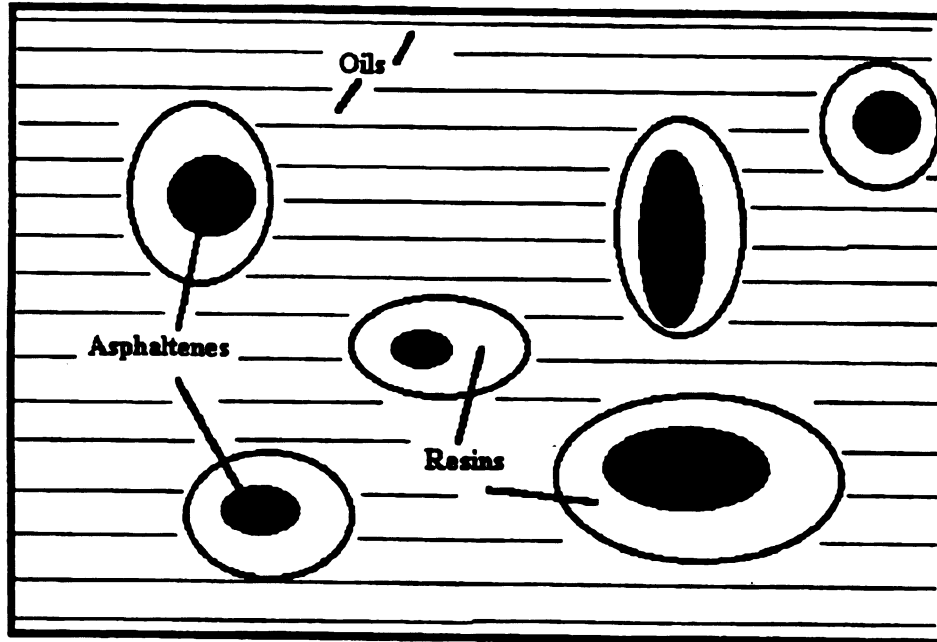


Figure 2.1 - *The two phase asphalt model*

Asphalt molecules contain many different organic functional groups. Asphalt is known to contain carboxylic acids, ketones, phenols, sulfoxides, acid anhydrides, pyrroles, and quinones⁸. These functional groups can react with a reactive polymer modifier, such as an epoxy. They are also important in age hardening, which is essentially oxidation of these functional groups which causes increased stiffness.

2.2 - Asphalt Failure Mechanisms

Asphalt manifests failure in a number of mechanisms. The most common forms of distress are thermal cracking, block cracking, fatigue cracking, rutting, and raveling or stripping. Table 2.3 summarizes the most common forms of pavement distress.

Thermal cracking can be caused by three mechanisms. First, fracture can be caused by the aggregate and binder having different coefficients of thermal expansion. As the temperature changes, the aggregate and binder expand at different rates causing cracking. Second, fracture can be caused by the presence of water in existing cracks in the asphalt. The freeze/thaw cycle found in climates like Michigan cause crack propagation. Third, fracture can be caused by increased brittleness in cold temperatures. This is usually a result of oxidative aging. When this brittle pavement is exposed to a load it is susceptible to fracture initiation.

Block cracking is similar to thermal cracking. It is caused at all temperatures by embrittlement of the pavements. Again, this embrittlement is usually caused by age hardening.

Fatigue cracking is the least understood pavement distress mode. This is because the results of the fatigue tests are dependent on the test methods. It is difficult to determine the period of time in which damage grows from an initial state to a critical failure level. This fatigue cracking is the result of repeated cyclic and static loads and the tensile strains that they produce in the bottom of the asphaltic layers.

Rutting is the major high temperature failure mode. It results from the asphalt flowing under loads at high temperature. The asphalt suffers permanent plastic deformation. A harder asphalt can be used to prevent rutting but will be more susceptible to low temperature distress.

Raveling or stripping occurs when the adhesion between aggregate and binder is poor. The fracture is at the aggregate/binder interface.

Table 2.3 - Asphalt distress modes

Distress Mode	Cause
Thermal Cracking	• thermal expansion differences between aggregate and binder • water freeze/thaw cycle • low temperature embrittlement
Block Cracking	• embrittlement of asphalt binder
Fatigue Cracking	• tensile failure
Rutting	• microstructural rearrangement due to asphalt plasticity under load
Raveling/Stripping	• interfacial fracture due to low binder/aggregate adhesion

2.3 - Reasons for Polymer Modification

Asphalt is a viscoelastic material whose properties are a very strong function of temperature. For optimum performance, asphalt must be soft at low temperatures to prevent cracking and hard at high temperatures to prevent rutting. This is the exact opposite of the way most materials behave. One way to improve the properties of asphalt is to add a modifier, such as polymer.

Goodrich proposed a model of asphalt that consists of a shock absorber and a spring as shown in Figure 2.2¹¹. The spring represents the elastic properties and the shock absorber represents the viscous properties. At high temperatures, the asphalt shows good viscous flow behavior and behaves mostly like a shock absorber. Rutting occurs because of the lack of elastic behavior. At low temperatures, the asphalt becomes a brittle elastic solid with little or no viscous character. In Goodrich's analogy, the spring becomes overloaded and snaps resulting in low temperature cracking. To reduce the

rutting and cracking potentials, various modifiers were added to asphalt. The goal is to increase the range of both the elastic and viscous properties of the asphalt binders. Convenient measures of these properties are G' , the elastic storage modulus, and G'' , the viscous loss modulus. The ideal case will have high temperature G' increasing and low temperature G'' increasing with modification.

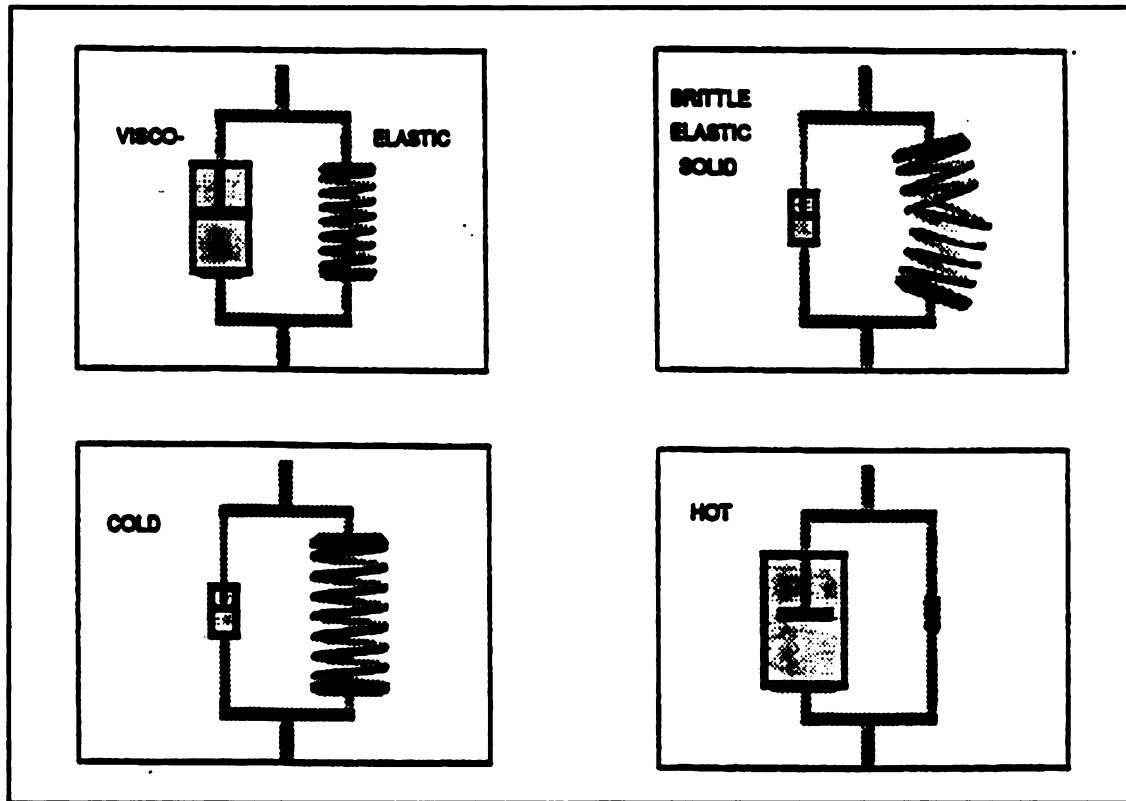


Figure 2.2 - Spring/shock absorber model of asphalt

2.4 - Polymers Commonly Used for Modification

The basic criteria for selecting a polymer modifier are performance, ease of processing, and economics. According to the functions and behaviors of various modifiers in asphalt, modifiers can be classified into five main types: dispersed thermoplastics, network thermoplastics, reacting polymers, fibers, and crumb rubber (CRM) particles. Dispersed thermoplastics behave like asphaltenes and normally require peptizing agents like resins to stabilize the modified system. Without peptizing agents, these polymers tend to phase separate from the asphalt binder. Usually it requires a considerable amount of dispersed thermoplastic material before formation of a macrostructural network occurs. Network thermoplastics behave somewhat like resins and will form a network of themselves inside asphalts. Network thermoplastics generally form a macrostructural network upon addition of 3% (w/w) to 7% (w/w) polymer. Reacting polymers bond chemically to the asphaltenes and form either asphalt/polymer networks or larger asphaltene groups. Fibers increase the available wetting surface area and behave as binder thickeners. Crumb rubber particles behave as aggregates if they are large ($> 100\ \mu\text{m}$) or as dispersed thermoplastics if they are small ($< 100\ \mu\text{m}$). Surface modification of CRM particles, such as sulfonation, can create functional groups to react with the asphalt. Figure 2.3 is a pictorial representation of four different phase behaviors seen in modified asphalt systems¹³. Table 2.4 lists many polymers that have been studied as additives. Reactive polymers are the most expensive, followed by network polymers and dispersed polymers. However, the amount of modifier needed for a given level of improvement generally evens out the costs.

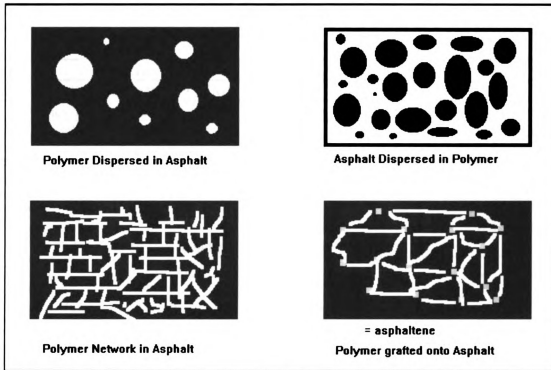


Figure 2.3 - Polymer/asphalt phase behavior

One or two of the most promising modifiers of each type were selected for this study. The polymers used were styrene-butadiene-styrene (SBS), styrene-ethylene-butylene-styrene (SEBS), styrene-butadiene rubber (SBR), Elvaloy® AM (EAM), ethyl vinyl acetate (EVA), polyethylene (PE), and crumb rubber particles (CRM). Work on SBS and SEBS was conducted prior to the author joining the research team and is summarized in section 2.6. This thesis focuses on SBR, EAM, EVA, and CRM modification.

Table 2.4 - Most common polymers used for modification

Polymer	Abbreviation	Cost (\$/lb.)	Tg (°C)
DISPERSED THERMOPLASTICS			
Ethylene-vinyl acetate	EVA	*	23 to 39
Polypropylene	PP	0.3	-30 to 20
Atactic Polypropylene	APP		
Polyethylene	PE	0.4	-130 to -15
Low Density Polyethylene	LDPE		
Polystyrene	PS	0.55	80 to 100
Polybutadiene	PBDt	*	-107 to -83
Hydroxyl Terminated Polybutadiene	HTPB		
NETWORK COPOLYMERS			
Styrene Butadiene Rubber	SBR	0.75	-64 to -59
Styrene-Butadiene-Styrene	SBS		
Styrene-Butadiene	SB	0.75	-60 to -90
Styrene-Ethylene-Butylene-Styrene	SEBS		
REACTIVE POLYMERS			
Elvaloy® AM	EAM	1.50	*

* Not measured at this time

2.5 - Recent Results from the Literature

A number of studies have been conducted investigating the effects of polymer modification on asphalt performance. While the results have varied from study to study, the general trend shows that polymer modification improves asphalt pavement performance. Figures 2.4 through 2.8 show the results of the literature survey conducted by MSU for the Polymers in Bituminous Mixtures, Phase I project ¹². All of these figures show the number of studies which reported positive and negative results of modification on various properties used to measure performance. These figures show that the majority of the studies have found that polymer modification does enhance pavement performance.

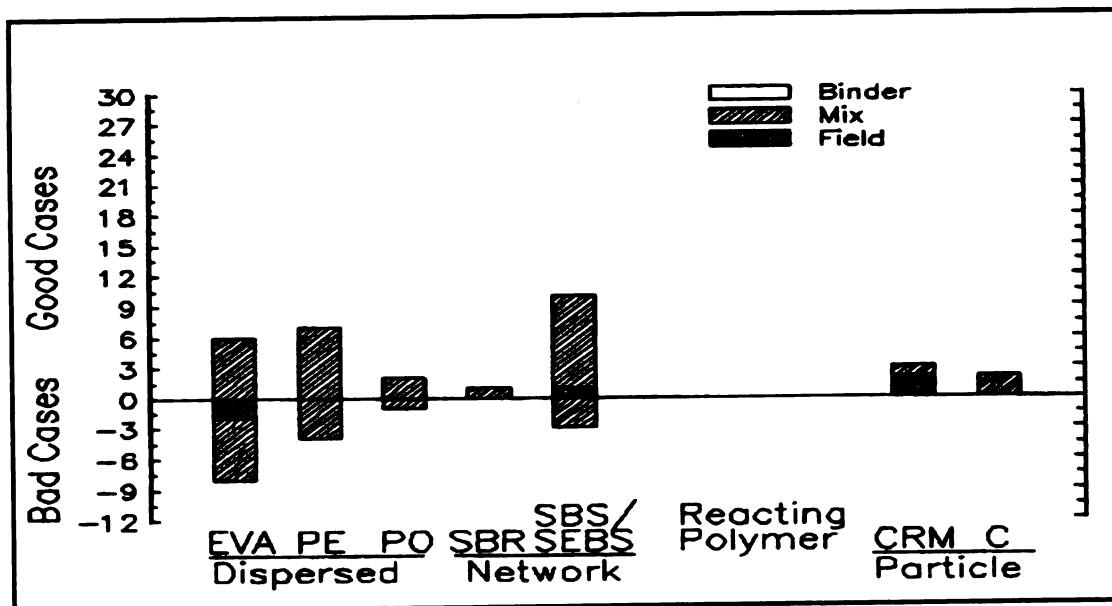


Figure 2.4 - Modifier effect on fatigue cracking

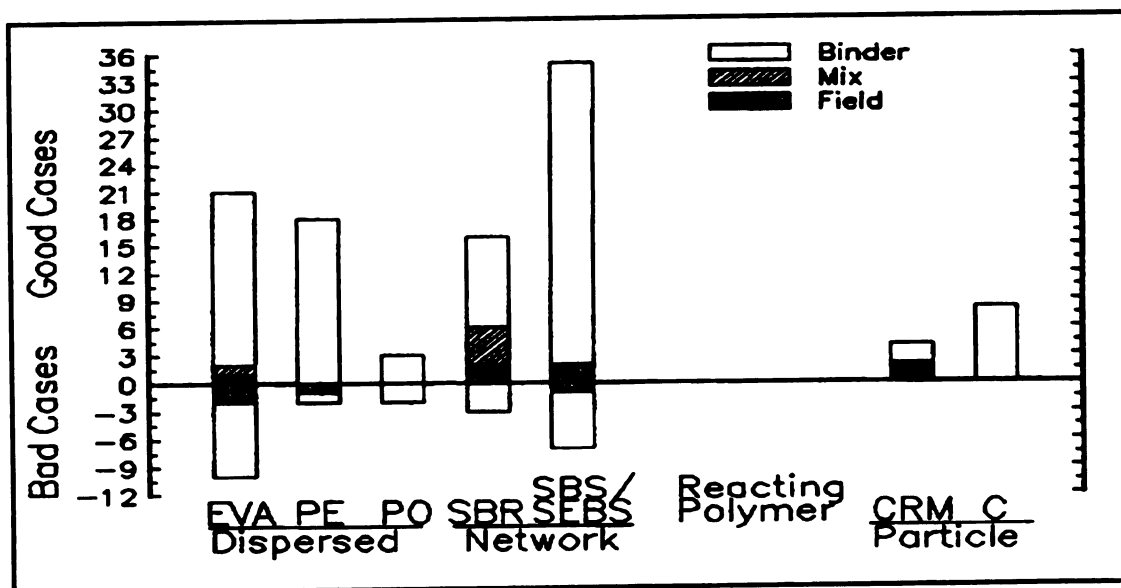


Figure 2.5 - Modifier effect on rutting

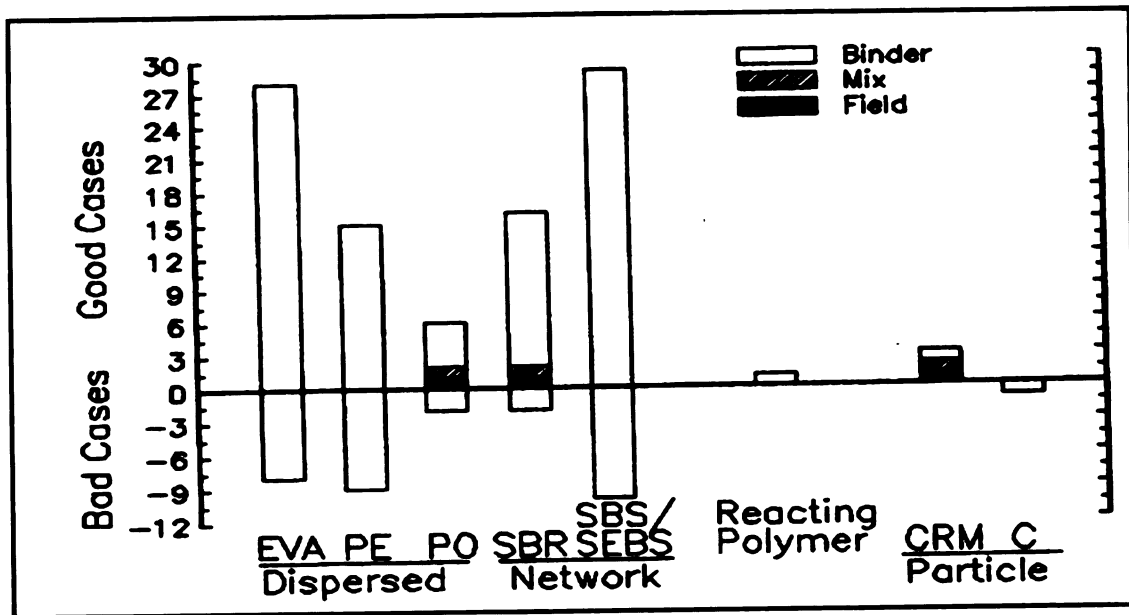


Figure 2.6 - Modifier effect on thermal cracking

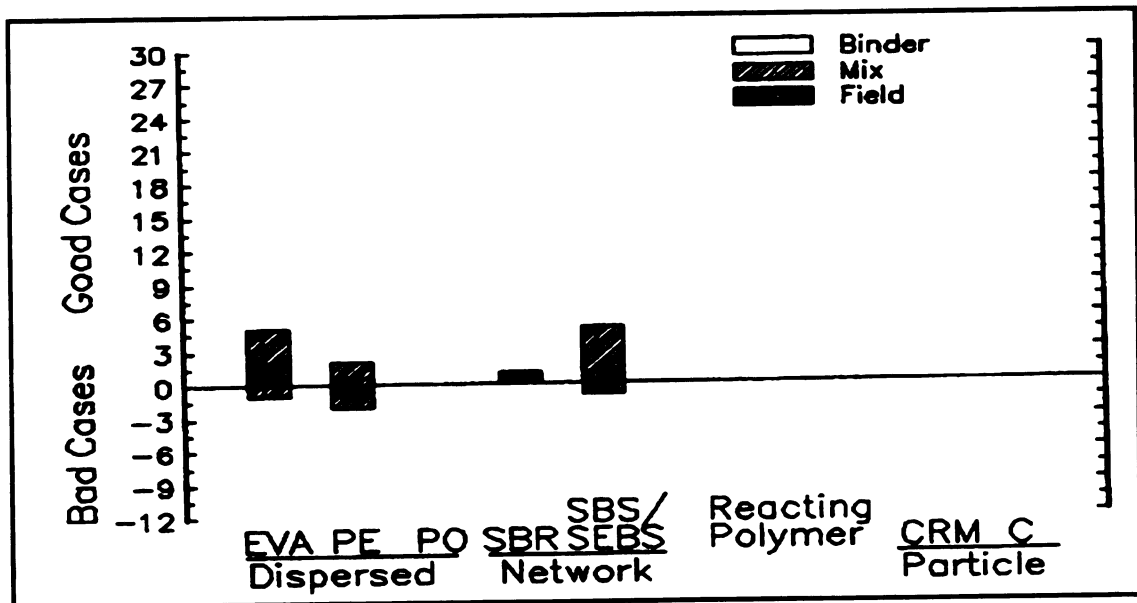


Figure 2.7 - Modifier effect on raveling

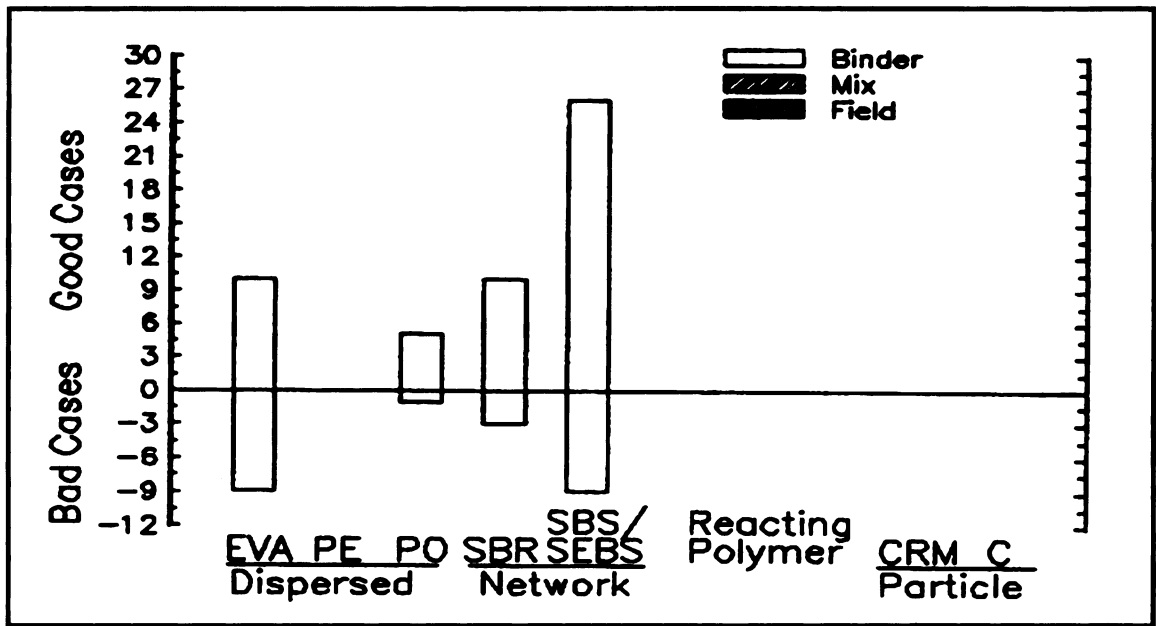


Figure 2.8 - Modifier effect on age hardening

For dispersed thermoplastics, modifiers that improved the low temperature susceptibility of asphalts included ethylene acrylic copolymer¹⁴, hydroxylterminated polybutadiene (HTPB)¹⁵, and polypropylene wax (PPW)¹⁵. Modifiers that improved the fatigue cracking resistance included HTPB¹⁵, and PPW¹⁵. When polyethylene (PE) was used to modify AC-20 asphalt, the modified binder had a higher resistance to permanent deformation and thermal cracking¹⁵⁻¹⁷.

Reviews of previous studies show that PE is the most promising candidate in the dispersed thermoplastics family. The glass transition temperature of PE ranges from -130 to -15°C. Polyethylene, however, is insoluble in asphalts (tends to phase separate in the asphalt/polymer blend). For example, PE will coagulate and separate from the asphalt phase in half an hour at 160°C after mixing if no stabilization technique is introduced.

The properties of a phase separated asphalt/polyethylene blend are less than those of straight asphalt. Therefore, phase separation needs to be prevented.

There are two ways to prevent phase separation. One is to reduce the storage time, such as done by Novophalt. This technique requires a huge mixing truck on the construction site so that asphalt, aggregate and PE can be mixed just prior to being laid down. Usually, the smaller the PE particle size, the better the performance of the PE modified pavement. Another way to prevent PE phase separation is through stabilization of the asphalt/PE blend.

Many methods can be used for stabilizing an asphalt/PE blend. They are, structural stabilization by gelling agents, specific polymer/asphalt functional reactivity, specific asphalt selection/modification, partial dissolution by polymer oxidation, and steric stabilization by a block or graft copolymer.

For structural stabilization by gelling agents, both inorganic and organic agents have been studied. When inorganic fillers are added to a liquid, a three dimensional network is formed ¹⁶. This has a thickening effect which tends to increase the brittle nature of the composite. Therefore, when inorganic agents are added to asphalt, the agents may introduce cracks at low temperatures. Organic gelling agents may give the blend macro scale stability but micro scale phase separation can still occur.

Through the introduction of certain functional groups to the polymer backbone, such as ester forming groups, polyethylene can be made partially soluble and stabilized in liquid bitumen. These methods include phosphonization, chlorosulfonation, maleic anhydride grafting, and acrylic acid grafting. If an asphalt only contains a small amount of polar aromatics (<5%), PE is a good modifier and the asphalt/PE blend will be stable.

Polyethylene chlorinated to less than 15 weight percent and polyethylene maleated to less than four weight percent were used to modify asphalts and resulted in improved properties¹⁸.

Partial dissolution by polymer oxidation is another method that can be used for asphalt/PE stabilization. The oxidation of polymer makes PE more compatible with asphalt. Oxidation techniques include hot air, high shear, and catalytic oxidation. However, the method causes deterioration of the low temperature properties of asphalt.

In steric stabilization, PE coalescence is prevented using a form of steric barrier to keep the particles apart far enough so that Van der Waals interactions can be overcome by thermal forces. The steric barrier should be soluble in asphalt and reactive with polyethylene. Stabilizers studied include styrene-butadiene rubber, Kraton G1652, and styrene hydrogenated butadiene-styrene tri-block copolymer.

This study used poly ethylene vinyl acetate in place of polyethylene. EVA results in performance similar to polyethylene without the need to stabilize the asphalt/polymer blend.

For network thermoplastics, modifiers that increased binder resistance to rutting included styrene-butadiene-styrene (SBS)^{15,19,22}, styrene-ethylene-butylene-styrene (SEBS)^{20,21}, and styrene-butadiene random copolymer (SBR)^{5,6,19,22}. However, they only improved binder low temperature properties slightly. SBR modified asphalts also had less fatigue cracks^{5,19,22}. However, ethylene-vinyl acetate (EVA) modified AC-20 showed more rutting and fatigue cracking as well as a tendency of stripping^{5,15,20,22}.

SBS/SEBS and SBR are the most promising candidates in the network thermoplastics family. SBR modifier is usually used in the latex form, a polymer/water

mixture. SBR latex is manufactured at temperatures of 100-110°F with a resulting polymer size of 0.1 micron and an overall solid weight percentage of 31%. Mechanical agglomeration is used to concentrate the latex and the final commercial product is 70 % (w/w) solids with a polymer size of half a micron. Typically, 3 to 5 % (w/w) of dry SBR is added to asphalt. Generally, a homogeneous blend is desired with asphalt as the continuous phase. In SBR modified asphalt, asphalt remains the continuous phase if the SBR concentration is below approximately 7 % (w/w). Molecular weight distribution and average polymer size in the latex are two variables that can be adjusted to increase compatibility between asphalts and polymers in the network thermoplastic family.

For reacting polymers, epoxy²⁴ and Elvaloy[®]AM modified asphalts showed less rutting, thermal cracking, and temperature susceptibility. Furfural^{23,25} modified asphalts had lower temperature susceptibility, higher resistance to rutting and low temperature cracking, higher freeze-thaw resistance, and better adhesion, but lower cohesion. Maleic anhydride (MAH)²⁶ modified asphalts had lower temperature susceptibility, higher resistance to rutting and low temperature cracking, and better adhesion, but lower cohesion. For the reacting polymers, previous studies are very limited.

Polymers with epoxide and hydroxyl groups are recommended for the reacting polymer family. Elvaloy[®]AM is a modified ethylene copolymer with a reacting epoxide group developed by DuPont/Chevron for the modification of asphalt cement. Most polymers, when added to asphalt cement, become dispersed and upon addition of more polymer, form a network which gives the desired properties. Elvaloy[®]AM, on the other hand, chemically reacts with asphalt cement creating a new material. Because of this reaction, DuPont claims that only 1-2 percent by weight of their material needs to be

added to asphalt cement versus 3-5 weight percent of most other polymers to obtain the same desired properties. Elvaloy®AM contains an epoxy functional group that DuPont believes reacts with aromatic carboxylic acid functional groups found in the asphaltene portion of asphalt cement. Figure 2.9 is a chemical schematic of Elvaloy®AM.

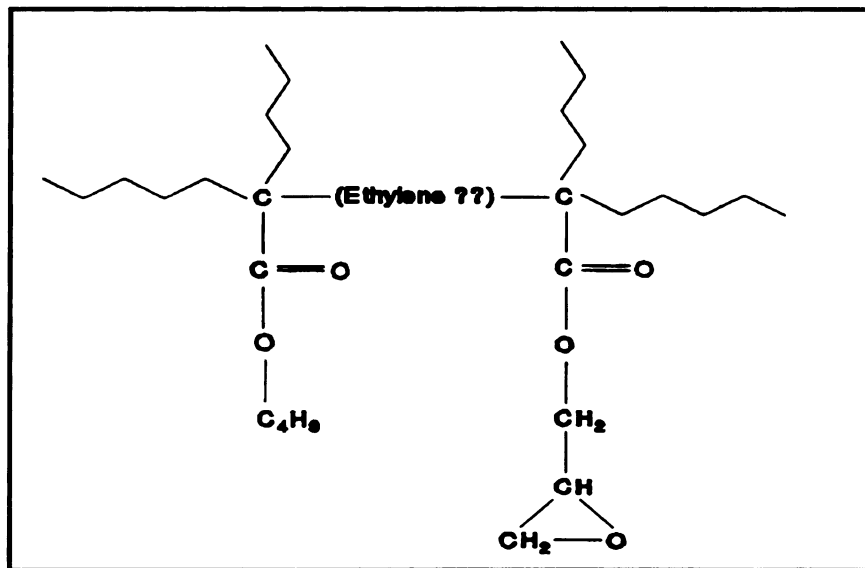


Figure 2.9 - Chemical structure of Elvaloy®AM

The reaction of Elvaloy®AM with asphalt cement was tested by looking at infrared measurements that showed the epoxy functional groups disappeared after being reacted with asphalt cement. Too much Elvaloy®AM will result in gelling the asphalt mixture due to the extensive crosslinking structures caused by the reacted epoxy functional groups. The amount of polymer needed for asphalts from different sources also varies.

DuPont tested Elvaloy®AM modified asphalt cements using dynamic mechanical analysis and found that the material remained elastic at high temperatures which would

help prevent rutting. The binder properties remained the same at low temperatures as those of straight asphalts. In order to improve both high and low temperature properties, a softer asphalt should be used with Elvaloy®AM.

DuPont and Chevron tested their product using the Chevron creep test, bending beam test, split tensile measurements, and resilient modulus measurements. All tests showed the DuPont product to be superior to SBS and SBR. It should be noted that all of these tests were conducted by the manufacturer of the superior polymer.

Mixing Elvaloy®AM with asphalt cement requires a low horse power stirrer, a heated tank, and an elevator assembly that will transfer the polymer to the tank. The polymer must be allowed to react with the asphalt cement for 2-48 hours at 350°F. The polymer is mixed in a solid form and DuPont claims to have never gelled a tank. Aging/oxidation was found not to be a problem when processing at these high temperatures because the tanks are sealed and no air is allowed to circulate in the system. The manufacturer stated a case where Elvaloy®AM modified asphalt cement was stored for 100 days at 350°F, and no viscosity change was recorded with only a one hour per day mixing period.

Elvaloy®AM is handled at temperatures similar to those of other polymer modified asphalts, but has been found not to be stringy and sticky like SBS and SBR modified asphalts. No recyclability experiments have been conducted on Elvaloy®AM modified asphalts. At the present time, Elvaloy®AM costs between \$1.20 and \$2.00 per pound.

For crumb rubber modifiers (CRM), both good and bad field results were reported. Good field performance^{27,28} was reported for low temperature susceptibility.

The reported bad field performances²⁹⁻³¹ included severe aging, lower tensile and shear strength, raveling, reflective cracking, and stripping.

Though the benefits of crumb rubber modification to asphalts are still being debated, CRM has to be studied due to environmental regulations. The principle source of CRM is scrap tire rubber in forms of whole tire, cut tire, shredded tire, or retread buffing waste. Tire rubber is primarily a composite of a number of blends of natural and synthetic rubbers and carbon black. There are three processing methods to produce CRM: granulator, crackmill, and micromill. The granulator process shears apart the scrap tire rubber and cuts the rubber with revolving steel plates that pass at a close tolerance. The product of this process is called granulated CRM which has a low surface area and particle size range of 9.5 mm to 2.0 mm (3/8'' - No.10 sieve). The crackmill process, the most common process, tears apart scrap tire rubber and reduces the size of the rubber by passing the material between rotating corrugated steel drums. The product of this process is called ground CRM which has a large surface area and particle size range of 4.75 mm to 425 μm (No.4 - 40 sieve). The micro-mill process further reduces the crumb rubber to very fine ground particles. The product of this process is called fine ground CRM which has a large surface area and a particle size range of 425 μm to 75 μm (No.40 - 200 sieve). The average cost of commercial CRM ranges from 20 to 35 cents per kilogram for coarse and medium crumb and up to 55 cents per kilogram for fine ground crumb.

Among the five types of modifiers, the order of importance in Michigan is network thermoplastics, reacting polymers, dispersed thermoplastics, fibers, and CRM particles. The CRM particles could become more important if congressional legislation is implemented requiring their use.

2.6 - Summary of SBS/SEBS Results

Year 1 of the MSU/MDOT study focused on SBS and SEBS as modifiers.³² Laboratory results indicate that there is measurable improvement in pavement performance for SBS and SEBS modified binders. The rheological properties of the binders were improved with increasing polymer content up to a certain "optimum" content, after which improvement was minimal. SBS showed an unexpected reduction in properties at around 3.5% - 4.5% (w/w) polymer. Figure 2.10 shows the storage and loss moduli as a function of SBS content for modified AC-5 binders. At first glance this appears to be an experimental artifact. However, a new series of AC5/SBS binders was mixed and tested resulting in similar phenomena. Figure 2.11 shows the storage and loss moduli for the second set of binders. It was theorized that at low polymer concentrations, SBS is slowly destroying the natural structure of the asphalt by absorbing the oils. At some intermediate polymer content, the asphalt suffers a sharp reduction in properties due to the disruption of the polar resin-asphaltene network by the SBS. At a slightly higher polymer content, the SBS forms a network structure and dominates the properties of the blend. Figure 2.12 is a graphical representation of this rheological theory.

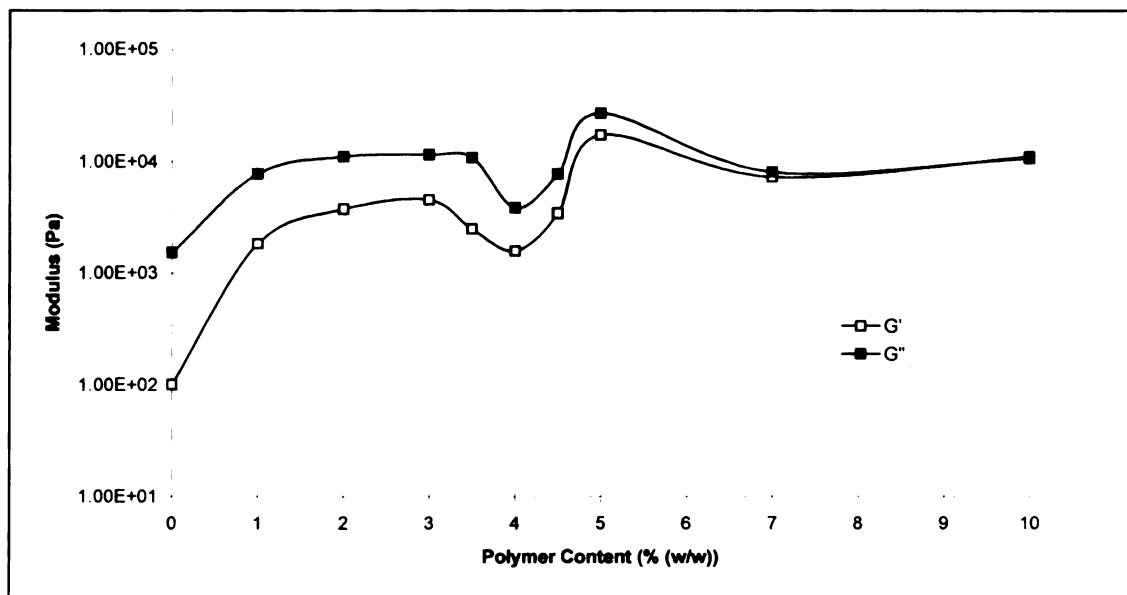


Figure 2.10 - Loss and storage moduli at 60°C of AC-5/SBS binders (Batch #1)

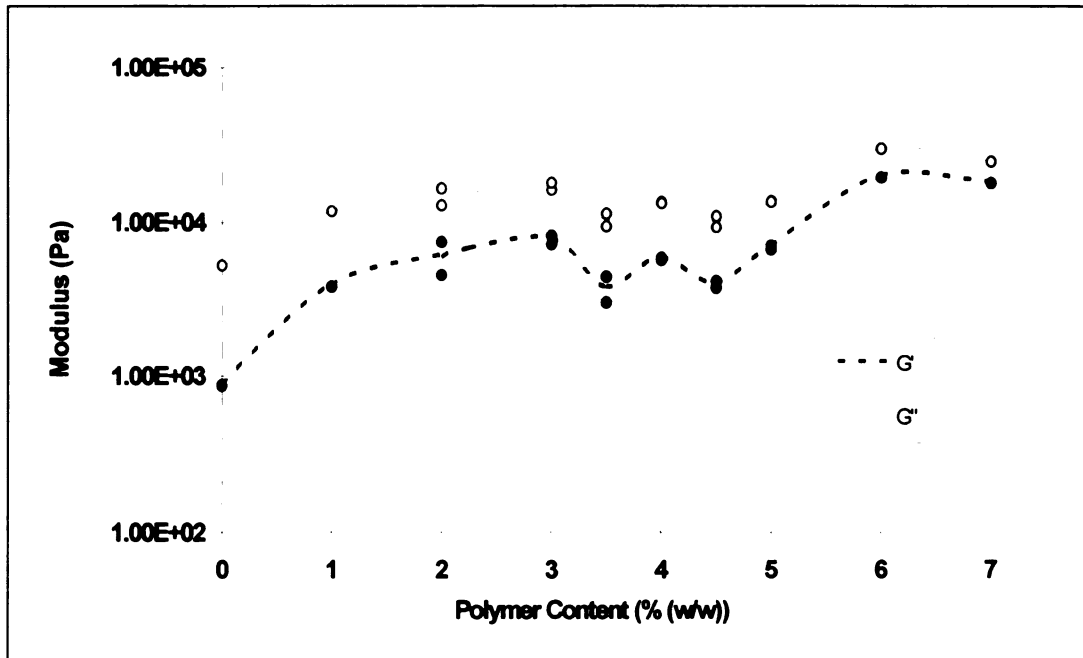


Figure 2.11 - Loss and storage moduli at 60°C of AC-5/SBS binders (Batch #2)

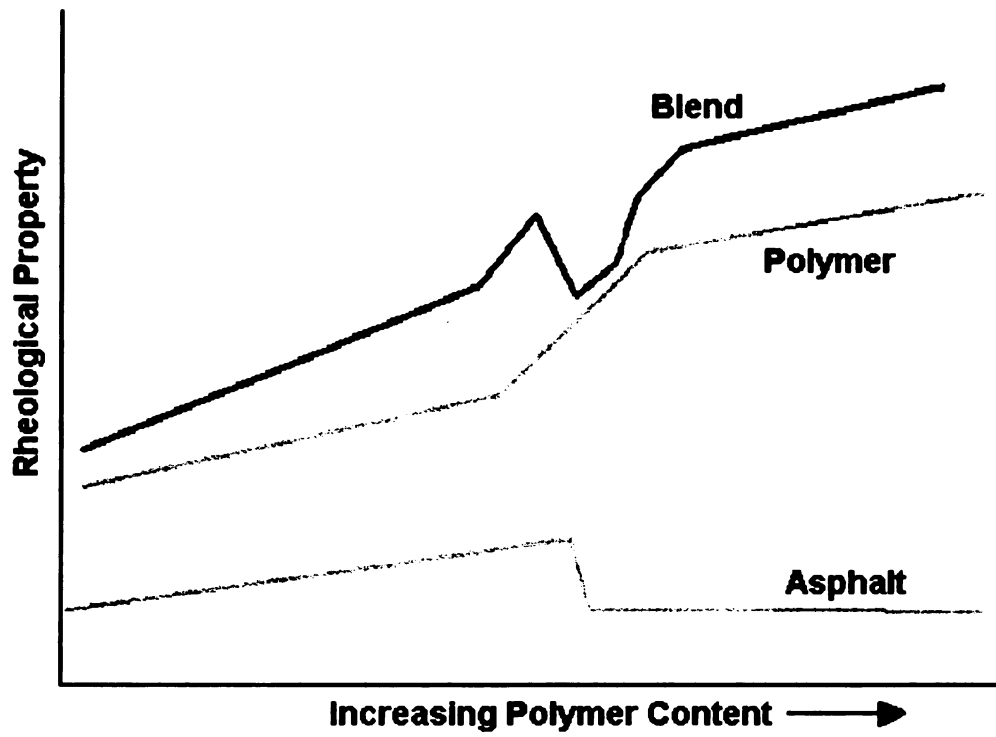


Figure 2.12 - Depiction of SBS modified asphalt theory at service temperatures

Chapter Three

Testing Procedures

Penetration and viscosity have traditionally been used to differentiate between different grades of asphalt. Both methods leave a lot to be desired. There are many chemical and physical differences between asphalts with the same penetration grade or viscosity grade. Figure 3.1 shows three asphalts that have the same viscosity grade ³³. It is apparent that these materials do not have the same physical properties and may exhibit extreme performance differences. State highway agencies recognized the deficiency in the current system. In 1987, the Strategic Highway Research Program (SHRP) was formed to develop a new method for grading asphalt cement.

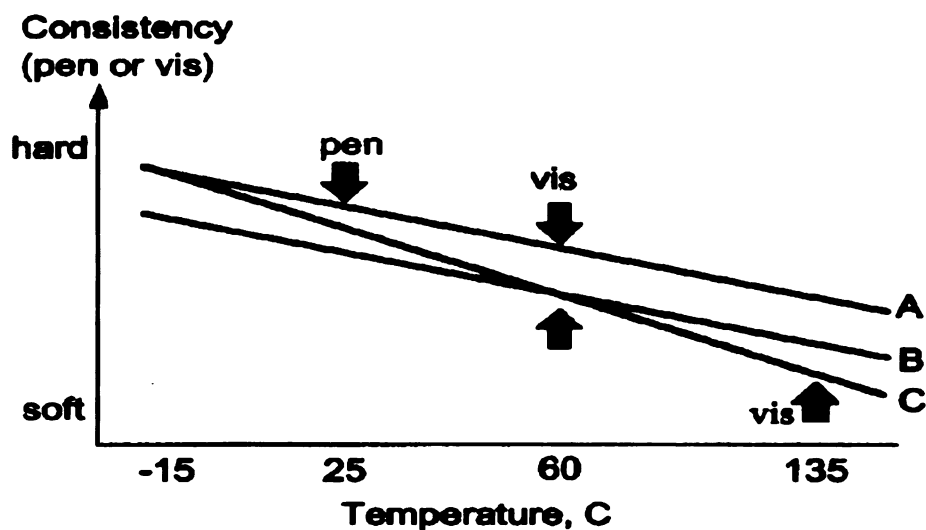


Figure 3.1 - Variations of three viscosity-graded asphalts

3.1 - SHRP Background

The major result of this initiative was the development of performance based binder specifications. Physical properties were selected that correlate well with pavement performance. A minimum specification value was determined that differentiated a good performing asphalt from a poor performing binder. The temperature at which the asphalt meets this specification determines its performance grade. The value of the specification remains constant because good pavement performance is expected in both Arctic and desert pavements. The SHRP tests simulate the three critical stages of the binder's service life: neat binders, processing and compaction, and long term aging. It is important to remember that these tests assume that the compaction and construction methods are sound. If not, even the best binder will perform poorly in an actual road.

3.2 - SHRP Binder Specifications

This section explains how the SHRP tests relate to pavement performance. Table 3.1 shows the SHRP binder specification sheet ³³. The PG contains two numbers, for example 52-40. The first number represents the average 7-day maximum pavement temperature that this asphalt can sustain, in this case 52°C. The second number represents the minimum instantaneous temperature that the pavement can withstand, in this case -40°C. By looking at climate data for the specific construction site a contractor can choose the appropriate asphalt grade. For example, Juneau, Alaska calls for a PG 46-26 while Phoenix, Arizona calls for a PG 70-10 ³³. Clearly different asphalts are needed for these two locations.

Table 3.1 - SHRP performance grading worksheet

Performance Grade	PG-76			PG-82		
	-16	-22	-28	-10	-16	-22
7-Day Maximum Pavement Temperature °C	<76			<82		
Minimum Pavement Temperature °C	>-16	>-22	>-28	>-10	>-16	>-22
Original Binder						
Flash Point Temp, Min. °C	230					
Viscosity, ASTM D 4402 Maximum 3 Pa·s Test Temp, °C	135					
Dynamic Shear, TP5 G*/sin δ, minimum 1 kPa Test Temp @ 10 rad/s, °C	76			82		
Rolling Thin Film Oven or Thin Film Oven Residue						
Mass Loss, maximum %	1.00					
Dynamic Shear, TP5 G*/sin δ, minimum 2.2 kPa Test Temp @ 10 rad/s, °C	76			82		
Pressure Aging Vessel Residue						
PAV Aging Temperature °C	100			100		
Dynamic Shear, TP5 G* sin δ, maximum 5000 kPa Test Temp @ 10 rad/s, °C	34	31	28	40	37	34
Physical Hardening	Report					
Creep Stiffness, TP1 S, Maximum 300 Mpa m-value, minimum 0.300 Test Temp @ 60 sec, °C	-6	-12	-18	0	-6	-12
Direct Tension, TP3 Failure Strain, minimum 1% Test Temp @ 1 mm/min, °C	-6	-12	-18	0	-6	-12

3.2.1 - Safety Test

The asphalt must have a minimum flash point of 230°C to be graded by the SHRP system. All binders in this study passed this test easily.

3.2.2 - Viscosity Test for Pumping

This test ensures that the asphalt binders can be processed using the currently employed equipment. To pass, the binder must not have a viscosity greater than 3 Pa·s at a temperature of 335°C. Any binder which fails this test cannot be graded.

3.2.3 - Permanent Deformation (Rutting) Test

Rutting is the major cause of pavement distress at high temperatures. Rutting resistance is measured using a Dynamic Shear Rheometer (DSR). The response of asphalt to load consists of two parts, elastic and viscous. Rutting is the accumulation of the non-recoverable viscous response. The high temperature stiffness, or rutting resistance, is characterized by the quantity $G^*/\sin \delta$. G^* is the complex shear modulus and δ is the phase angle. To minimize rutting, this value must be at least 1.00 kPa for neat binders and 2.20 kPa for RTFO aged binders. The specification promotes the use of stiff, elastic binders to prevent rutting³³. The temperature at which the binder meets both of these specifications determines the high temperature PG of the material.

3.2.4 - Excessive Aging Test

Excessive aging susceptibility is determined by measuring the mass loss during aging. The mass loss can be no greater than one percent of the original mass to meet the

specification. This prevents the use of an asphalt that would lose an excessive amount of volatiles during processing.

3.2.5 - Fatigue Cracking Test

Fatigue cracking occurs at low to moderate temperatures in pavements that have been in service for a while. G^* and δ are important in determining fatigue cracking resistance. Unlike rutting resistance, these values are determined at lower temperatures on binders which have been aged using RTFO and PAV. They are measured using a DSR, however the important value in fatigue cracking is $G^* \sin \delta$. The specification requires a maximum value of 5000 kPa. Low values of G^* and δ are desirable to prevent fatigue cracking³³.

3.2.6 - Thermal Cracking Test

The most important form of low temperature distress is thermal cracking. When the pavement temperature decreases, the asphalt shrinks and causes tensile stress build-up. When these stresses exceed the tensile strength of the binder, a crack forms³³. A Bending Beam Rheometer (BBR) is used to apply a creep load to the aged sample and measure the creep stiffness at low temperatures. To prevent cracking, the creep stiffness must be less than 300 MPa. The rate at which the binder stiffness changes with time is also important and is represented by the m-value. The m-value represents the slope of the stress-strain curve. A high m-value is desirable because it results in lower stresses and, consequently, less opportunity for cracking. The m-value must be at least 0.300 after 60 seconds of loading. A third factor in thermal cracking is direct tension strain. This

specification is only used if the stiffness is between 300 and 600 MPa and the m-value is over 0.300. This occurs rarely and therefore the direct tension specification is of less importance. The temperature at which the binder passes the fatigue cracking and thermal cracking tests determines the low temperature PG.

3.3 - Detailed Test Procedures

This section offers detailed procedures for all of the SHRP tests as well as all additional tests used to characterize neat and modified binders. Mixing procedures for each asphalt/polymer system are included in Chapter 4.

3.3.1 - Flash Point

The flash point test is conducted at the MDOT laboratory. The sample is heated to 230°C in accordance with the standard test method (AASHTO T 48).

3.3.2 - Dynamic Shear Rheometry

Dynamic Shear Rheometry (DSR) is used to measure the rheological properties of aged and unaged binders. The experiment is conducted by sandwiching a thin (1.6 mm) asphalt sample between two parallel plates. One of the plates oscillates at a user-determined frequency and the other plate is fixed. The response of the material as the plate oscillates is measured by a transducer connected to the opposite plate.

The DSR is used to characterize both elastic and viscous behavior by measuring the phase angle (δ) and the complex shear modulus (G^*). G^* contains an elastic component (G') and a viscous component (G''). G' is often referred to as the storage

modulus and G'' is called the loss modulus. The SHRP specification uses the dynamic shear modulus for the rheological properties. This modulus, defined as $G^*/\sin \delta$, incorporates both the phase angle and complex modulus into one number to give a simple measure of the rheological characteristics. The rheological properties are related by the following equations:

$$G^* = \sqrt{G'^2 + G''^2} \quad \text{and} \quad \tan \delta = \frac{G''}{G'}$$

The values of the rheological properties are highly dependent on temperature. At high temperatures, asphalt behaves as a completely viscous fluid. In this case, G' would be small and δ would be 90° . At low temperatures asphalt behaves like an elastic solid with a large G' , small G'' and δ equal to 0° . Under normal operating temperatures asphalt behaves as a combination of the two. This behavior is called viscoelastic. Figure 3.2 shows a plot of G^* and δ for two asphalts with the same G^* ³³. Even though both asphalts have the same value of G^* , Asphalt 2 is more elastic than Asphalt 1 because its δ is smaller. Asphalt 2 will recover much more deformation than Asphalt 1. It is important to consider both G^* and δ when describing asphalt rheology.

G' is a measure of the elastic response of the binder. At high temperatures, elastic response is an important factor in rutting resistance. A large value of G' indicates that the binder is better at preventing rutting, assuming all other variables are the same. G'' is a measure of the viscous response of the binder. At low temperatures, viscous response is an important factor in thermal cracking. A large value of G'' indicates less resistance to flow under load which corresponds to lower stiffness. This lower stiffness causes an increase in the cracking resistance of the binder.

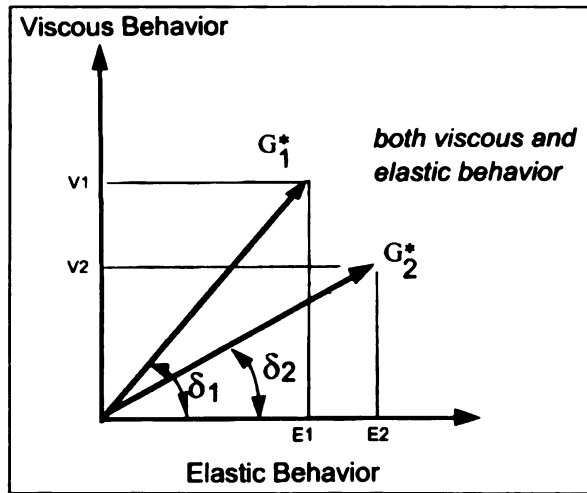


Figure 3.2 - Viscoelastic behavior of asphalt

In this study, a Rheometrics RMS-800 apparatus was used for measuring rheological properties. Experiments on unaged binders were conducted using 25 mm diameter plates and those on aged binders used 8 mm diameter plates. A gap width of 1.6 mm was used for both aged and unaged binders. Sample handling procedures were consistent with those used for the SHRP Bohlin instrument in which the sample is poured hot directly on the plates and allowed to cool to room temperature. Figure 3.3 shows the sample setup. Temperature sweeps were conducted from 25°C to 80°C with measurements taken at five degree intervals. The equilibration period between temperatures was two minutes. A frequency of 10 rad/sec was used in compliance with the SHRP specification. Strain levels were controlled to ensure that the testing was conducted in the viscoelastic range. Tests were conducted multiple times to ensure reproducibility. Figure 3.4 shows the reproducibility of storage modulus versus temperature for a triplicate. This reproducibility is excellent.

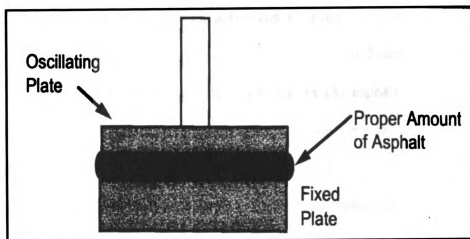


Figure 3.3 - Sample setup for DSR

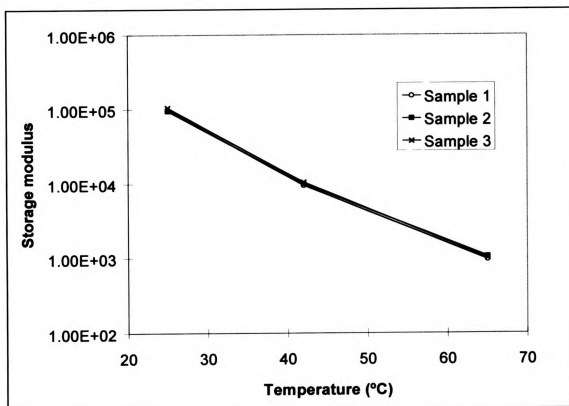


Figure 3.4 - Reproducibility of rheological data

3.3.3 - Rotational Viscometry

Rotational viscometry is conducted to ensure that the binder will be able to be pumped at the hot mix facility. The viscosity of the sample is determined by measuring the torque required to keep the spindle suspended in the asphalt turning at a given rotational velocity. The torque is directly related to the material viscosity at the test temperature. Figure 3.5 shows a schematic of the test setup.

This study used a Brookfield viscometer for these measurements. Samples were heated at $\sim 135^{\circ}\text{C}$ until they flowed well. Ten grams of the asphalt was poured into a preheated sample container. A No. 27 spindle was suspended in the sample and the temperature was allowed to equilibrate for 15 minutes. The spindle was rotated at 5 to 100 rpm depending on the viscosity. The rotation rate was set so that the strain was as close to 10% as possible without being less. This ensured that the viscosity was being measured in a newtonian region. Each sample was tested at 30°F intervals from 220°F to 370°F . The temperature was allowed to equilibrate for 15 minutes after each temperature change.

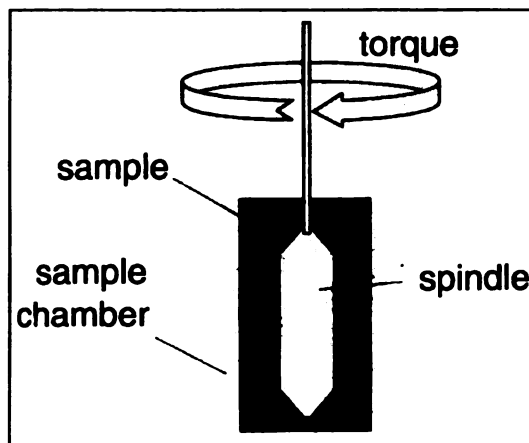


Figure 3.5 - Rotational viscosity setup

3.3.4 - Thin Film Oven Aging (ASTM D 1754-87)

Aging occurs by two main mechanisms, loss of volatiles due to high temperatures and oxidation of the binder at moderate temperatures and high oxygen exposure. During processing, both mechanisms are important. The Thin Film Oven Test (TFOT) was used to simulate aging that occurs during processing. The SHRP program calls for use of the Rolling Thin Film Oven Test for simulation of processing aging. However, this equipment was unavailable during this study and TFOT was used as a substitute. Figure 3.6 is a schematic of the TFOT apparatus. It consists of a convection oven with a suspended, horizontal, rotating shelf suspended from the center. The test calls for a temperature of 163°C for a period of five hours. The shelf rotates at a rate of 5.5 ± 1.0 RPM.

Samples are prepared by heating the asphalt at 135°C until a good melt is achieved. Approximately 50 grams of material are poured into the sample containers. The sample containers are 140 mm deep in diameter and 9.5 mm deep. They are made of aluminum and have a flat bottom. The pans are allowed to cool to room temperature and then are weighed to the nearest 0.001 grams. The pans are put into the preheated TFOT oven and allowed to heat for five hours after the system has regained the equilibrium temperature. After heating, the pans are removed and allowed to cool to room temperature. They are again weighed to the nearest 0.001 grams to determine the percent mass loss. If it is more than one percent the sample does not meet the excessive aging specification. The material is then left in the pans for further aging in the Pressure Aging Vessel.

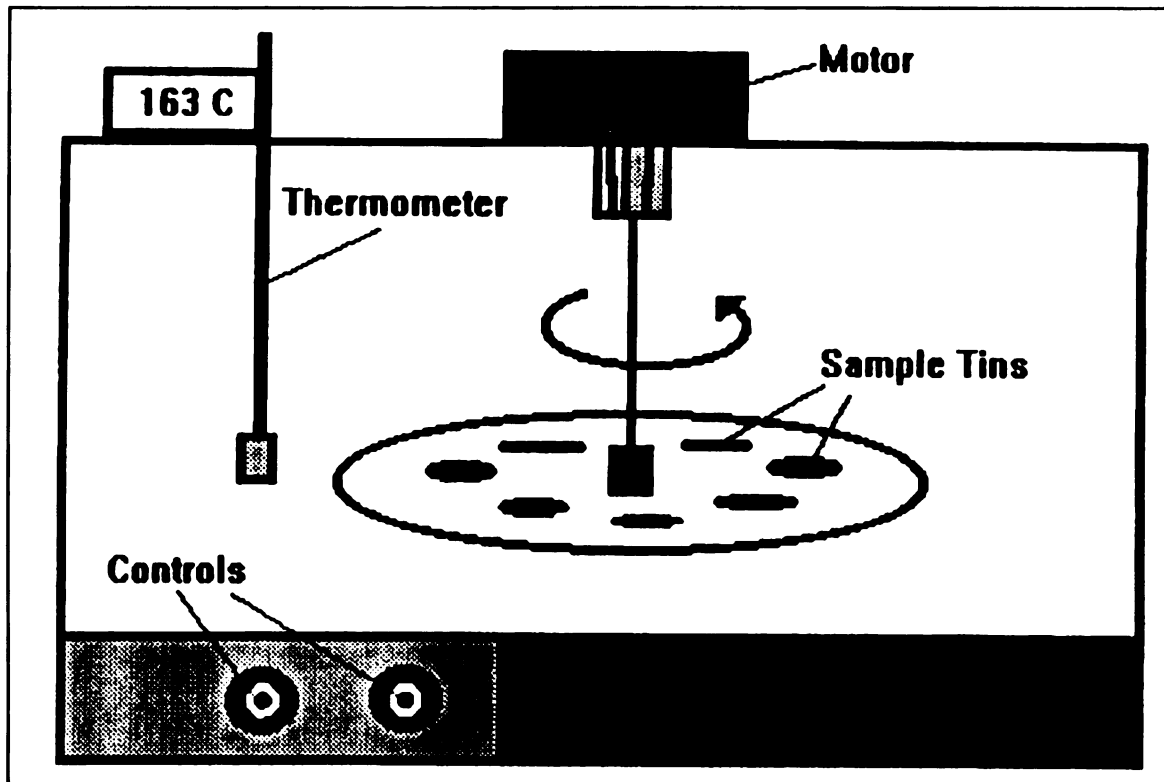


Figure 3.6 - Thin film oven test apparatus

3.3.5 - Pressure Vessel Aging

Prior to Superpave, long term in-service aging effects were not included in any specifications. This was a major oversight because the properties of the asphalt during its service life can be significantly different than the properties of the asphalt during construction. The Pressure Aging Vessel (PAV) was used to simulate in-service aging. The PAV exposes TFOT aged binder to high pressure air and elevated temperatures for 20 hours³³.

The PAV consists of the high pressure vessel and a forced draft oven. Oxygen is supplied as clean, dry, compressed air in a regulated cylinder. The PAV operates at 2070 kPa and 100°C. The oven is able to control the temperature to $\pm 0.5^\circ\text{C}$.

The pressure vessel is preheated to the desired test temperature prior to loading. After the samples are loaded, the temperature is allowed to reach the test temperature before pressurization. After 20 hours at high pressure, the pressure is slowly reduced over about 10 minutes to prevent foaming. The samples are removed and degassed in a 163°C oven for 30 minutes. Figure 3.7 is a schematic of the PAV apparatus.

3.3.6 - Bending Beam Rheometer

The Bending Beam Rheometer (BBR) is used as a predictor of low temperature cracking of asphalt pavements. The SHRP specification calls for the test to be done on TFOT and PAV aged binders to gauge low temperature performance during service life. The BBR is a standard three-point bending apparatus submersed in a bath of ethylene glycol, methanol, and water. Figure 3.8 shows the BBR apparatus. Test temperatures are in the range of -6°C to -36°C. The BBR is used to measure how much a binder deflects under a constant load at a constant temperature. This data is converted to a binder stiffness (a measure of how fast stress builds up for a given strain) and m-value (a measure of the binders ability to dissipate stresses). High stiffness and low m-value are indicative of a large low temperature cracking potential.

The asphalt beams have dimensions of 6.25 mm X 125 mm X 12.5 mm. They are prepared by pouring hot asphalt into metal molds from one end to the other in a continuous motion. They are allowed to cool to room temperature for an hour, placed in a freezer for 15 minutes, and then allowed to equilibrate at the test temperature for an additional hour before testing.

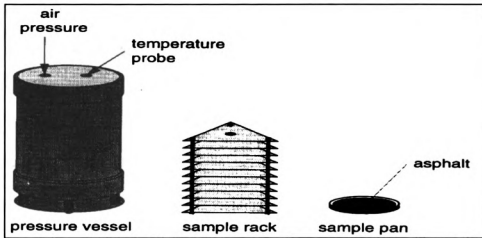


Figure 3.7 - Pressure aging vessel and components

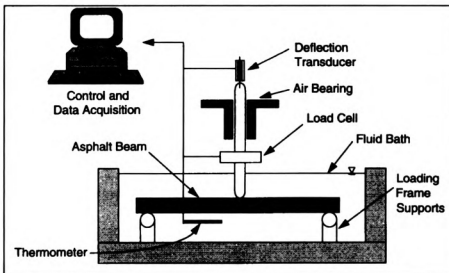


Figure 3.8 - Bending beam rheometer apparatus

The sample is tested under load for a period of 240 seconds. Using the time-temperature superposition principle, the stiffness at 60 seconds correlates to the stiffness after two hours at a temperature 10°C lower than the test temperature. Figure 3.9 shows a graphical representation of the stiffness and m-value measurements. The m-value is

simply the slope of the stiffness vs. time curve at 60 seconds on a log-log plot. There is some debate as to whether the SHRP specification values are correct for use with modified asphalts. This topic is addressed in detail in Chapter Six.

3.3.7 - Thermal Mechanical Analysis

Thermal Mechanical Analysis (TMA) was used to measure the softening point and melt temperature of asphalt binders. The samples were heated at a specified rate under a probe loaded with one gram. The pressure exerted by this probe is similar to that exerted by a truck tire on pavement. The change in height of the probe was measured and used to determine the softening point and melt temperature.

TMA tests were conducted using a DuPont Instruments 943 Thermal Mechanical Analyzer. The samples were placed in a 7 mm diameter by 5 mm deep aluminum holder at room temperature and packed firmly forming a flat top surface. The sample was then quenched to a temperature of approximately -100°C and allowed to equilibrate. The sample was heated at a rate of 5°C per minute under a one gram load and its height change was measured until a total melt (corresponding to a 1 mm depression of the sample) was achieved. A typical TMA curve is shown as Figure 3.10. The softening point was taken as the intersection of the extrapolation of the two straight portions of the TMA curve. The melt temperature corresponds to the temperature at which the sample shows a 1 mm depression.

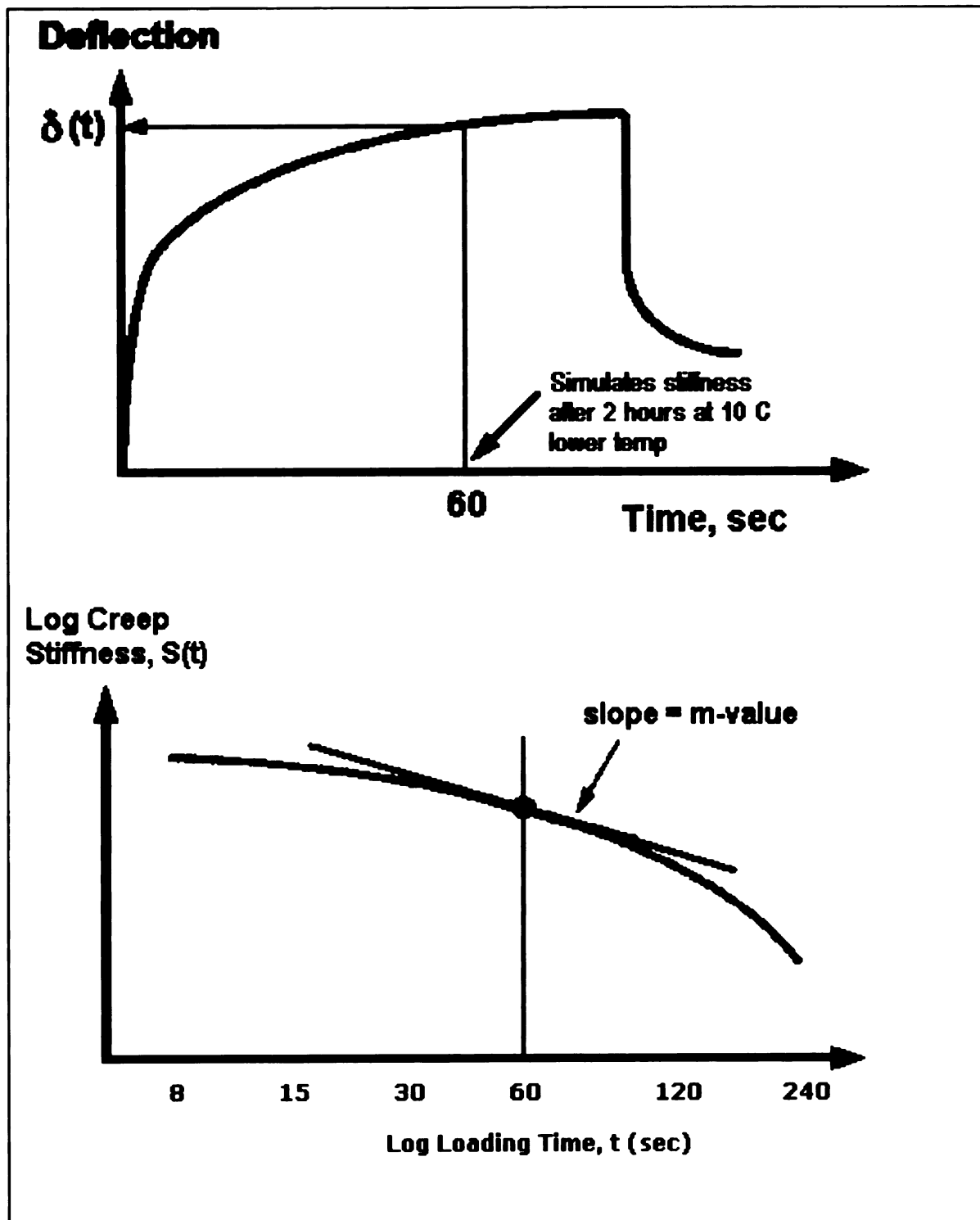


Figure 3.9 - BBR deflection and m-value

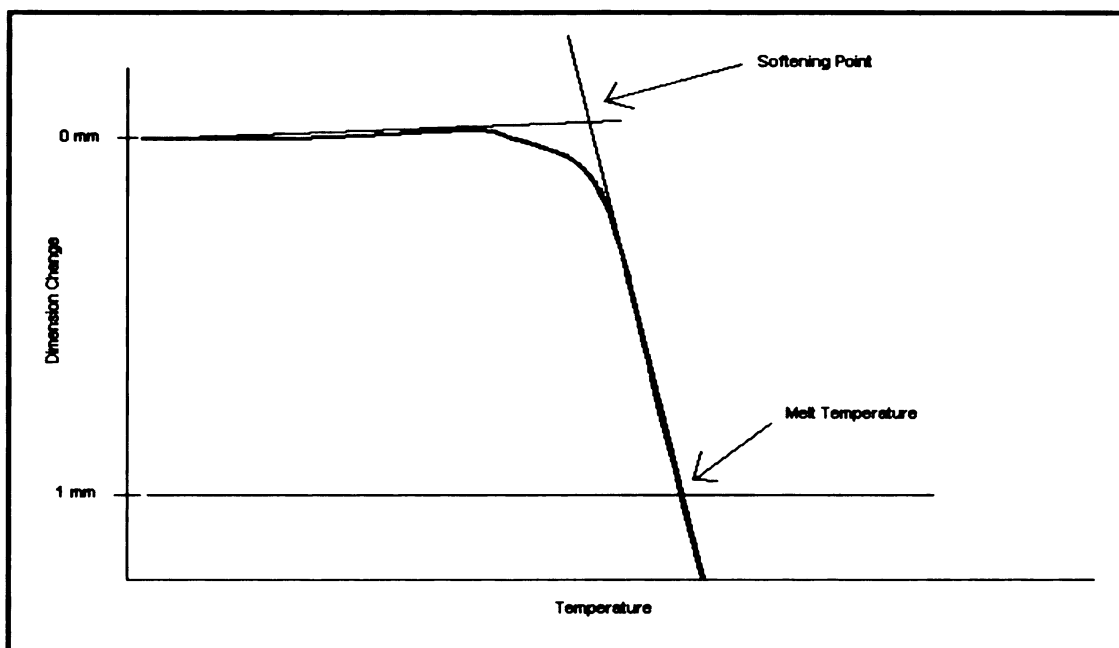


Figure 3.10 - Typical TMA curve showing softening point and melt temperature

3.3.8 - High Performance Gel Permeation Chromatography

High Performance Gel Permeation Chromatography (HP-GPC) is used to determine size and molecular weight distributions in an asphalt sample. A sample is injected into a solvent stream which flows through columns packed with a porous silica gel. The larger particles encounter fewer pores and are eluted first while the small particles which encounter many pores are eluted last. The molecular weight of the material can be calibrated to molecular size to determine molecular weight distributions. This assumes that the molecules are similar in shape to the standards used for calibration. The molecular weight range of the equipment is about 50 - 600,000 g/mol.

For this study, a Waters' HP-GPC system was used to analyze modified and unmodified binders as well as asphaltene fractions of unmodified asphalts. The system was equipped with a refractive index detector to measure molecular size, a photo diode

array to measure UV absorption spectra, a dual reciprocating pump, and a manual injection port. A PC with Millennium software was used to control the apparatus and to collect and analyze data. The system uses four Waters' Styragel columns that gave an effective molecular weight range of 50 - 600,000 g/mol. The mobile phase used for this study was tetrahydrofuran (THF) at a flow rate of 1.0 ml/min. The sample concentration was kept constant at 10 grams per liter and the injection volume was 250 μ l.

3.3.9 - Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is used to identify chemical functional groups. All molecules possess natural resonating frequencies due to bond stretching, bending, or twisting that can be detected by examining the infrared absorbance spectrum. Wavelengths that are the same as those of the molecule are absorbed and this absorbance is converted to an infrared spectrum.

FTIR was used to examine aged, unaged, and modified binders. The samples were prepared by evaporating a THF/binder solution on a potassium bromide pellet leaving a thin film of material. The solution was mixed at a concentration of 0.5 g of sample per 10 ml of THF. The pellets were allowed to dry overnight at room temperature followed by 15 minutes at 135°C in a vacuum oven.

This study used a Perkin Elmer Model 1800 spectrometer. Each sample was scanned 16 times at a resolution of 4 cm^{-1} . The system is controlled using a PC with Perkin Elmer Spectrum software.

3.3.10 - Compatibility Index

The compatibility index was first reported by Heithaus in 1960³⁴. It is a measure of how well the asphaltenes are held in solution by the resins and the oils in the asphalt. A modified procedure used by Glover, et al.³⁵ was used in this study. The compatibility index (I_C) was determined from the amount of heptane required to initiate precipitation of asphaltenes in an asphalt-toluene solution. Starting with 0.1 gram of asphalt in 1 ml toluene, the I_C is calculated as

$$I_C = \frac{(\text{volume of toluene}) + (\text{volume of heptane})}{\text{volume of toluene}}$$

The more heptane required to initiate precipitation indicates better compatibility. A large I_C indicates better compatibility than a small I_C . Because of the qualitative nature of determining onset of flocculation, these tests were done three times to ensure accuracy.

3.3.11 - Asphalt Fractionation

Asphalt was separated into four fractions (asphaltenes, naphthene aromatics, polar aromatics and saturates) using ASTM D4124-86 Method B³⁶. Asphalt is dissolved in heptane (100 ml/gram asphalt) and stirred with a magnetic stirrer for approximately two hours. The precipitated asphaltenes are vacuum filtered and air dried for at least 24 hours.

3.3.12 - Asphalt/Polymer Blending

Industry often recommends a mixing time based on visual homogeneity of the asphalt and polymer blend. It was found that this is inadequate for laboratory practice. A

mixing procedure for each polymer system was developed based on an improvement in the high temperature rheological properties of the blends. The experiments used to make this determination are described in detail in Chapter Four. Table 3.2 lists the mixing time and temperature for all of the polymers studied.

The actual mixing was done using a Fischer-Scientific Jumbo 115V low shear mixer equipped with a four blade, 5 cm diameter impeller. The stirring speed was determined for each polymer according to experiments and manufacturer suggestions. The asphalt was heated during mixing in an oil bath held at constant temperature. The temperature of the bath was different for each polymer system.

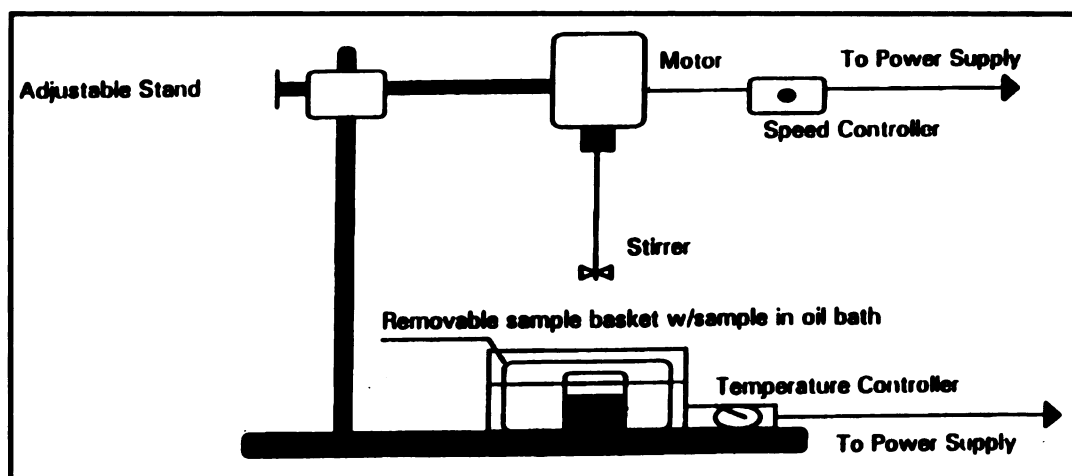


Figure 3.11 - Mixing apparatus

Table 3.2 - Mixing time and temperature for all modifiers

Polymer	Temperature (°F)	Mixing Time
SBS/SEBS	350	2 hours
SBR	325	30 minutes
EVA	350	2 hours
Crumb Rubber	350	30 minutes
Elvaloy® AM	375	2 hours

Chapter Four

Experimental Results and Discussion

Four different modifiers were considered in this study. This chapter will detail and discuss the experimental results for each of the modifiers. The general outline of each section will be an introduction to the modifier followed by a presentation of the physical and chemical properties of the binders.

4.1 - Styrene Butadiene Rubber

Styrene-butadiene rubber (SBR) is one of the most promising polymers in the family of network thermoplastics. An SBR latex was obtained from the Ultrapave division of the Textile Rubber and Chemical Company. The water-based UP®70 SBR latex solution contains approximately 70% (w/w) polymer confirmed by thermogravimetric analysis. The polymer is a high molecular weight, random block copolymer consisting of 24 mole % styrene and 76 mole % butadiene. The material maintains a stable latex at room temperature with pH of 10 and has a viscosity of about 1.65 Pa·s. The consistency of the polymer is similar to that of latex paint. Two other Ultrapave polymers were studied briefly. UP®7576 is a medium molecular weight SBR latex while UP®7289 is a low molecular weight SBR latex. The effect of the polymer molecular weight on binder properties was investigated.

4.1.1 - Mixing Procedure

The SBR polymer was mixed with asphalt binders by using a preparation method developed in the laboratory. It is believed that this material behaves as dispersed thermoplastics at low SBR content and then forms an entangled polymer network within the asphalt as the SBR content is increased. This network structure manifests itself in an increase in the rheological properties of the modified binder. The mixing procedure for SBR modification was determined to maximize its rheological properties and to minimize asphalt degradation. Approximately 150 g of neat asphalt was heated in an oven to 135°C to obtain a good melt. The asphalt in a beaker was placed in a pre-heated (180°C) oil bath and SBR was added slowly while stirring at low-shear. It was important to add the latex slowly to allow the water to evaporate without gelling the SBR. Each asphalt/polymer blend was mixed for only 30 minutes at 180°C. The stirring speed varied as a function of the consistency and concentration of the blend. The current industry practice is to flash evaporate the latex into the hot mix. This may provide sufficient mixing because of the violent nature of the flash evaporation. The mixing procedure is consistent with that recommended by Ultrapave. Figure 4.1 shows the storage modulus as a function of polymer content for various mixing times for modified AC-5 binders. It is apparent that the majority of the improvement is seen with only 30 minutes of mixing, especially for temperatures below 60°C. Figure 4.2 shows the Tan δ curves for the same binders. A flat Tan δ is desired because it represents a consistency in the rheological properties with temperature changes. The figure shows that at a mixing time of 30 minutes the Tan δ curve is essentially flat and that further mixing does not significantly effect the flatness of the curve.

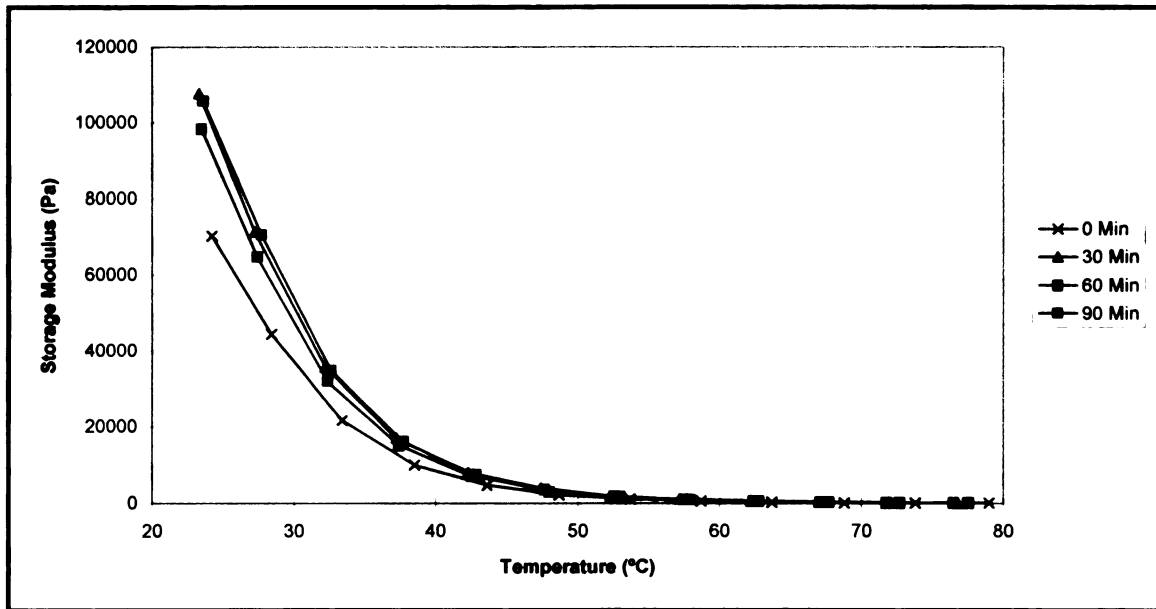


Figure 4.1 - Storage modulus of AC-5/SBR binders with different mixing times

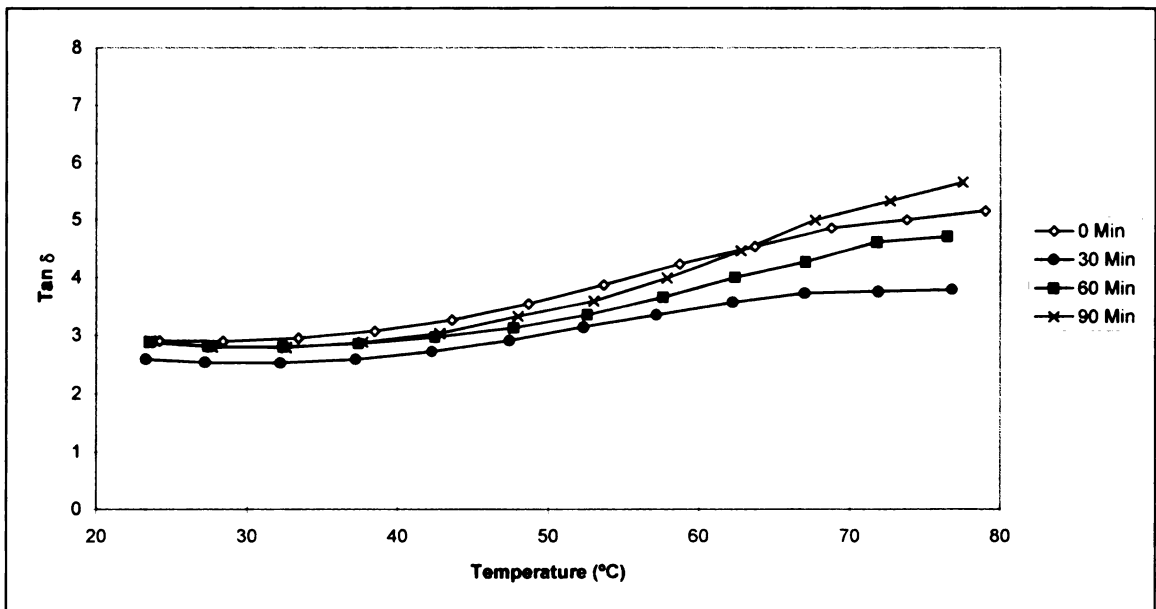


Figure 4.2 - Tan δ curves of AC-5/SBR binders with different mixing times

4.1.2 - Dynamic Shear Rheometry

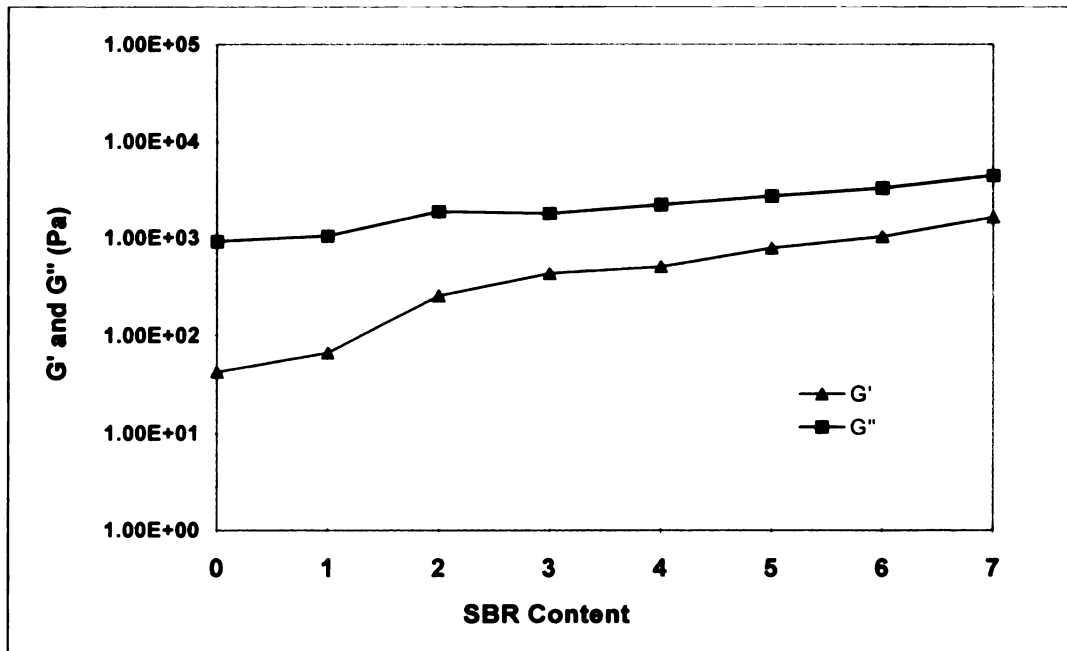
Dynamic Shear Rheometry (DSR) testing served two purposes. First, it is the initial test in the SHRP performance grading specifications. Secondly, it was used to determine the optimum polymer content. The optimum content is defined as the content at which further increases in polymer amount do not significantly improve the high temperature rheological properties as measured by DSR.

4.1.2.1 - Optimum Polymer Content

Table 4.1 summarizes the optimum contents for the SBR modified binders. These optimum contents were chosen by examining both the modulus curves at 60°C and the Tan δ curves. Sixty degrees was chosen because it is a likely maximum pavement temperature for Michigan roads. Figure 4.3 shows the loss and storage modulus versus polymer content of AC-5/SBR binders. It shows that the increase in moduli slows after a content of 3% (w/w). Figure 4.4 shows the tan δ curves of the AC-5/SBR binders. It is desirable to have a flat tan δ vs. temperature curve which indicates constant relative loss modulus and storage modulus with varying temperature. It can be seen in Figure 4.4 that no appreciable increase in the "flatness" of the Tan δ curve is realized with polymer contents greater than 3% (w/w). The optimum contents for the other asphalt grades were determined using the same procedure.

Table 4.1 - Optimum SBR content

Asphalt Grade	Optimum SBR Content
AC-2.5	4% (w/w)
AC-5	3% (w/w)
AC-10	3% (w/w)
AC-20	3% (w/w)

**Figure 4.3 - Loss and storage moduli of AC-5/SBR binders**

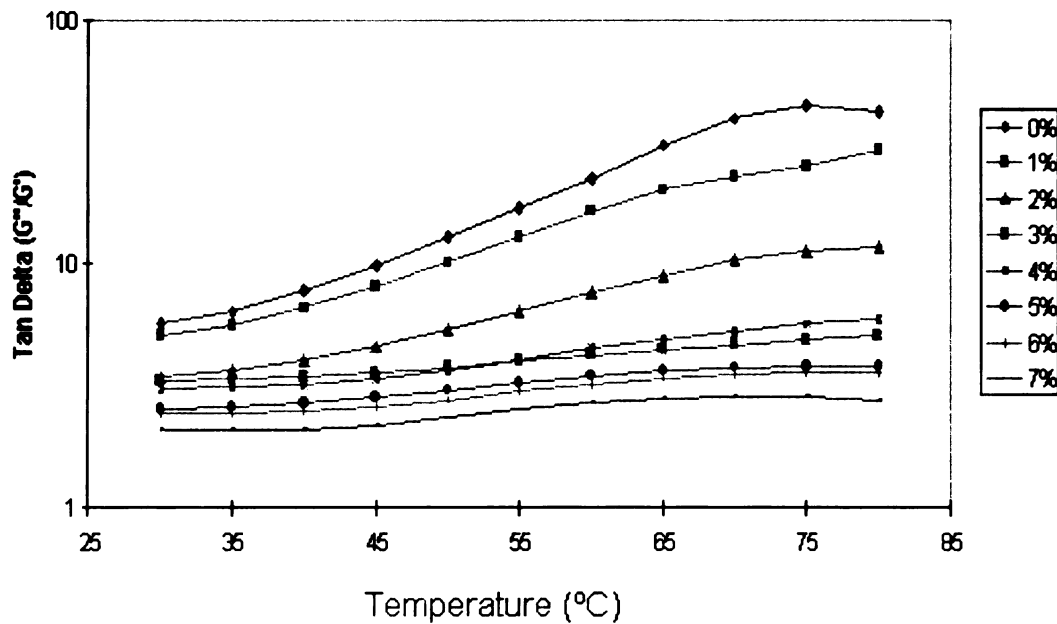


Figure 4.4 - Tan δ curves of AC-5/SBR binders

4.1.2.2 - SHRP High Temperature Performance Grade

The SHRP performance grading system, as discussed in Chapter Three, was used to characterize SBR modified binders. The high temperature performance grade is determined by computing the dynamic shear modulus, $G^*/\sin \delta$. The Performance Grade is then the temperature at which the dynamic shear modulus of the unaged binder is equal to 1000 Pa. To complete the SHRP high temperature grading, the RTFO residue must be analyzed with DSR. The specification calls for a minimum dynamic shear modulus of 2200 Pa. In all cases, the testing of the aged binder did not affect the performance grade determined by the original binder. Figure 4.5 shows a typical curve of dynamic shear vs. temperature. The temperature scale has been divided into the gradations specified in the

SHRP system. The graph shows that polymer contents of 2% (w/w) to 5% (w/w) result in an increase of one PG. Polymer contents of greater than 5% (w/w) did not pass the viscosity specification and were therefore ungradable by the SHRP system. Table 4.2 summarizes the SHRP high temperature performance grades for all four asphalts.

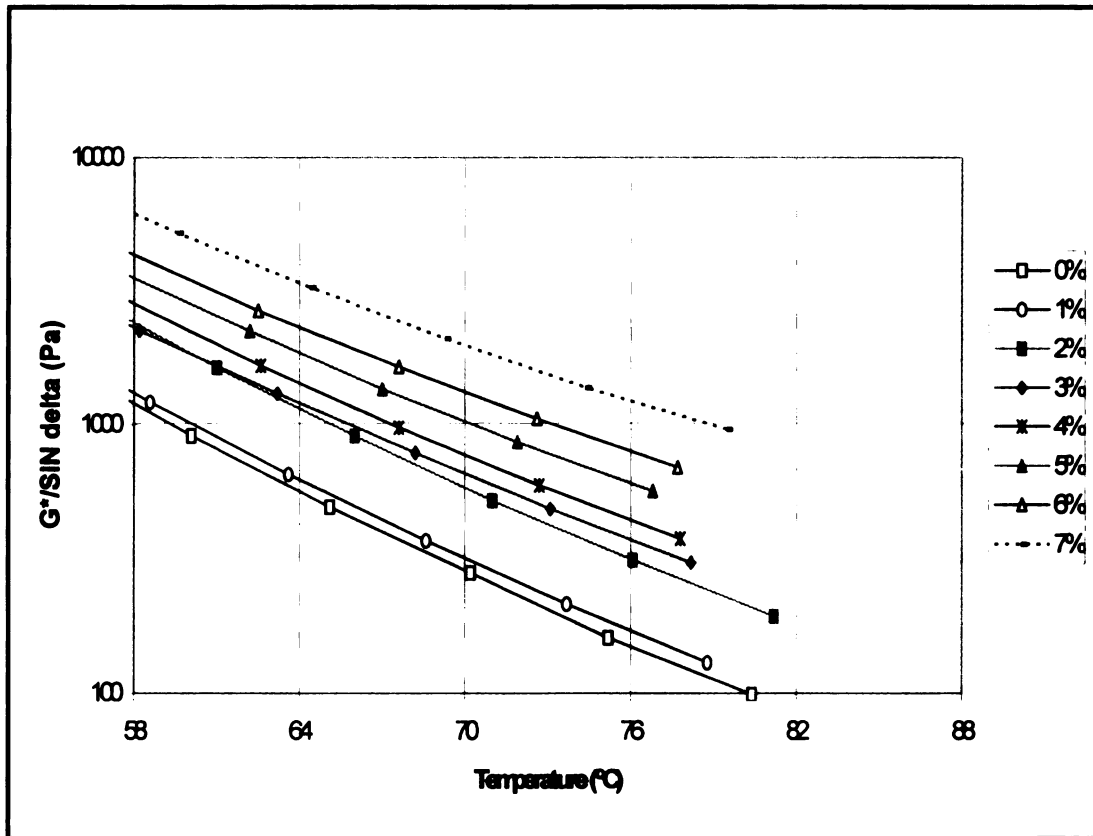


Figure 4.5 - Dynamic shear modulus of AC-5/SBR binders

Table 4.2 - High temperature SHRP PG of SBR modified binders

SBR Content	AC-2.5	AC-5	AC-10	AC-20
0% (w/w)	52	58	64	70
1% (w/w)	58	58	70	70
2% (w/w)	58	64	70	70
3% (w/w)	58	64	76	70
4% (w/w)	58	64	76	76
5% (w/w)	64	70	76	82

4.1.3 - Rotational Viscometry

The melt viscosity of SBR modified binders was determined using rotational viscometry. All binders with polymer contents of 5% (w/w) or less passed the SHRP specification for melt viscosity. Figure 4.6 shows the melt viscosity curves for AC-5/SBR binders. Viscosity increases at all temperatures with increasing polymer content with the exception of 1% (w/w). There is no increase in viscosity seen upon the addition of 1% (w/w) SBR. This is likely because the polymer is too dispersed to have any affect on the viscosity. Significant increases are seen between 1% (w/w) and 2% (w/w) and between 4% (w/w) and 5% (w/w). These two facts suggest that SBR is forming a localized network structure at about 2% (w/w) SBR and forming a global network at 5% (w/w) SBR. The formation of the SBR network at 5% (w/w) can be seen using fluorescence microscopy. At contents less than 5% (w/w) the SBR can be seen as discrete particles or micro-networks. At 5% (w/w) and greater, the SBR forms a fibril macro-network within the asphalt.

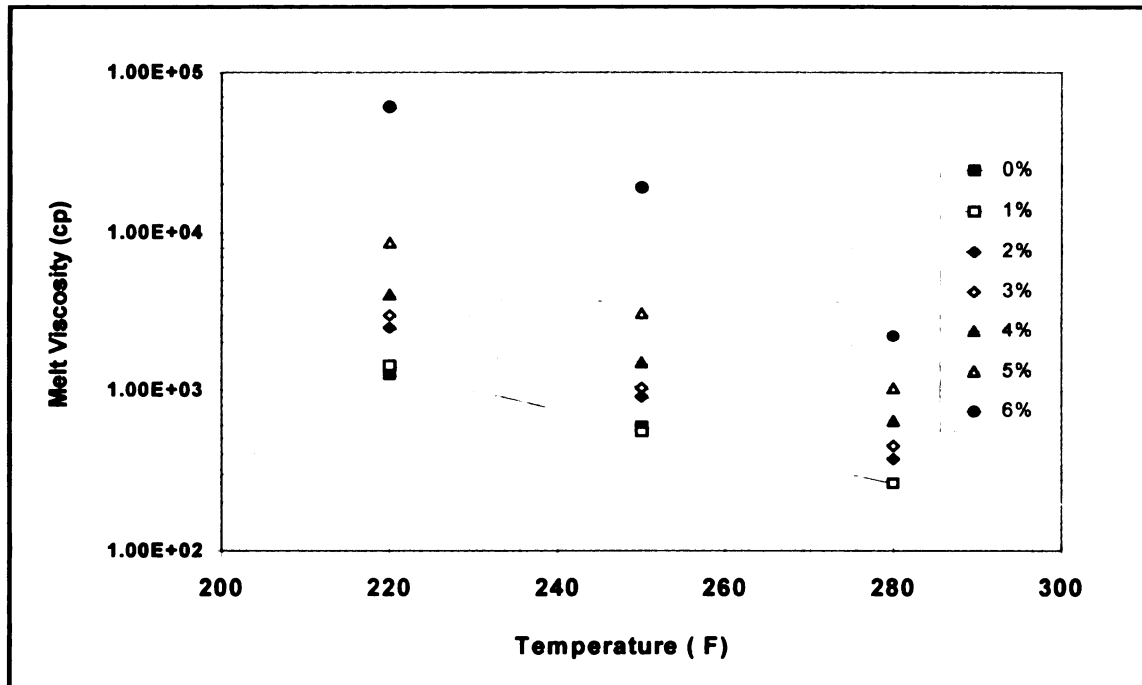


Figure 4.6 - Melt viscosity of AC-5/SBR binders

4.1.4 - Bending Beam Rheometry

Bending beam rheometry was conducted to determine the low temperature SHRP PG of SBR modified AC-2.5 and AC-5 binders. In all cases, the m-value specification was the limiting factor in determining the performance grade. Table 4.3 summarizes the low temperature performance grade for the SBR modified asphalts. All of the samples tested had a low temperature PG of -28. There was no improvement in performance grade upon addition of SBR. There was some improvement in the creep stiffness of the binders with SBR modification. Some of the binders did meet the specification for creep stiffness at -24°C (PG of -34) but they failed to meet the m-value specification at that temperature. Figure 4.7 shows the creep stiffness curves for AC-5/SBR at various temperatures and polymer contents. Figure 4.8 shows the m-value curves for the same

binders. It can be seen that there is no trend for creep stiffness except at -24°C. At this low temperature, the creep stiffness improves significantly and linearly with increasing SBR content. This improvement did not manifest itself in the performance grade because the m-value specification was not met at -24°C. There were no trends evident in m-value at any temperature. SHRP assumed that the m-value would increase with the increase of polymer content³⁷. It appears that the m-value is not a function of polymer content, at least for SBR, and is instead determined by the properties of the base asphalt used for modification.

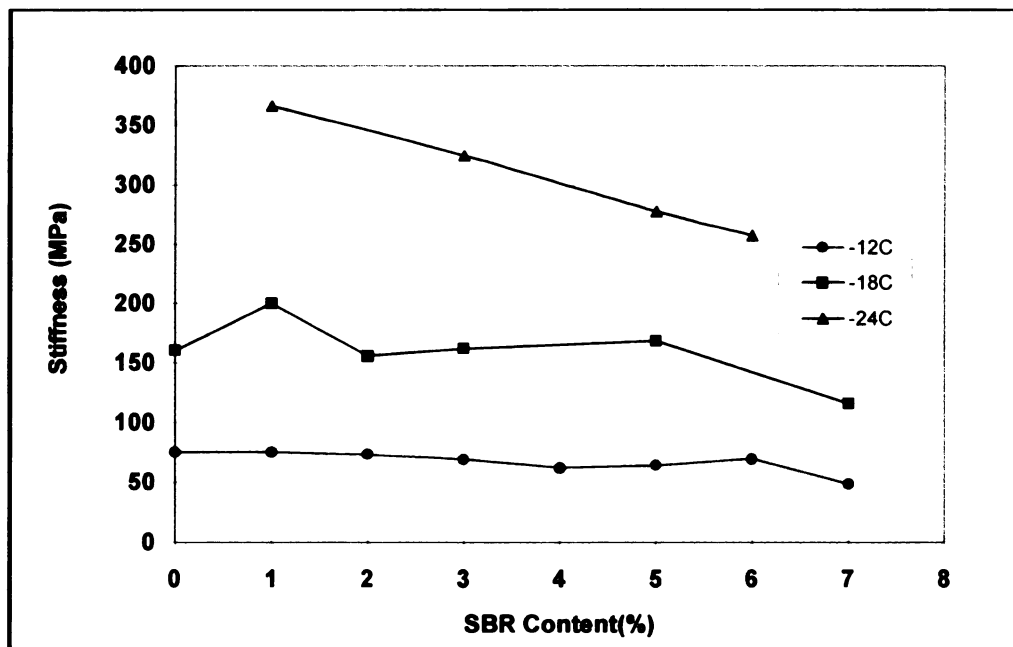


Figure 4.7 - Creep stiffness of AC-5/SBR binders

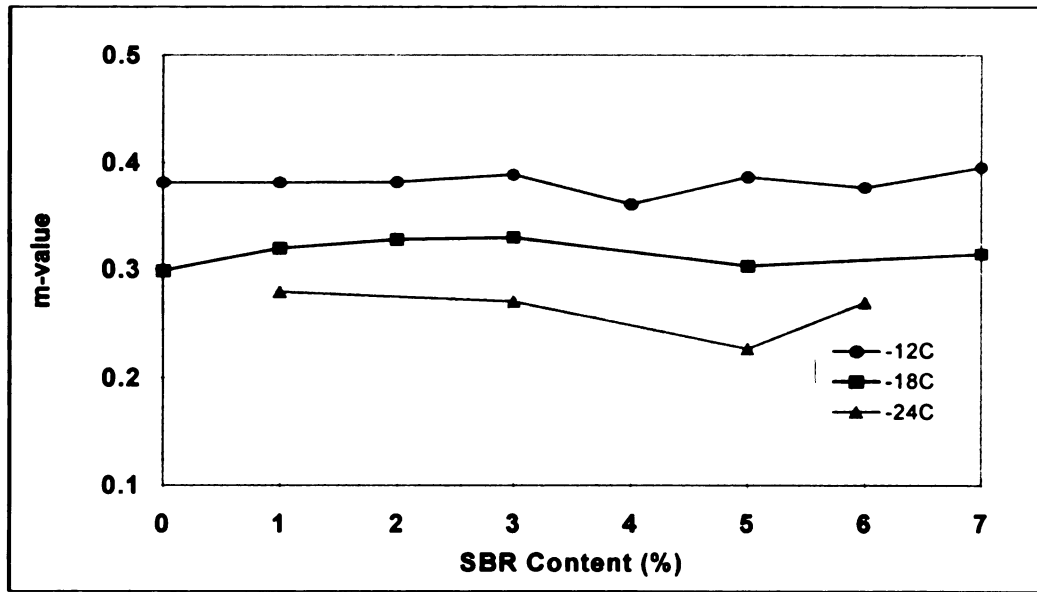


Figure 4.8 - *M-value of AC-5/SBR binders*

Table 4.3 - *Low temperature SHRP PG of SBR modified binders*

SBR Content	AC-2.5	AC-5
0% (w/w)	-28	-28
1% (w/w)	-28	-28
2% (w/w)	-28	-28
3% (w/w)	-28	-28
4% (w/w)	-28	-28
5% (w/w)	-28	-28

4.1.5 - Fourier Transform Infrared Spectroscopy

Fourier-Transform Infrared Spectroscopy (FTIR) was used to characterize various functional groups in the asphalt and the polymer. FTIR has been used to analyze the unaged SBR modified asphalt binders. A typical FTIR spectrum for SBR/AC-2.5 blends is shown in Figure 4.9. The aliphatic C-CH₃ peak at wavelength of 1375 cm⁻¹ in asphalt and the trans-1,4 contribution of butadiene (C-C=C-C) at 965 cm⁻¹ in SBR were used as the content indicator. These peaks were chosen because they are unique to the asphalt and the polymer respectively. The ratio of the two characteristic absorption peaks is supposed to be linearly proportional to the SBR content in the asphalt. A calibration curve is constructed by preparing samples that contain known concentrations of SBR polymer in the asphalt binders and plotting this information against the respective absolute absorbance band ratios. It is important to note that the calibration curves are valid only for the given asphalt/polymer blends. A new calibration curve must be constructed for each new asphalt. The calibration curves for all SBR systems tested are ;

$$\text{Polymer content (\% (w/w))} = (\text{Ratio} - 0.2189) / 0.0626 \quad \text{for SBR/AC-2.5 ;}$$

$$\text{Polymer content (\% (w/w))} = (\text{Ratio} - 0.0628) / 0.0539 \quad \text{for SBR/AC-5 ;}$$

$$\text{Polymer content (\% (w/w))} = (\text{Ratio} - 0.0858) / 0.0438 \quad \text{for SBR/AC-10 ;}$$

$$\text{Polymer content (\% (w/w))} = (\text{Ratio} - 0.3007) / 0.0463 \quad \text{for SBR/AC-20.}$$

All of the above calibration curves had an R² value of 0.95 or greater.

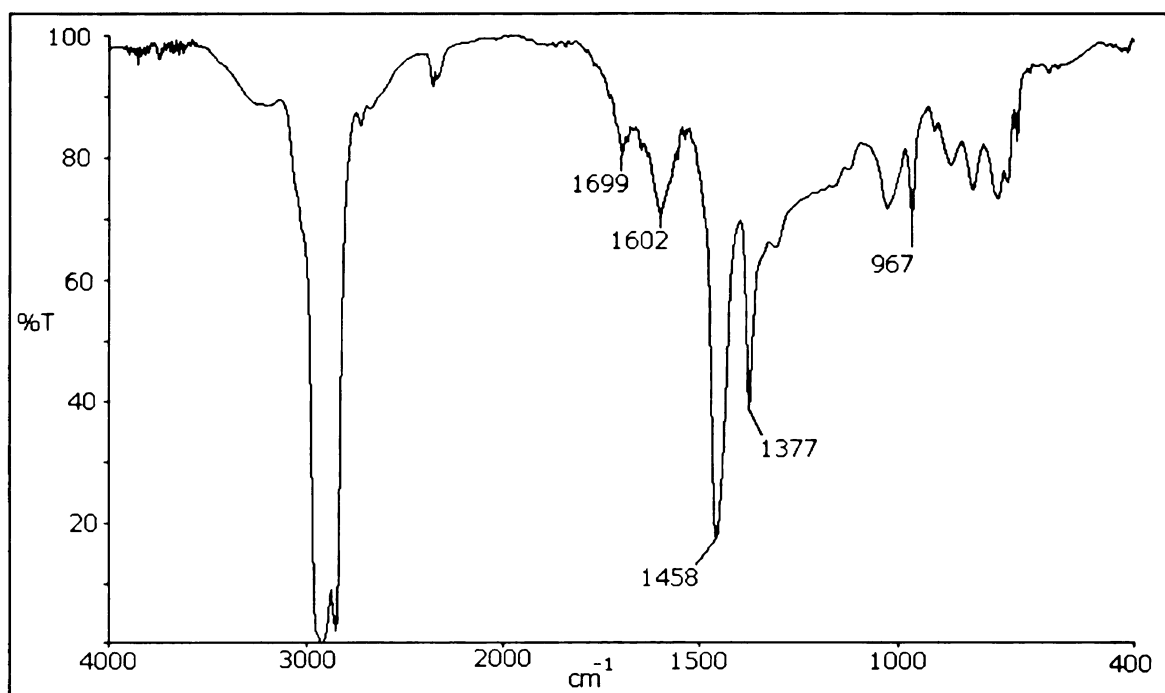


Figure 4.9 - Typical FTIR spectrum of AC-2.5/SBR binders

Aging studies with FTIR used the absorption peak at 1700 cm^{-1} corresponding to carboxyl groups in the asphalt as an indicator of aging.. Since the number of C=O bonds in the asphalt increases during aging due to oxidation of the binder, while the numbers of aryl C-C and C-CH₃ bonds are not affected by oxidation, the change in the ratio of the C=O peak (1700 cm^{-1}) to the C-CH₃ peak (1375 cm^{-1}) due to aging is used as a measure of aging.

PAV aged AC-2.5 and AC-5 binders modified with SBR have been investigated to determine extent of aging. Aging is characterized by the ratio of the 1700 cm^{-1} C=O peak which indicates oxidation, to the 1375 cm^{-1} C-CH₃ peak. Aging has also been characterized by looking at the 1700 cm^{-1} peak to the aryl C-C peak at 1600 cm^{-1} . The

ratios for the aged binders are shown in Table 4.4 and Table 4.5. There does not appear to be any effect of polymer modification on the oxidation ratios determined by FTIR.

Table 4.4 - FTIR oxidation ratios of AC-2.5/SBR binders

AC-2.5	Aged Binders	
	1700/1600	1700/1375
0% SBR	0.73	0.38
1% SBR	0.72	0.39
3% SBR	0.76	0.35
5% SBR	0.55	0.25

Table 4.5 - FTIR oxidation ratios of AC-5/SBR binders

AC-5	Aged Binders	
	1700/1600	1700/1375
0% SBR	0.76	0.35
1% SBR	0.70	0.40
3% SBR	0.63	0.36
5% SBR	0.58	0.31
7% SBR	0.66	0.30

4.1.6 - Gel Permeation Chromatography

Gel Permeation Chromatography did not prove to be a useful tool in analyzing SBR modified binders. SBR itself could not be characterized in our system because it was insoluble in THF due to its latex form in water. GPC was also used to examine the SBR modified asphalt binders. SBR modified asphalt binders were not characterized well even though the water in the blends was believed to be evaporated during the mixing. The most likely reason is that the low molecular weight range of the SBR overlapped with the high molecular weight range of the asphalt making much of the SBR

indistinguishable from the asphalt. It is also possible that the SBR, being insoluble in THF, was filtered from the solution before injection.

4.1.7 - Thermomechanical Analysis

Thermomechanical analysis (TMA) was used to characterize both the softening point and melt temperature of SBR modified binders. These temperatures are important in predicting rutting potential by determining the temperature at which the asphalt begins to flow. Table 4.6 summarizes the softening and melt temperatures for the four asphalt grades modified with SBR. With addition of more than 4 % (w/w), there is an increase of approximately 4°C in the final softening point for the AC-5/SBR blends with respect to the unmodified binders. It is important to note that the 0% SBR binders were subjected to the same mixing condition as the SBR modified binders. For comparison purposes, Table 4.6 also shows the softening points and melt temperatures of neat (unprocessed) asphalt.

4.1.8 - Effect of Polymer Molecular Weight on Modified Binder Properties

Three different molecular weight SBR polymers were studied to determine the effect of the polymer molecular weight on the modified binder properties. All three binders were provided by Ultrapave. The polymers in increasing order of molecular weight are UP® 7289, UP® 7576, and UP® 70. UP® 70 was the polymer used for all of the SBR modification presented in sections 4.1.1 - 4.1.7. There was significant variation

Table 4.6 - Softening and melt temperatures of SBR modified binders

AC-2.5/SBR Blends		
Polymer Content (%)	Softening Point (°C)	Melt Temperature (°C)
neat	22	31
0	24	33
1	26	34
3	27	39
4	25	38

AC-5/SBR Blends		
Polymer Content (%)	Softening Point (°C)	Melt Temperature (°C)
neat	26	33
0	28	38
1	27	36
2	30	42
3	27	39
4	27	42
5	31	46
6	30	46

AC-10/SBR Blends		
Polymer Content (%)	Softening Point (°C)	Melt Temperature (°C)
neat	31	40
0	32	41
1	35	48
2	36	49
3	35	49
4	36	46
5	37	49

AC-20/SBR Blends		
Polymer Content (%)	Softening Point (°C)	Melt Temperature (°C)
neat	35	47
0	39	48
1	40	48
3	38	50

in the physical properties of the binders mixed with different molecular weight polymers. All three SBR modifiers were blended with the asphalt using the mixing procedure described in Section 4.1.1. AC-5 grade asphalt was used for all of these tests.

The softening point and melt temperature of the SBR modified binders was greatly affected by SBR molecular weight. Table 4.7 and 4.8 show respectively the softening and melt temperatures for these binders. The differences in initial softening point are small (3°) while the difference in final melt temperature is rather large (9-10°C). This is because the initial softening point depends primarily on the base asphalt while the SBR network helps support the binder and prevent flow necessary for a total melt.

Table 4.7 - Softening point of AC-5 modified with three different SBR polymers

	0 % (w/w)	3% (w/w)	5% (w/w)
UP® 70	29	33	33
UP® 7576	29	32	33
UP® 7289	29	30	32

Table 4.8 - Melt temperature of AC-5 modified with three different SBR polymers

	0 % (w/w)	3% (w/w)	5% (w/w)
UP® 70	37	47	52
UP® 7576	37	42	46
UP® 7289	37	38	42

The high temperature dynamic shear modulus of AC-5 binders modified with 0% (w/w), 3% (w/w), and 5% (w/w) of each SBR polymer was measured. These results are presented in Figure 4.10. The figure shows that there is significant differences in the modulus value as well as in the SHRP performance grade among the samples with the

same content but different molecular weight polymer. For example, the temperature at which the samples meet the SHRP specification for 3% (w/w) polymer ranges from 63°C for the low MW UP@7289 to 69°C for the high MW UP@70. The 5% (w/w) samples show a similar range of 68°C to 78°C. There is some overlap in the two groups. The 3% (w/w) UP@70 has virtually identical modulus characteristics as the 5% (w/w) UP@7289.

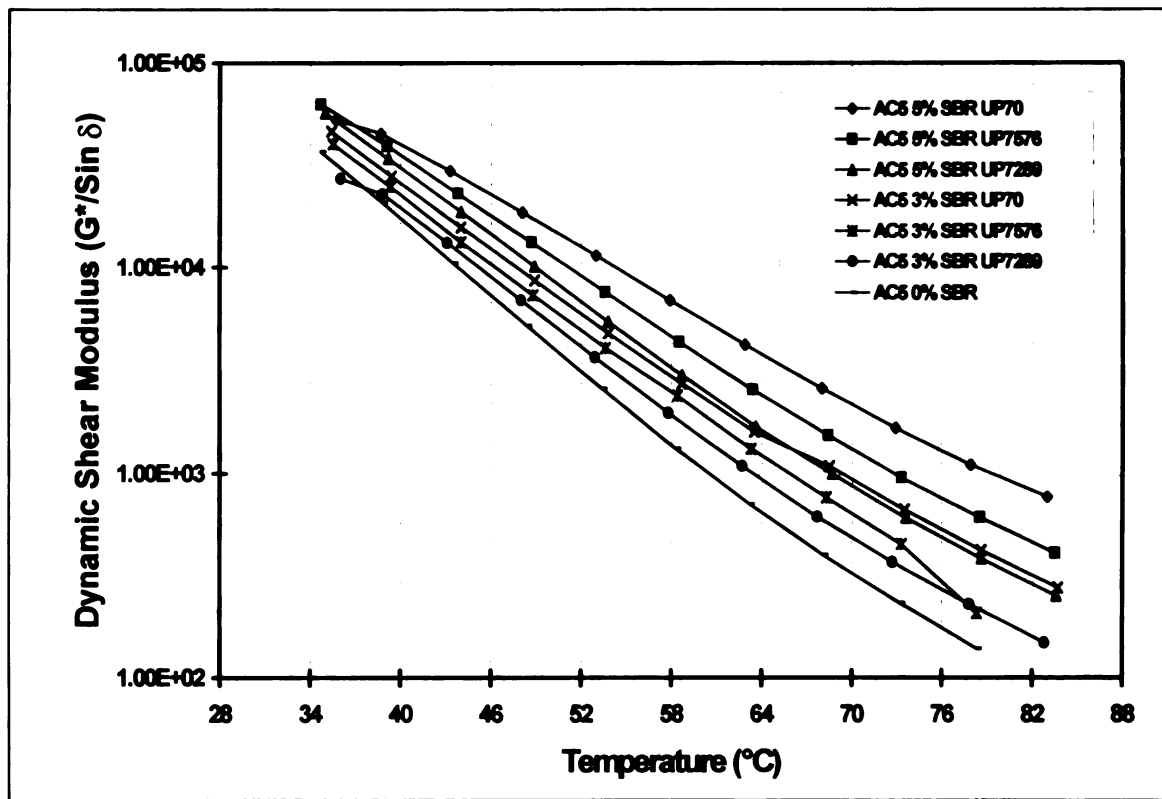


Figure 4.10 - Dynamic shear modulus of AC-5 with three different SBR polymers

The same test was run at low temperatures (0°C - 25°C) to determine low temperature rheology. Figure 4.11 shows the results of the low temperature dynamic shear modulus. There is very little difference between any of the samples. This indicates that the base asphalt is controlling the rheological properties at low temperatures.

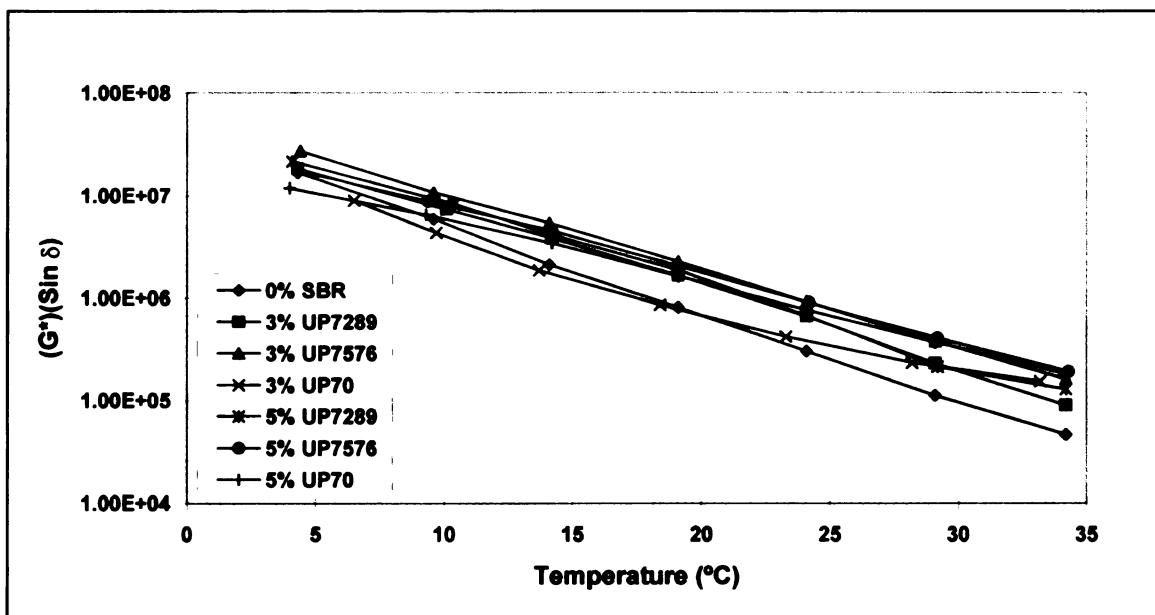


Figure 4.11 - Low temperature rheology of AC-5/SBR blends

Melt viscosity of the AC-5/SBR binders is plotted in Figure 4.12. The viscosity is a strong function of polymer molecular weight. The effect is so significant that the 3% (w/w) UP®70 and the 5% (w/w) UP®7289 have virtually identical viscosities.

The effect of polymer molecular weight on low temperature properties was investigated. Figure 4.13 shows that there is little effect of either MW or polymer content on creep stiffness. Figure 4.14 shows that the m-value deteriorates with increasing polymer content, however the effect of molecular weight is minimal.

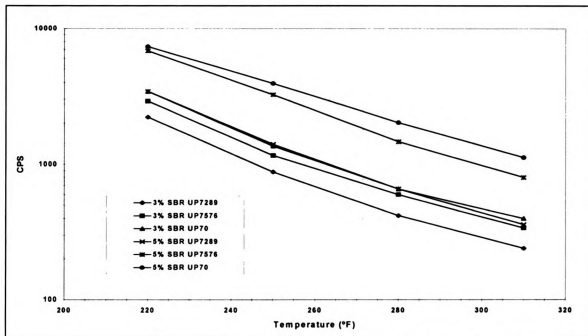


Figure 4.12 - Melt viscosity of AC-5/SBR binders.

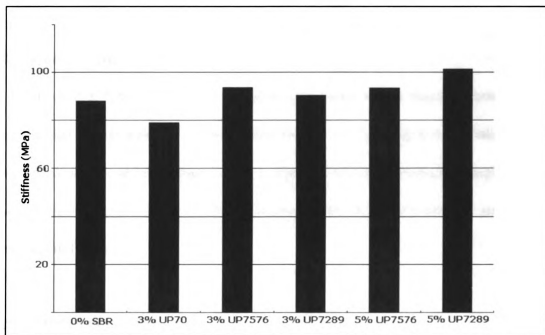


Figure 4.13 - Creep stiffness of AC-5/SBR binders at -12°C.

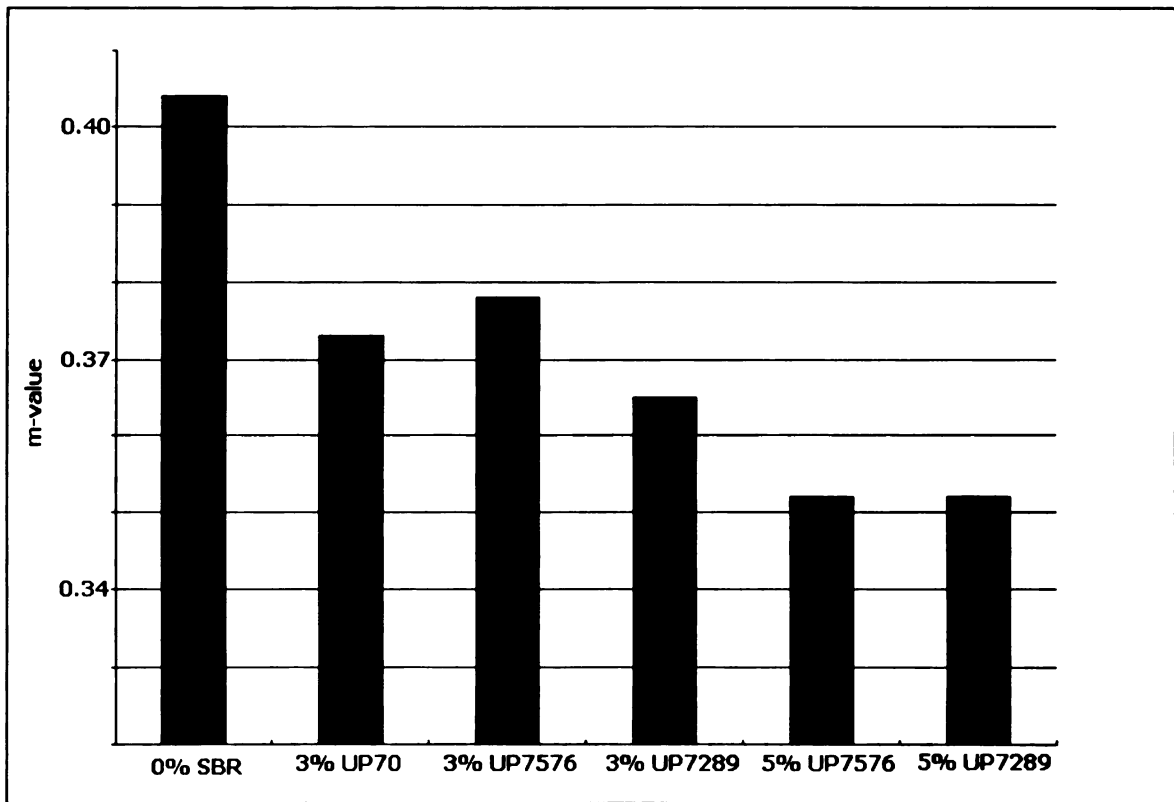


Figure 4.14 - M-value of AC-5/SBR binders at -12°C.

4.2 - Elvaloy® AM

Elvaloy® AM is a modified ethylene copolymer with a reacting epoxide group. When added to the asphalt, it reacts with the asphalt creating a new material. This reaction takes place at high temperature causing extensive oxidation of the asphalt binder. The chemical structure of Elvaloy® AM is proprietary, however a possible structure was presented in Figure 2.9.

4.2.1 - Mixing Procedure

Elvaloy® AM was mixed with asphalt using the procedure recommended by the manufacturer. The three main variables to consider in the mixing procedure are time,

temperature, and shear rate. Because Elvaloy® AM reacts with asphalt, a temperature of 195°C was required to overcome the reaction activation energy. Shear rate was chosen to be high shear to be consistent with the other polymer systems studied. Therefore, mixing time was the only variable to be investigated. The manufacturer suggested a mixing time of two hours with additional curing at 195°C for 23 or 69 hours. Typical Elvaloy® AM content is one to three percent by weight. AC-5 with three polymer contents (1% (w/w), 2% (w/w) , and 3% (w/w)) as well as controlled AC-5 (0% (w/w)) were evaluated at different mixing times. All of the samples were mixed according to the following procedure:

- About 150 g of the asphalt was heated in an oven until it melted. The temperature of the oven was set at 135 °C and the asphalt was allowed to heat for 40-60 minutes.
- After a good melt of the asphalt was obtained, the container was placed in a hot oil bath which was preheated to 195 °C. The asphalt was stirred slowly (~800 rpm) for 10 minutes before adding the polymer.
- The desired amount of Elvaloy® AM was slowly added to the asphalt and the stirring speed was gradually increased to ~1600 rpm. The blend was stirred for an additional two hours at the same temperature.
- After two hours of mixing, a part of blend was poured into a separate container which was stored in a freezer for testing at a later date. The sample was recorded as the '2 hours mixing' and '0 hour cure time' sample.
- The container of the remaining blend was covered in order to not be exposed to air and then placed in the hot oil bath (~380 °F) for the desired cure time.
- After 23 hours of curing, some of the sample was removed for later testing. The rest of the material was allowed to cure for 69 hours.

Figure 4.15 shows the $\tan \delta$ curves for AC-5/EAM binders with no additional cure time. It is evident that addition of Elvaloy® AM improves the $\tan \delta$ behavior of the asphalt. There is a big increase in $\tan \delta$ flatness with addition of 2% (w/w) polymer.

Figure 4.16 and Figure 4.17 show $\tan \delta$ curves for samples cured for 23 hours and 69 hours, respectively. These figures also include the 3% (w/w) Elvaloy® AM binder with no additional cure time for comparison. It is clear from these two figures that mixing for only 2 hours enhances the rheological properties of the blend and that additional curing time is not beneficial. This phenomenon was also seen during the SBS and SBR mixing studies and is attributed to either thermal degradation of the base asphalt or shearing of the polymer.

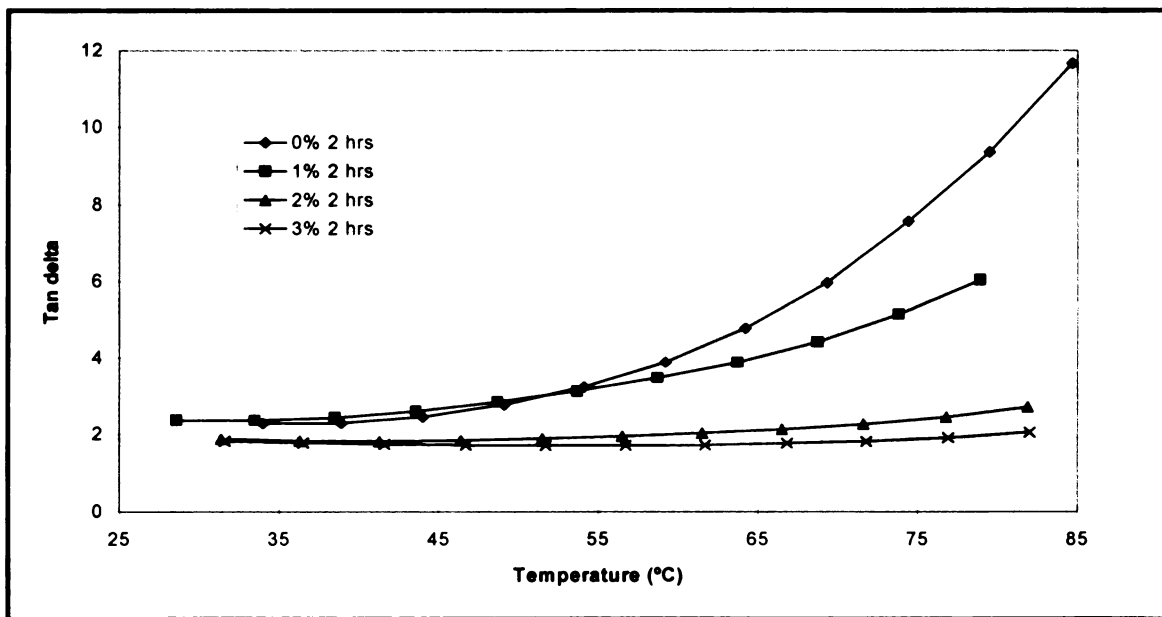


Figure 4.15 - $\tan \delta$ curves of AC-5/EAM binders mixed for two hours (no cure)

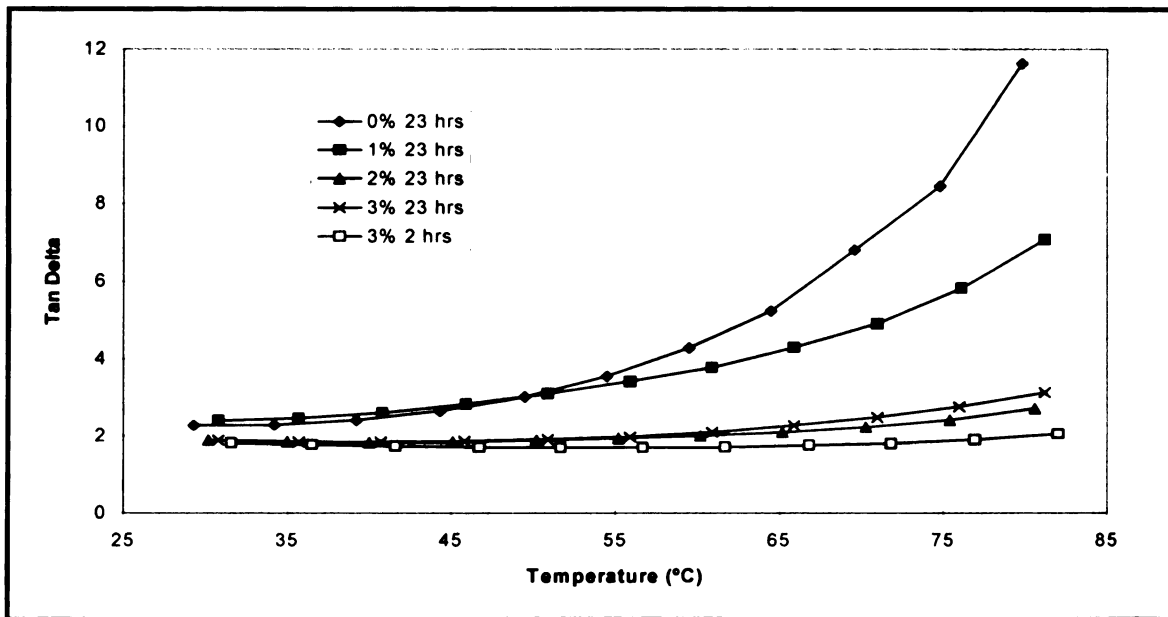


Figure 4.16 - $\tan \delta$ curves of AC-5/EAM binders with 23 hours cure time

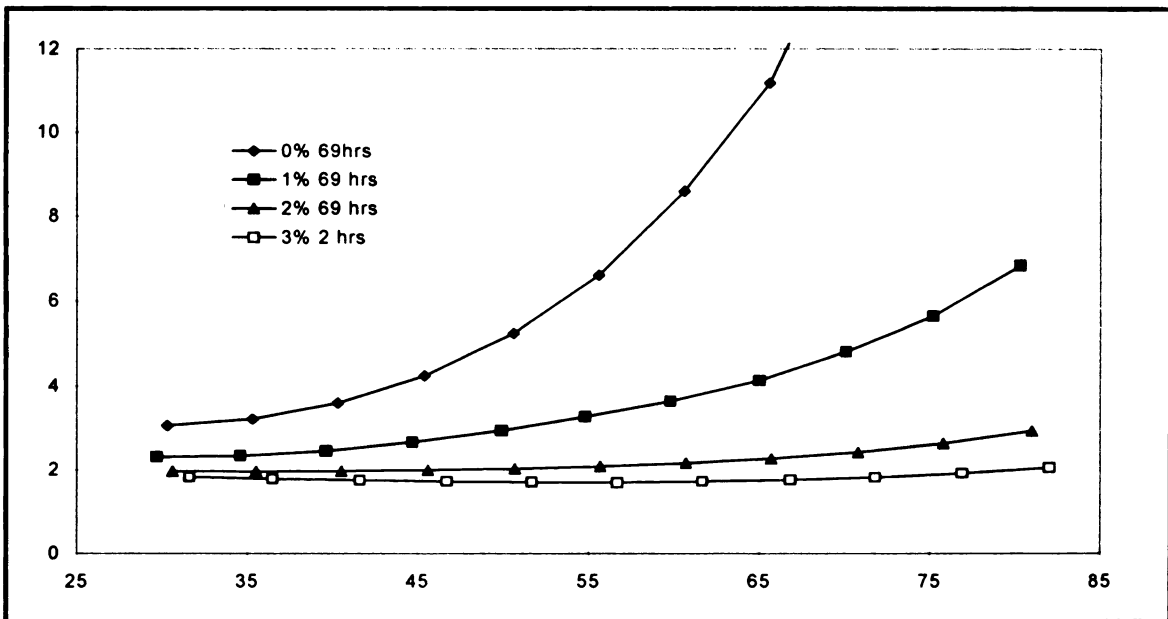


Figure 4.17 - $\tan \delta$ curves of AC-5/EAM binders with 69 hours cure time

4.2.2 - Mixing Scale-Up

The mixing procedure developed for Elvaloy® AM is only valid for mixing 150 gram batches. Direct scale-up to 300 gram batches gave vastly different, as well as less desirable, properties. The other polymers studied to date have scaled up perfectly to large batches. The network formation in these polymers is much less dependent on perfectly replicating the small batch mixing in the large batch. The reaction of Elvaloy® AM with the asphalt can be affected by shear rate, asphalt turnover, access to oxygen, and any number of other factors affected by the mixing process. To get identical properties in the large batch would require duplicating the three dimensional flows and thermal gradients produced in the small batch during mixing. This is beyond the scope of this project. Figure 4.13 illustrates the differences between the two batches. It is a graph of the high temperature dynamic shear modulus for two large batches and one small batch of 1.5% (w/w) Elvaloy® AM modified AC-5. Dynamic shear modulus for small batches was reproducible to within ten percent. Figure 4.13 shows not only the inferior properties of the large batch but also the irreproducibility.

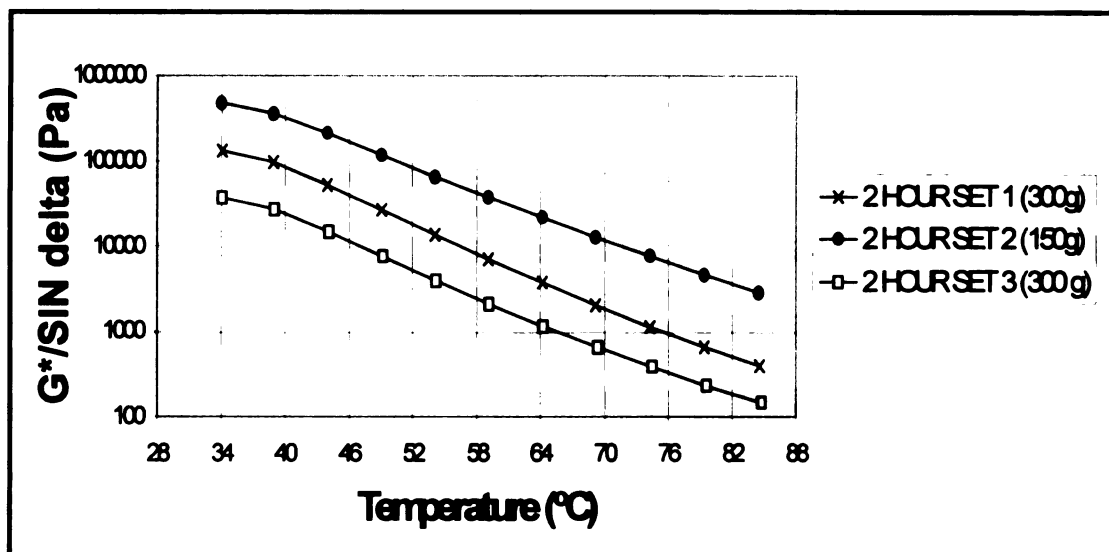


Figure 4.18 - Dynamic shear modulus of different batch sizes of AC-5/EAM blends

4.2.3 - Dynamic Shear Rheometry

Dynamic shear rheometry was used to determine the optimum Elvaloy® AM content for each asphalt. The manufacturer claims that half as much Elvaloy® AM is needed to get properties similar to those of SBS modified asphalts. Because of this, the Elvaloy® AM is priced at twice the price of SBS. Our data confirm this claim. Table 4.9 shows the optimum Elvaloy® AM content for the four asphalt grades. The optimum contents were determined using the same method as outlined in Section 2.2.1.

Table 4.9- Optimum Elvaloy® AM content

Asphalt Grade	Optimum Elvaloy® AM Content
AC-2.5	2.5% (w/w)
AC-5	1.5% (w/w)
AC-10	1% (w/w)

DSR was also used to determine the SHRP high temperature performance grade. Table 4.10 shows the high temperature performance grade for Elvaloy® AM modified binders. There is a large increase in SHRP grade due to oxidation as seen by the high PG of the 0% (w/w) Elvaloy® AM samples. These samples have a PG three or four grades higher than the neat asphalt used for the mixtures. There is little increase in the performance grade upon addition of Elvaloy® AM. While the SHRP PG for Elvaloy® AM samples is very high, the performance may be degraded in a real road application because much of the improvement is from oxidation in the mixing process and not the polymer itself.

Table 4.10 - SHRP high temperature PG of Elvaloy® AM modified binders

Asphalt → Cure Time →	AC-2.5 2 hr.	AC-5 2 hr.	AC-10 2 hr.	AC-5 23 hr.	AC-5 69 hr.
0% (w/w)	70	76	76	70	70
1% (w/w)	70	76	82	76	70
2% (w/w)	70	82	82	82	82
3% (w/w)	82	82	82	82	N/A
4% (w/w)	N/A	82	N/A	N/A	N/A

4.2.4 - Rotational Viscometry

The viscosity of Elvaloy® AM modified binders was much higher than SBR modified binders. This is mainly due to the oxidative hardening that occurs during processing. Figures 4.19 and 4.20 are the viscosity versus temperature curves for AC-5 and AC-2.5 blends respectively. Of the AC-5 blends, only samples with less than 1.5% (w/w) Elvaloy® AM passed the SHRP viscosity test. AC-2.5 blends, on the other hand, pass the specification at up to 3% (w/w) Elvaloy® AM due to the softer base asphalt. Excessive viscosity increases may limit the amount of Elvaloy® AM and/or the hardness of the base asphalt that can be used to prepare Elvaloy® AM modified binders.

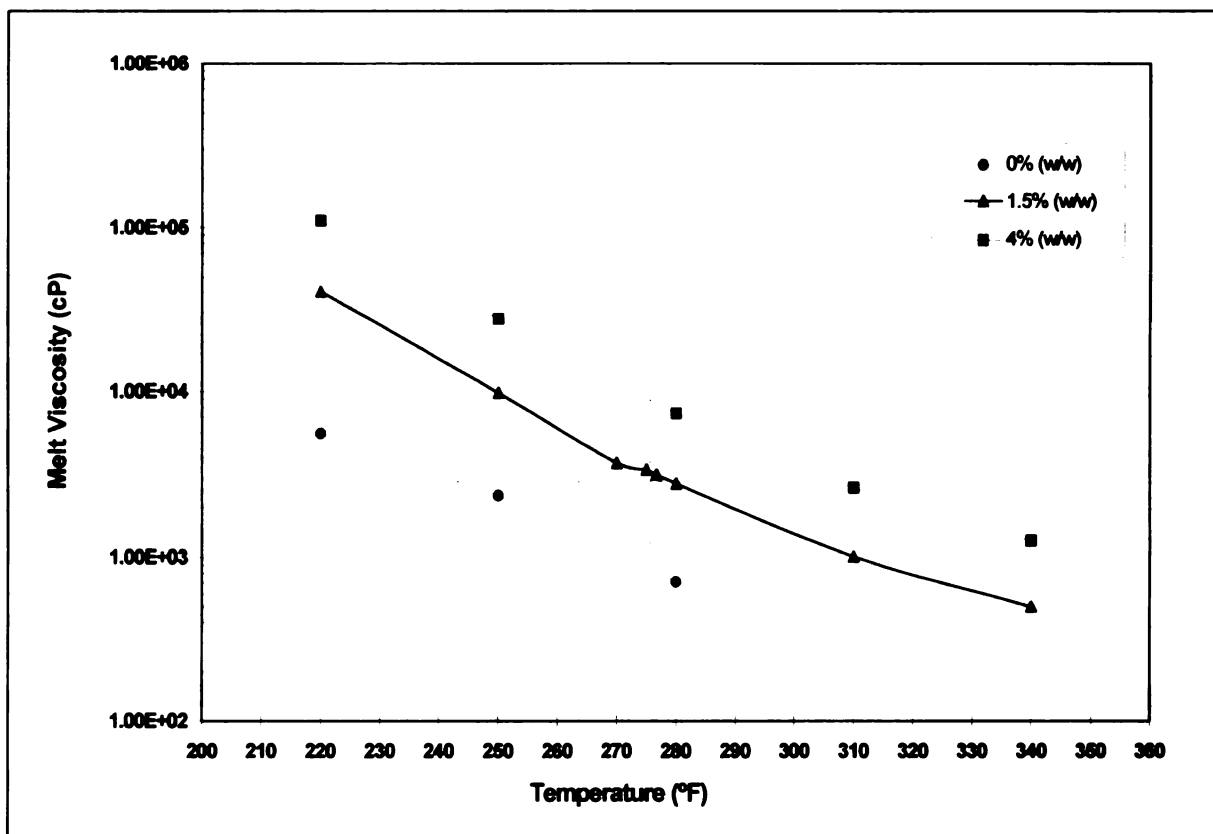


Figure 4.19 - Melt viscosity of AC-5/Elvaloy® AM modified binders

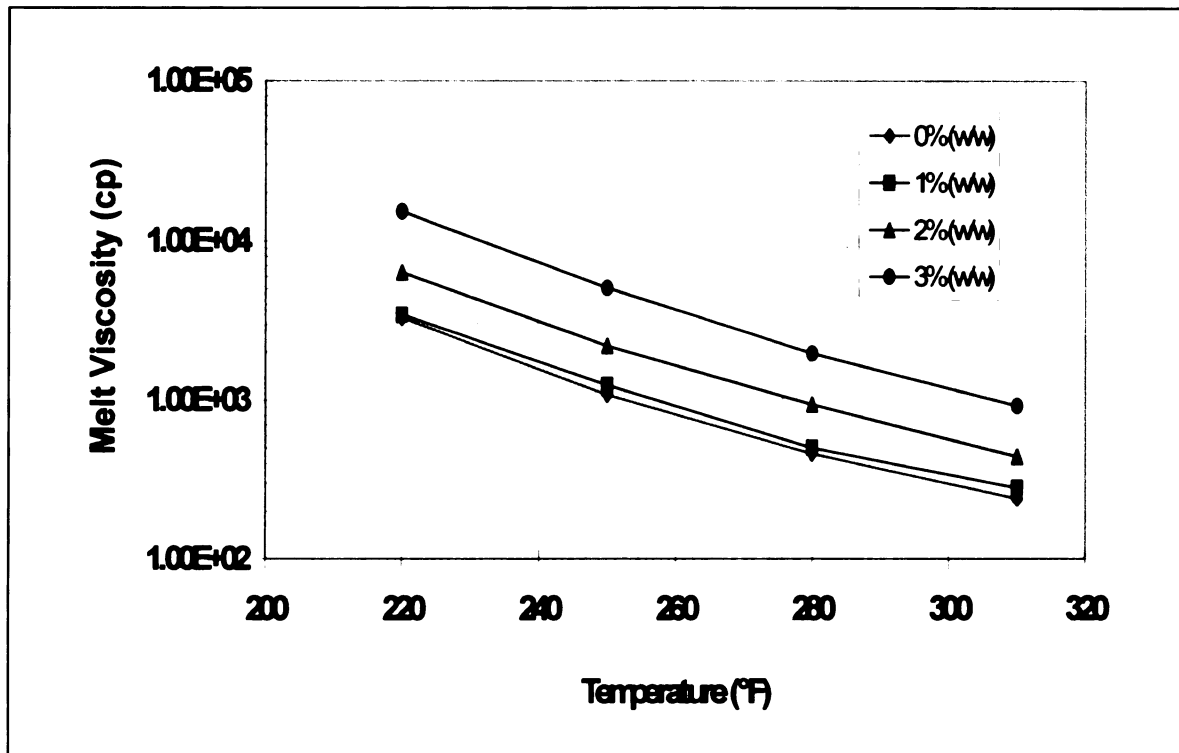


Figure 4.20 - Melt viscosity of AC-2.5/Elvaloy® AM modified binders

4.2.5 - Bending Beam Rheometry

Bending beam rheometry was conducted to determine the low temperature performance grade of Elvaloy® AM modified binders. In all cases, the m-value was the limiting factor in determining the SHRP PG. Table 4.11 contains the low temperature PG for Elvaloy® AM modified AC-5 and AC-2.5 samples. The AC-5 performance grades are significantly worse than those of the SBR modified AC-5. This is because of the severe oxidation which occurs during Elvaloy® AM processing. The AC-2.5 performance grades are the same as the SBR modified binders, however this is because the coarse temperature scale used to determine the PG.

Table 4.11 - Low temperature SHRP PG of Elvaloy® AM modified binders

	AC-2.5	AC-5
0% (w/w)	-28	-16
1% (w/w)	-28	-16
2% (w/w)	-28	-16
3% (w/w)	-28	-16

Figure 4.21 shows the m-value and stiffness of AC-2.5 binders modified with SBR and Elvaloy® AM at -18°C. This figure clearly indicates that the low temperature properties of SBR binders are better than Elvaloy® AM binders despite the lack of difference in their performance grades. There was minimal changes in low temperature properties with increasing Elvaloy® AM content. AC-5 blends showed decreased stiffness at -12°C with increasing Elvaloy® AM content but showed no differences when tested at -6°C. AC-2.5 blends showed no changes for contents of 0% (w/w) to 2% (w/w) with a 20% reduction in stiffness at 3% (w/w) Elvaloy® AM. The low temperature properties of asphalt, as measured by BBR, are not improved upon addition of Elvaloy® AM. They are in fact degraded due to the high level of oxidation which occurs during processing. It is important to note that these tests do not confirm that Elvaloy® AM modified pavements will have poor low temperature performance. The SHRP specification ignores many factors, such as tensile properties, plastic deformation, and toughness which will likely play an important role in determining the low temperature performance of PMA pavements. This topic is addressed in detail in Chapter Seven.

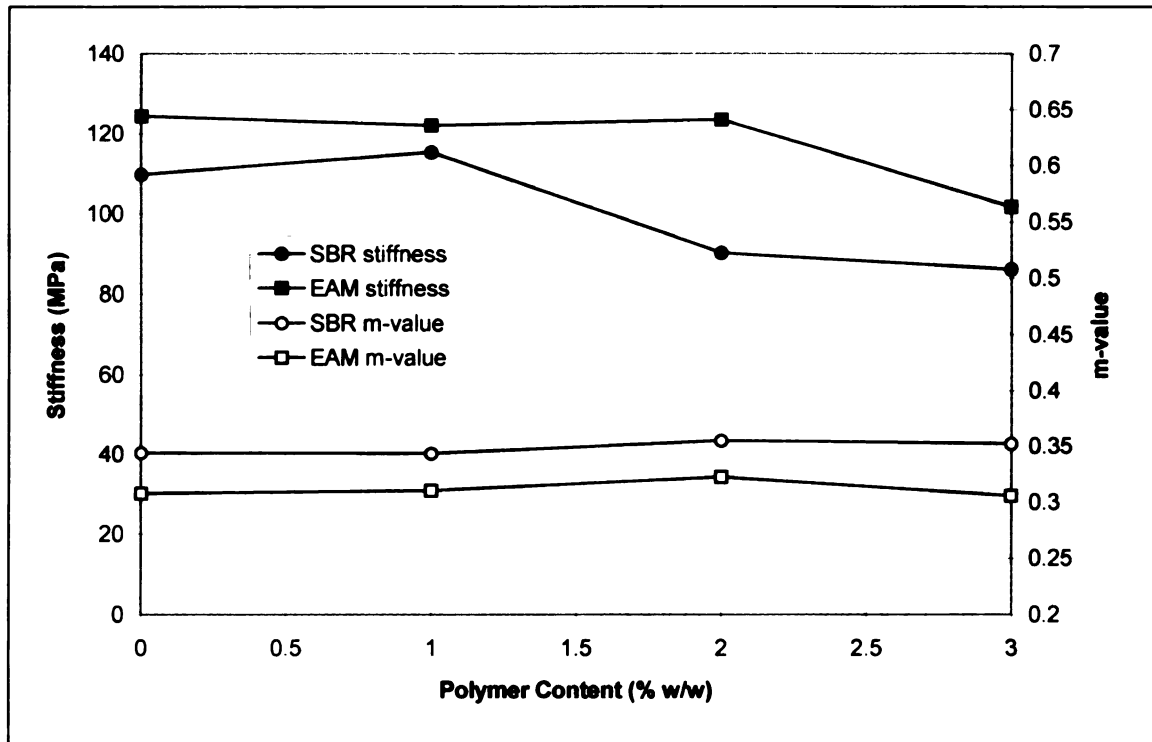


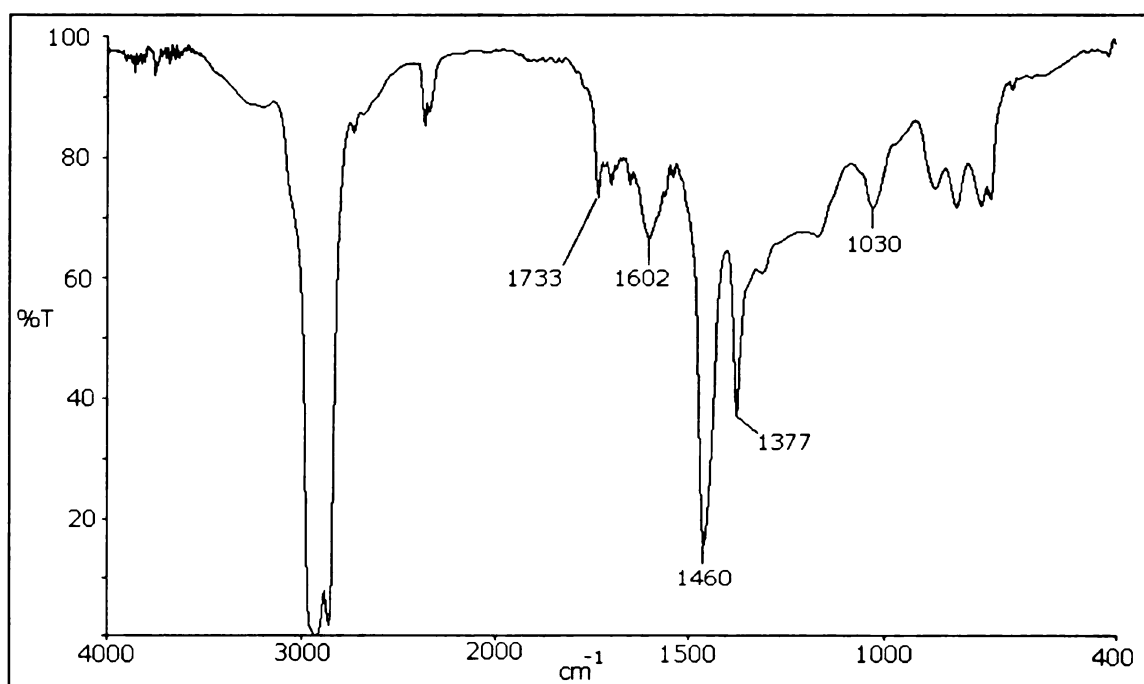
Figure 4.21 - BBR data of AC-2.5/SBR and AC-2.5/EAM binders at -18°C

4.2.6 - Fourier Transform Infrared Spectroscopy

Fourier-Transform Infrared Spectroscopy (FTIR) was used to analyze the original binders as well as the unaged Elvaloy® AM modified binders. The characteristic IR absorption peak for the asphalt is the aryl C-C peak at 1600 cm^{-1} . The characteristic IR absorption peak of Elvaloy® AM is 1740 cm^{-1} , which corresponds to a C=O bond found in Elvaloy® AM. A typical FTIR curve for EAM/AC-5 blends is shown in Figure 4.22. The absolute ratio of the 1740 cm^{-1} absorption band to the 1600 cm^{-1} band of an Elvaloy® AM modified asphalt can be used to determine the polymer content in the binder. The calibration curve is valid only for the given asphalt/polymer blend. Table 4.12 details the calibration curves for AC-2.5, AC-5, and AC-10 binders modified with Elvaloy® AM. In all cases, the R^2 regression coefficient was greater than 0.990.

Table 4.12 - FTIR calibration curves of Elvaloy® AM modified binders

Sample	Calibration Curve Equation
AC-2.5/EAM	Polymer Content = (Ratio - 0.3041) / 0.1680
AC-5/EAM	Polymer Content = (Ratio - 0.3551) / 0.1427
AC-10/EAM	Polymer Content = (Ratio - 0.2743) / 0.1657

**Figure 4.22** - Typical AC-5/Elvaloy® AM FTIR spectrum

IR experiments were conducted to investigate the difference between the small size batch (150g) and the large size batch (300g). In Table 4.13 below, two important ratios of the characteristic peaks are shown. One is the ratio of C=O peak (1740 cm⁻¹) of Elvaloy® AM to the aryl C-C peak (1600 cm⁻¹) of asphalt and the other is the ratio of the C=O peak (1700 cm⁻¹) from oxidation of asphalt to the aryl C-C peak (1600 cm⁻¹).

Table 4.13 - FTIR ratios of different batch size Elvaloy® AM modified binders

AC-5/EAM 1.5% (w/w) (Small Batch)		
Curing Time	1740 / 1600	1700 / 1600
2 hours	0.5740	0.6010
5 hours	0.5576	0.6970
10 hours	0.5858	0.7676

AC-5/EAM 1.5 % (w/w) (Large Batch)		
Curing Time	1740 / 1600	1700 / 1600
1 hour	0.5511	0.6079
2 hours	0.5590	0.6521
5 hours	0.5460	0.5570
10 hours	0.4880	0.6547
15 hours	0.5000	0.7012

The small batch ratios behave as expected. The 1740/1600 ratio does not change with additional heating time as expected because the amount of Elvaloy® AM does not change. The 1700/1600 ratio increases with increased heating time, which is expected because oxidation occurs for longer time. The large batch ratios do not behave as expected. The small batch system, which had good mixing efficiency, showed greater oxidation peak ratios (0.7676 vs. 0.6547 for 10 hours mixing). This was consistent with the lower storage and loss modulus of the large batch binders. The large batch might have had poor mixing efficiency which is related to thermal induction and reaction as well as thermal oxidative degradation occurring simultaneously during the curing. The differences in both physical properties and chemical properties of the different batch size mixes should be examined further.

4.2.7 - Gel Permeation Chromatography

GPC was used to analyze Elvaloy® AM modified binders. Figure 4.23 shows a typical chromatogram for Elvaloy® AM modified asphalt. The chromatogram has been divided into two regions. Region A represents the relatively high molecular weight portion which was formed, possibly by the reaction of the epoxy group in Elvaloy® AM with a nucleophilic functional group like carboxylic acid in the asphalt. Since straight AC-10 has more high molecular weight asphaltenes (A region) and more reactive sites than straight AC-2.5, the ratio of region A to region B is higher for AC-10 binders. It is important to note that even the unmodified binders subjected to the Elvaloy® AM mixing procedure show relatively high portion of region A due to the thermal oxidation. Whether this high MW material in the modified binders was due to oxidation, reaction, or both could not be determined directly from the GPC results.

In addition, GPC tests for two different batch sizes of AC-5/Elvaloy® AM blends were conducted. The small batch samples showed a much larger Region A than the large batch samples. This is consistent with both the rheological properties and the FTIR data.

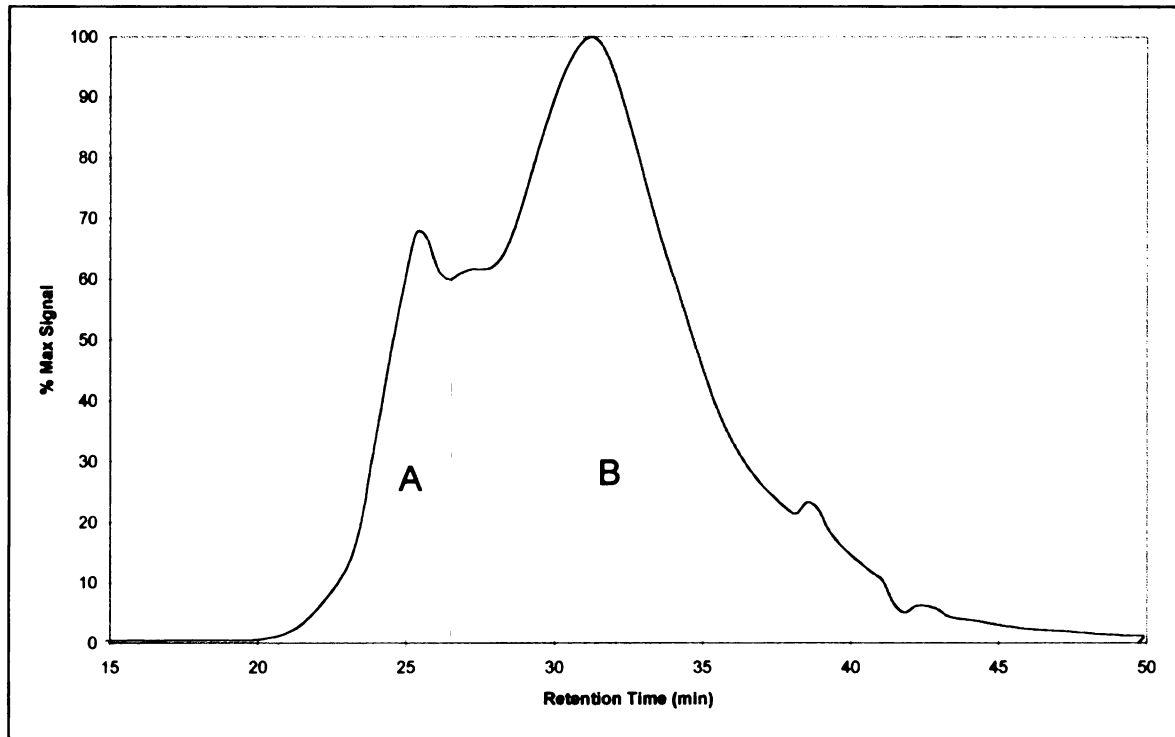


Figure 4.23 - Typical AC-5/Elvaloy® AM GPC curve

4.2.8 - Thermomechanical Analysis

The softening points of straight and Elvaloy® AM modified AC-2.5, AC-5, and AC-10 binders were measured using thermal mechanical analysis. Table 4.14 is the complete softening point and melt temperature data for the Elvaloy® AM modified binders. The softening point and melt temperature showed considerable improvement upon addition of polymer. There was an average increase of 16°C in the softening point of the three asphalt grades due to the processing conditions. The addition of 2-3 % (w/w) resulted in an additional increase of approximately 10-15°C in the softening point. The melt temperatures measured also showed similar trends as outlined in Table 4.14. TMA indicates that while much of the high temperature performance improvement is due to

processing, the polymer itself does contribute to that increase somewhat. This is contrary to the dynamic shear results which suggested the polymer's role was minimal in performance enhancement.

Table 4.14 - Softening and melt temperatures of Elvaloy® AM modified binders

AC-2.5/EAM Blends

Polymer Content (%)	Softening Point (°C) (by intercept)	Melt Temperature (°C) (by 1 mm depression)
virgin	22	31
0	38	46
1	38	48
2	42	54
3	49	60

AC-5/EAM Blends

Polymer Content (%)	Softening Point (°C)	Melt Temperature (°C)
virgin	26	33
0	43	51
1	42	49.5
1.5	45	55
2	48	57.5
3	45	56
4	55	56

AC-10/EAM Blends

Polymer Content (%)	Softening Point (°C)	Melt Temperature (°C)
virgin	35	47
0	41	52
1	55	58
2	56	69

4.3 - Recycled Crumb Rubber

There is a great deal of interest in the feasibility of using ground tire rubber to modify asphalt. Because of the environmental problem of tire disposal any way to reuse the tire rubber would be greatly beneficial. The amount of crumb rubber (CRM) used for modification is much higher than the other polymers, with double-digit weight percentages common. This indicates that recycling CRM pavements may be problematic and should be considered in any evaluation of CRM modification.

Crumb rubber modifiers which were supplied by Rouse Rubber Industries were used in this study. The crumb rubber modifier is a mixture of natural and synthetic rubbers, carbon black, fillers, and oils. Three different modifiers were obtained: Ultrafine™ GF-80A, GF-80AE, and XP-14. These Ultrafine™ crumb rubber modifiers were graded by their size. For example, Ultrafine™ GF-80A is an ambiently produced tire rubber powder that passes the 80 mesh sieve (174 microns) screen with a resulting 200 mesh (74 micron) mean particle size and a surface area of $\sim 2 \text{ m}^2/\text{g}$. All three were investigated to determine the best rubber for use with the Amoco asphalt. The Ultrafine™ Wet method was used for blending as recommended by Rouse. This method can produce all types of rubber modified asphalt binders including membrane interlayers and surface treatments but requires additional equipment. The ‘Wet’ process goal is to achieve a finite degree of plasticization or reclaiming without degassification or pyrolysis. Fine rubber reacts and solvates very rapidly for a stable asphalt rubber modified mixture. The advantage of the use of the fine rubber in ‘Wet’ process is the ease of dispersion and imparting the properties of the tire rubber readily into the asphalt matrix.

The major concern is the reactivity of the tire rubber itself that can easily occur with elevated temperature of 350°F on a relatively short time scale (< 6 hours). Heating rubber in an asphalt for defined periods of time can result in devulcanization or scission of long chain macromolecules into shorter chains while preserving the main rubber polymer, or pyrolysis to complete decomposition of the rubber polymer into its basic components of oil, gas and carbon black. Reactivity is a direct function of surface and particle size. The smaller the particle size, the greater the reactivity, and thus, the less the capital and operating costs. The GF-80A crumb rubber modifier, which is ultra-fine, allows the asphalt producer, distributor, or hot mix plant operator to economically handle, disperse, react and produce a very uniform, stable and flowable rubber modified asphalt cements in all types of asphaltic processes and application needs. The physical properties of Ultrafine™ GF-80A also allow the inherent properties of the tire rubber to be impacted into the asphalt binder itself to achieve asphalt modification. However, reactivity or solvation can also be hampered by high heating temperatures which can lead to environmental and polymer degradation problems.

The high temperature properties of CRM modified AC-10 and AC-20 binders were investigated in this study. The aging characteristics and low temperature properties will be investigated in the future

4.3.1 - Mixing Procedure

AC-10 or AC-20 are generally recommended for CRM blends but, in colder climates, lower viscosity AC can be used. High temperatures are not required for blending. For example, the blending temperature of GF-80A is between 325-350°F.

Because it can be a continuous process, time required for incorporation is less than one hour. For the wet applications, the fine tire rubber is fully dispersed into the asphalt binder prior to addition to any type of hot mix unit or surface treatment application. Rubber modified asphalt concrete binders have a shelf life in excess of eleven days and are stable with minimal settling occurring.

A mixing procedure was developed based upon the improvement of rheological properties for varying temperatures and mixing times. The method of preparation of crumb rubber modified asphalt binders followed the suggested guidelines from Rouse Rubber Industries. Since low viscosity asphalt binders are not recommended, AC-10 was first mixed with CRM Ultrafine™ GF-80A. Mixing temperature was determined based on the investigation of rheological properties as well as homogeneity of binders. For determination of the optimum mixing temperature, 10% (w/w) CRM asphalt binders were mixed for one hour at three different temperatures (250°F, 300°F, 350°F). Figures 4.24 and 4.25 show the dynamic shear modulus and $\tan \delta$, respectively, as a function of temperature for the three different mixing temperatures. Higher temperature showed slightly higher moduli and slightly lower $\tan \delta$ due to possible oxidation of the binders.

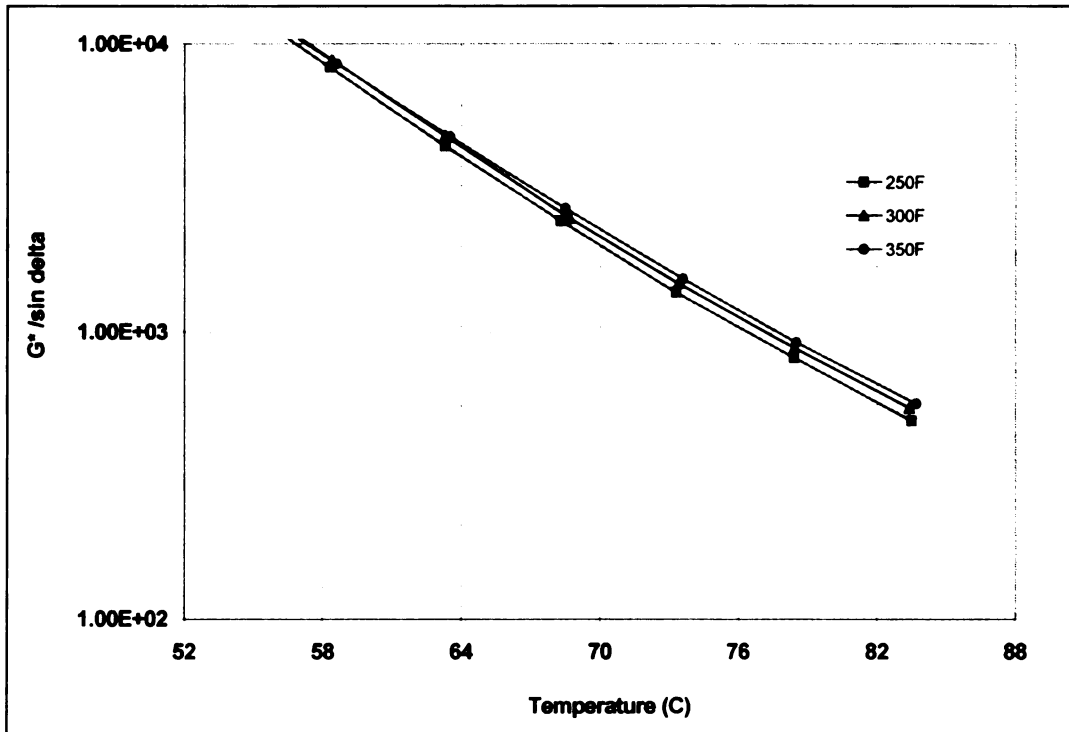


Figure 4.24 - Dynamic shear modulus of 10% (w/w) CRM modified AC-10 mixed for one hour at various temperatures

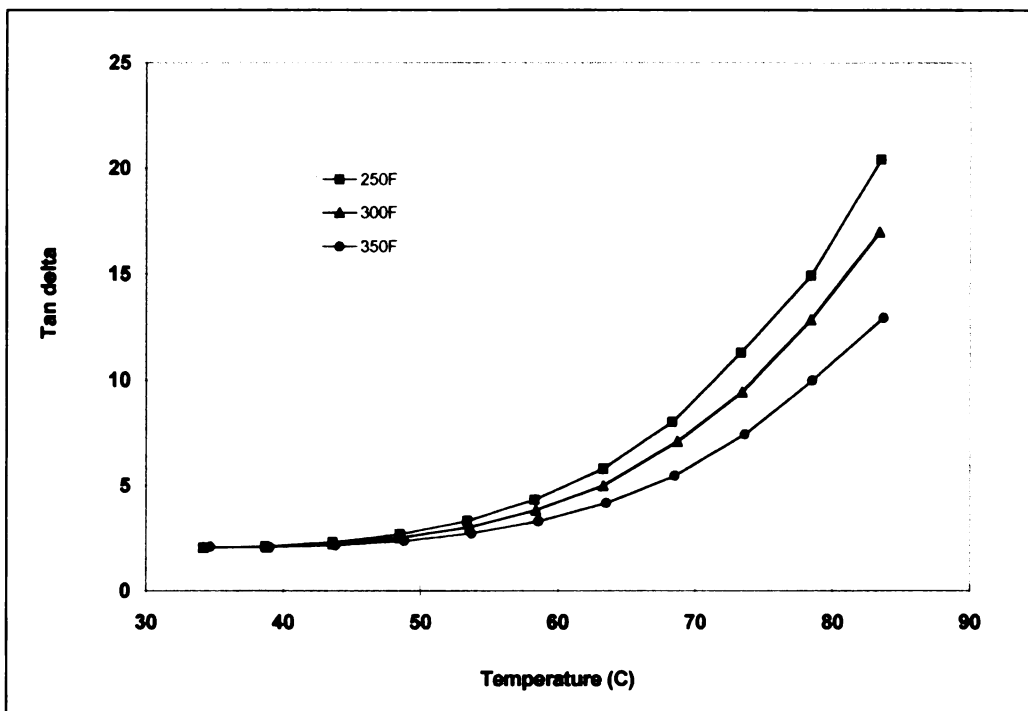


Figure 4.25 - $\tan \delta$ curves of 10% (w/w) CRM modified AC-10 mixed for one hour at various temperatures

Additional samples were mixed using several different mixing times (15, 30, 45, 60, and 120 minute) at 300°F and then tested to examine any rheological property improvements as well as melt viscosity change due to increased mixing times. Figures 4.26 shows the dynamic shear modulus as a function of temperature of these samples. It is not clear that longer mixing enhances the rheological properties of the blend. There was also minimal differences in the melt viscosity of all five samples. Based on the above studies, the best mixing time and temperature were determined to be 30 minutes and 350°F. This is consistent with the recommendations of the supplier.

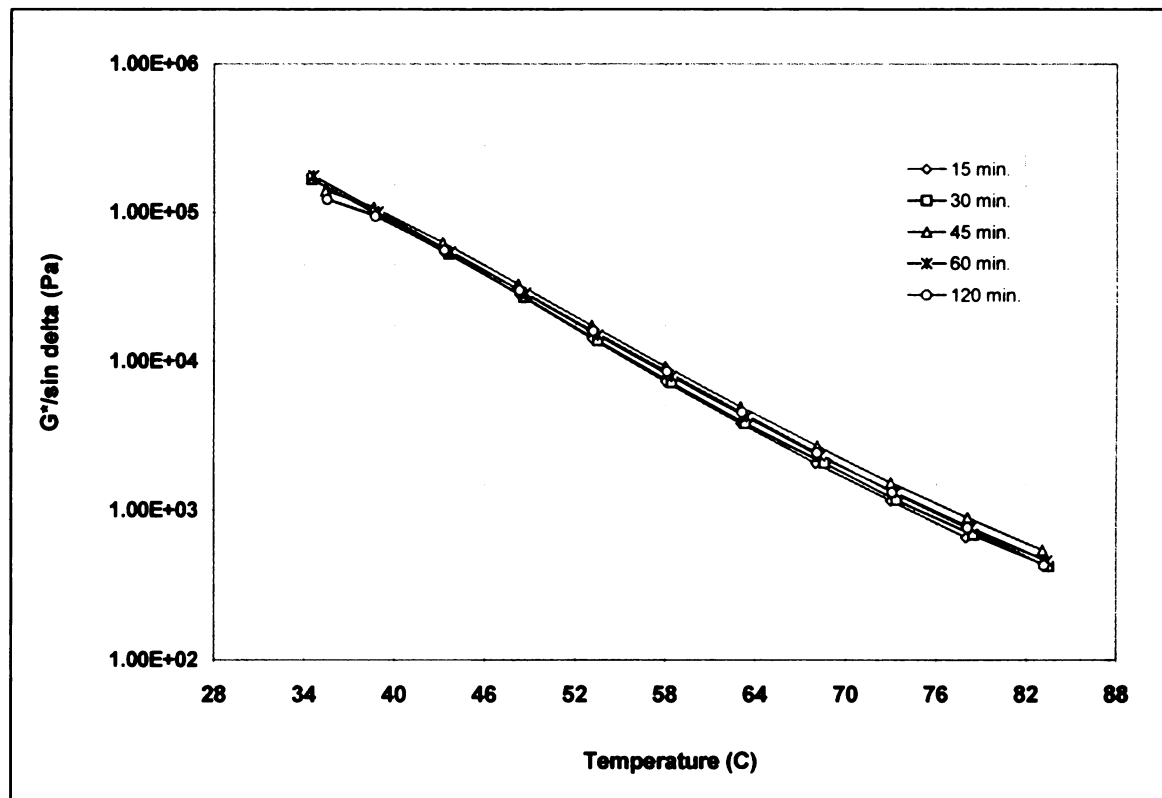


Figure 4.26 - Dynamic shear modulus of 10% (w/w) CRM modified AC-10 mixed at 300°F for various amounts of time

4.3.2 - Dynamic Shear Rheometry

DSR was used to determine optimum polymer contents as well as high temperature performance grade. Unlike previous systems, CRM showed no optimum polymer content. That is, there was no content above which the rheological properties improvement was minimal. CRM modification continued to increase properties with additional modifier up to 20% (w/w). At this content, the asphalt became untestable using the SHRP specifications due to excessive viscosity.

The AC-10/CRM system was studied using CRM contents of 0%, 5%, 10%, 15%, and 20% (w/w). Contents of 20% (w/w) and greater could not be classified using SHRP because they did not meet the viscosity specification. Figure 4.27 shows the dynamic shear modulus of AC-10/CRM blends after spending an additional hour at elevated temperature. It clearly shows that there is no optimum content as defined earlier. Likewise, the $\tan \delta$ curves for the same samples displayed continued improvement with additional CRM as shown in Figure 4.28.

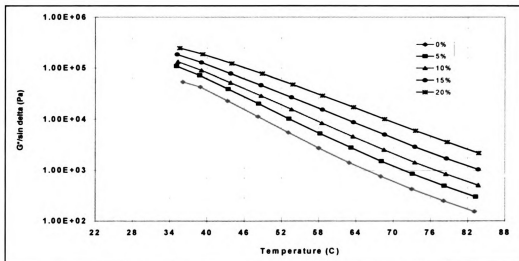


Figure 4.27 - Dynamic shear modulus of AC-10/CRM binders

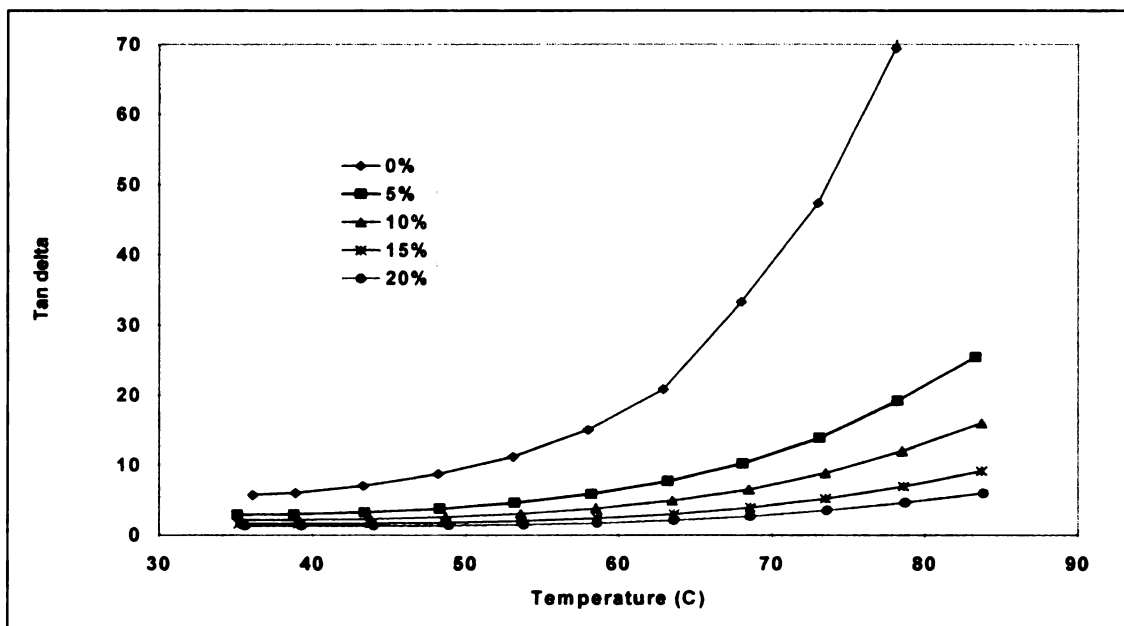


Figure 4.28 - *Tan δ curves of AC-10/CRM binders*

The dynamic shear curves were also used to assign high temperature performance grades to the AC-10/CRM binders. Table 4.15 details the high temperature PG of each of the samples. The PG continues to increase with increasing CRM content. The PG for 10% (w/w) CRM can also be achieved using 2% (w/w) SBR or simply heating the asphalt at 380°F for two hours. Each sample was also subjected to additional time at high temperature to determine the effects of storage time on the SHRP PG. There was minimal effect of storage for times up to two hours.

Table 4.15 - *SHRP high temperature PG of AC-10/CRM binders*

CRM amount	30 min. mixing	+ 1 hr at 350°F	+ 2 hr at 350°F
0 %	64	64	64
5 %	70	70	70
10 %	70	76	76
15 %	82	82	82
20 %	88	88	88

4.3.3 - Rotational Viscometry

CRM modified binders were tested for processibility using rotational viscometry. The viscosity of the modified binders increased with increases in CRM content. For example, at 135°C the viscosity of AC-10 increased from 0.32 Pa·s for the 0% (w/w) CRM to 2.42 Pa·s for the 15% (w/w) CRM. Contents greater than 15% (w/w) were too viscous to be tested. All binders with 15% (w/w) or less CRM passed the SHRP specification for viscosity. Figure 4.29 shows the viscosity versus temperature curves for AC-10/CRM binders. The dashed lines indicate the SHRP specification temperature and viscosity value. It is important to note that the plot is linear for all contents on a log scale.

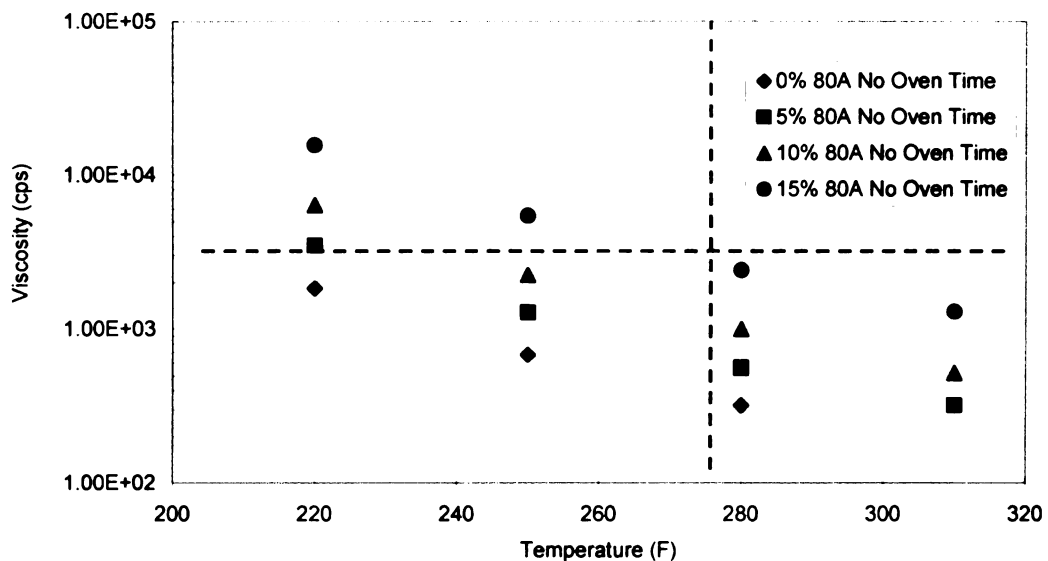


Figure 4.29 - Viscosity of AC-10 binders with various CRM contents (w/w)

The viscosity change associated with long term high temperature storage was also investigated. The samples were stored at 350°F for five hours and 24 hours after being mixed using the normal procedure. The percentage change in viscosity after this aging is shown in Figure 4.30. These results are inconclusive. The 24 hour aging data shows that all of the CRM binders increased more rapidly than the control sample. This indicates that the increase in viscosity is not simply due to oxidation of the asphalt binder and that the CRM affects the viscosity increase. The increase is possibly due to solvation of the rubber, crosslinking of the rubber, or some other phenomenon. This should be studied further.

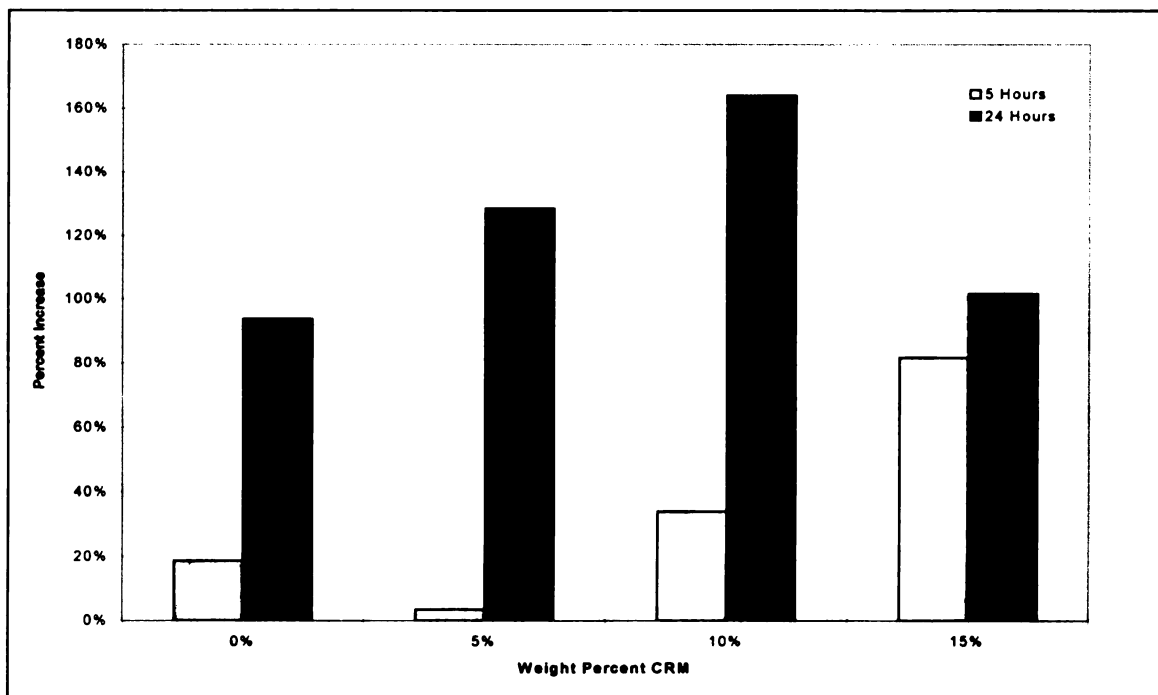


Figure 4.30 - Percent increase in viscosity of AC-10/CRM binders after high temperature storage

4.3.4 - Thermomechanical Analysis

The softening point and melt temperature of AC-10/CRM binders was measured using thermal mechanical analysis. Table 4.16 contains the TMA data of AC-10/CRM mixtures that have been aged for up to 24 hours at 350°F. Unlike other polymers, the softening point increase does not level off with increasing polymer content. This is consistent with the dynamic shear rheometry results. There is a sharp increase in melting temperature of the 0% (w/w) CRM sample after 24 hours aging which indicates thermal oxidation. This effect becomes less pronounced with increasing CRM content. At a CRM content of 20% (w/w), there is only a four degree increase in the melt temperature after 24 hours compared with a 10 degree increase in the control. This seems to indicate that the CRM is either preventing or masking the effects of oxidative aging.

4.4 - Ethylene Vinyl Acetate

Ethylene vinyl acetate (EVA) is a member of the dispersed thermoplastics family. Polyethylene (PE) is the most common dispersed thermoplastic used for modification. However, PE has a tendency to phase separate in asphalt which causes undesirable results. EVA is much more compatible with asphalt.

Two different EVA polymers (Polybilt 152 and Polybilt 104) were supplied by Exxon Chemical and were used to modify AC-5 asphalt binders. The manufacturer claims that EVA modification is used to increase binder softening point and decrease penetration, to maintain base asphalt low temperature behavior, and to provide modified blends with good storage stability and handling characteristics. Polybilt (PB) 152 and 104 are available as free-flowing translucent pellets and can be processed using

Table 4.16 - Melt temperature and softening point of AC-10/CRM binders

0% GF80A	Softening Point (°C)	Melting Point (°C)
No Oven Time*	29	38
One Hour at 350°F	32	39
Two Hours at 350°F	32	39
Five Hours at 350°F	32	40
24 Hours at 350°F	40	48

5% GF80A	Softening Point (°C)	Melting Point (°C)
No Oven Time*	28	39
One Hour at 350°F	32	41
Two Hours at 350°F	32	41
Five Hours at 350°F	37	41
24 Hours at 350°F	41	50

10% GF80A	Softening Point (°C)	Melting Point (°C)
No Oven Time*	36	46
One Hour at 350°F	38	47
Two Hours at 350°F	37	48
Five Hours at 350°F	39	47
24 Hours at 350°F	40	52

15% GF80A	Softening Point (°C)	Melting Point (°C)
No Oven Time*	37	50
One Hour at 350°F	38	49
Two Hours at 350°F	40	50
Five Hours at 350°F	42	52
24 Hours at 350°F	43	54

20% GF80A	Softening Point (°C)	Melting Point (°C)
No Oven Time*	41	55
One Hour at 350°F	40	56
Two Hours at 350°F	43	60
Five Hours at 350°F	45	60
24 Hours at 350°F	46	59

conventional equipment. Blending time will depend on the shear rate of the equipment used and temperature. Recommended blending temperature for Polybilt 152 is 330°F to 350°F. The recommended blend temperature for Polybilt 104 is about 10°F lower. Table 4.17 shows typical properties of the EVA modifiers. The EVA dissolves in several solvents such as tetrahydrofuran, chloroform, carbon tetrachloride, and toluene. THF was mainly used for the IR work of EVA modified asphalt binders because of its convenience and availability in the lab. Typical EVA has 30 or 40 % vinyl acetate on a mole/mole basis. Polybilt 152 is a higher molecular weight polymer than Polybilt 104 as indicated by the lower melt flow rate. Polybilt 152 also has a higher melt temperature which requires a higher blending temperature with the asphalt.

Table 4.17 - Physical properties of EVA modifiers

Property*	Polybilt 152	Polybilt 104	Test Method
Melt Flow Rate, dg/min.	2.5	20	ASTM D-1238
Density, g/cm ³	0.942	0.941	ASTM D-792
Softening Point, °F	350	260	ASTM E-28
Hardness, Shore A	90	85	ASTM D-2240
1% Scant Modulus, psi	7000	7100	ASTM D-638
Elongation at Break, %	650	675	ASTM D-638

* Property information supplied by Exxon Chemical.

4.4.1 -Mixing Procedure

Polybilt blends have been successfully made using a variety of blend equipment. Blending requirements are different for the various Polybilt grades with the higher molecular weight grades (lower melt flow rate) requiring more time. Increasing mixing temperature and/or shear rate will reduce the blending time required. The selected

temperature and time is based on the production of a homogeneous blend of EVA with asphalt. Polybilt polymers, like most other polymers, have a density of 0.92-0.95 as compared to 1.0+ for most asphalt. This results in a tendency for the EVA Polybilt to float and stay at the surface. It is important that Polybilt polymers must melt into the asphalt bulk at high enough temperature without agglomerating into a molten mass or skin which becomes very difficult to mix. Laboratory mixes can be made using high or low shear mixers. To reduce laboratory blending time in the lab, the low shear conditions used are higher speed than commercial installations. The key consideration in lab blending is to achieve turn over in the mix so that polymer pellets are pulled below the surface. The mixing speed for EVA Polybilt 152 and 104 binders was about 1600 rpm. Low viscosity grade asphalt binder, such as AC-5, with low molecular weight EVA like Polybilt 104 required milder mixing conditions than that of AC-10/ EVA Polybilt 152 system. Phase separation is best checked by turning off the mixer and observing for incorporated polymer floating to surface. Mixing temperature was determined based on the investigation of rheological properties as well as homogeneity of binders. For determination of the optimum mixing temperature and time, 5% (w/w) EVA PB152 and PB104 modified asphalt binders were mixed at three different conditions (300°F/1hr, 325°F/2hrs, 350°F/2hrs). In Figure 4.31, the dynamic shear modulus of the three samples is plotted against temperature. It is not clear that longer mixing at higher temperature enhances the rheological properties of the blend. The mixing conditions of 350°F and two hours blending was selected to maintain consistency with the SBS/SEBS mixing procedure. This allows direct comparison to the SBS/SEBS results. The mixing time and temperature are within the guidelines suggested by Exxon.

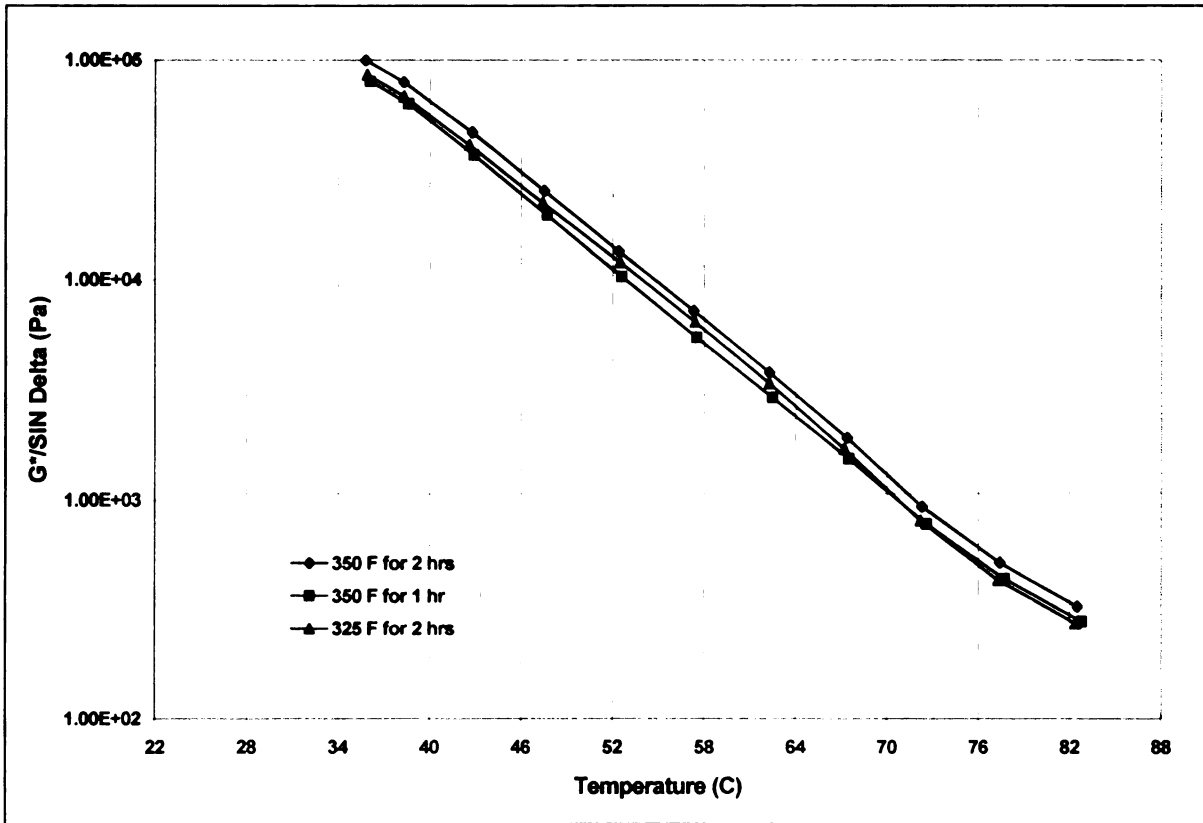


Figure 4.31 - Dynamic shear modulus of AC-5/EVA binders with different mix conditions

4.4.2 - Dynamic Shear Rheometry

DSR was used to determine optimum polymer content as well as high temperature performance grade. The optimum EVA content was determined for AC-5 grade asphalt binder. The optimum content was determined using the same method as other polymers. Figure 4.32 shows the $\tan\delta$ curves for different polymer kinds (PB152 and PB104) and contents as a function of temperature. In case of AC-5, adding more than 3-5 weight percent polymer did not significantly enhance the rheological properties in the range of service temperatures regardless of EVA molecular weight. Figure 4.33 shows the storage

modulus values as a function of polymer content. Unlike the $\tan \delta$ curves, the storage modulus of the binders enhanced almost linearly with increasing EVA contents. This trend is more clear when G' and G'' at 60°C are plotted in a function of polymer content in Figure 4.34. Based on all of these factors, the optimum content is 5% (w/w). This optimum is not as obvious as that determined for SBS, SBR, or Elvaloy® AM.

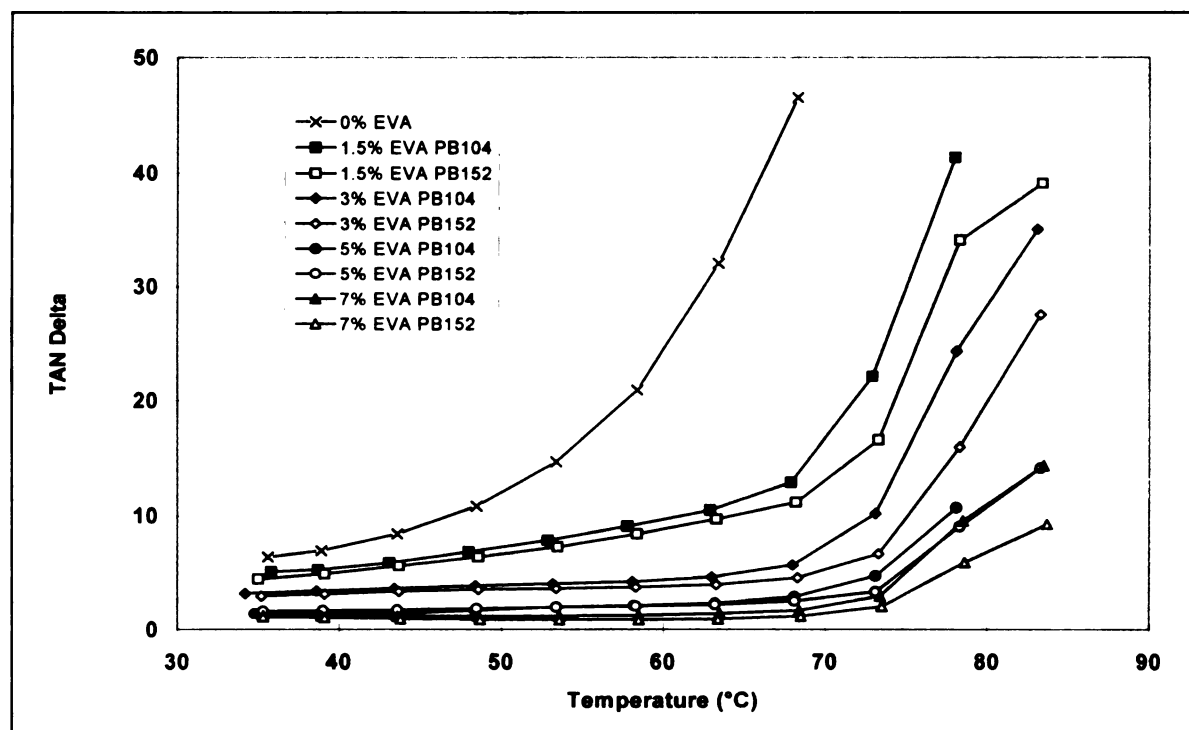


Figure 4.32 - $\tan \delta$ curves of AC-5/EVA binders

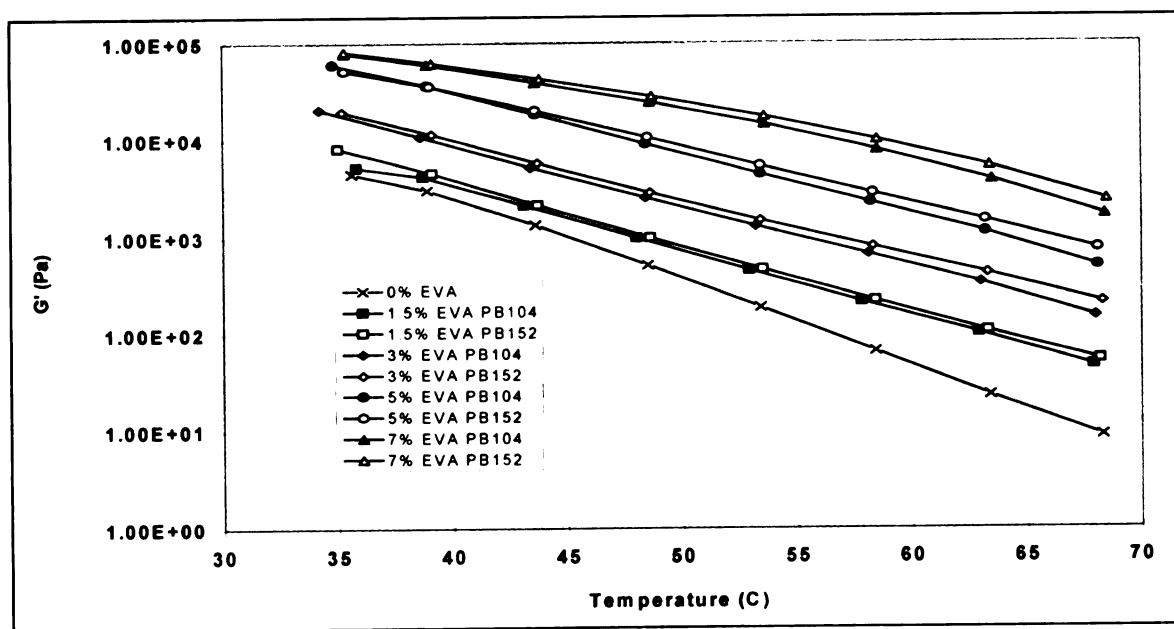


Figure 4.33 - Storage modulus of AC-5/EVA binders

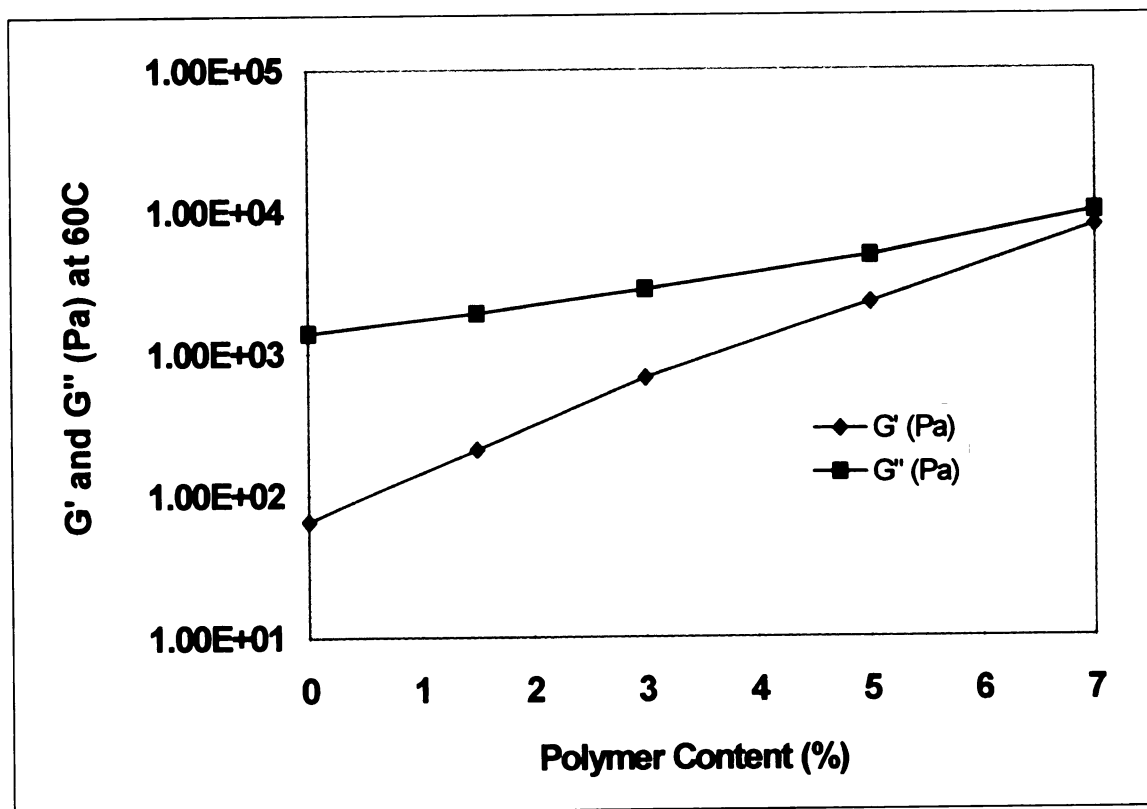


Figure 4.34 - Storage and loss modulus at 60°C of AC-5/EVA (PB104) blends

There was very little difference between the two molecular weight polymers. This is evident in the dynamic shear modulus plot used to assign a performance grade. Figure 4.35 shows the dynamic shear modulus as a function of temperature. At all polymer contents, the SHRP PG of the blends was the same for PB104 and PB152. PB152 had slightly better high temperature properties in each case. However, the ability to mix PB104 at a lower temperature, although not done in this study, could help preserve the low temperature properties of the base asphalt by reducing oxidation. Table 4.18 details the SHRP high temperature PG of the AC-5/EVA samples.

Table 4.18 - High temperature SHRP PG of AC-5/EVA blends

EVA Content (w/w)	SHRP PG (PB104)	SHRP PG (PB152)
0%	64	64
1.5%	64	64
3%	70	70
5%	76	76
7%	82	82

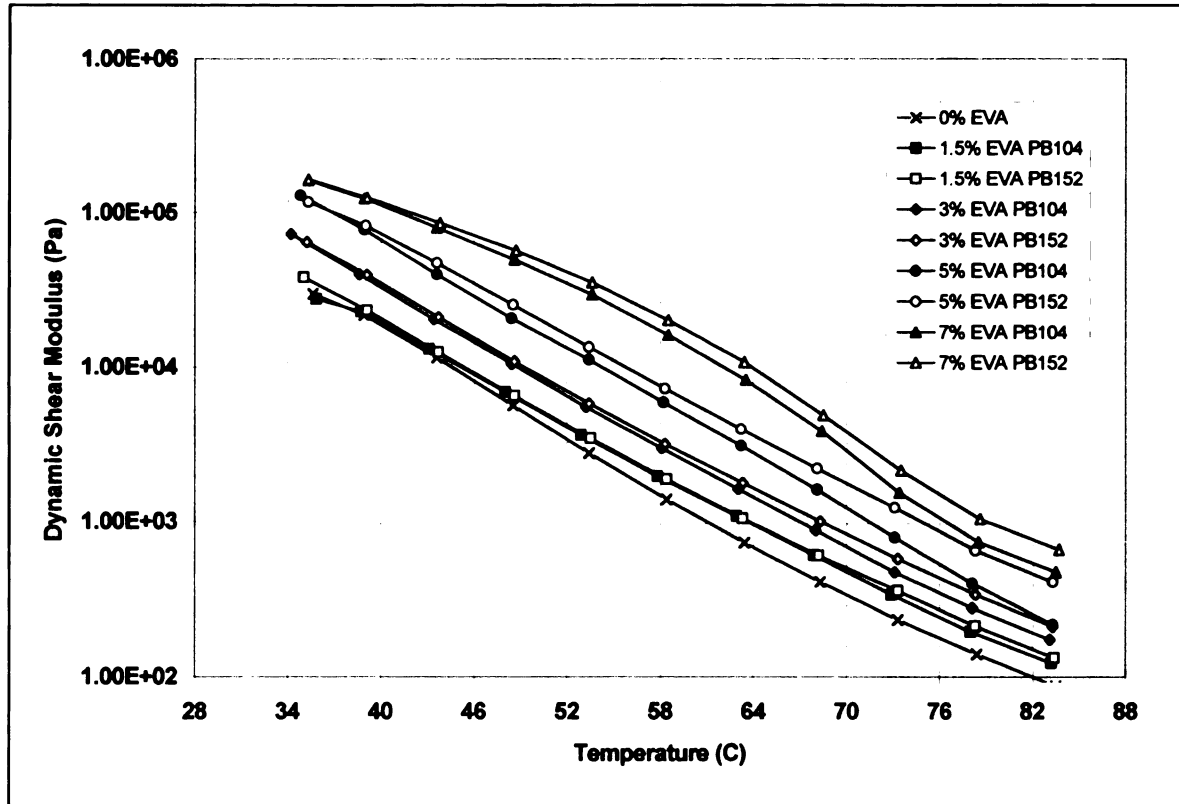


Figure 4.35 - Dynamic shear modulus of AC-5/EVA blends

4.4.3 - Rotational Viscometry

The viscosity of AC-5/EVA PB152 and AC-5/EVA PB104 blends was measured at various polymer contents and temperatures using a Brookfield viscometer. Figure 4.36 is the collected data for some AC-5/EVA polymer modified binder samples. All EVA modified AC-5 samples met the SHRP specification (maximum 3 Pa·s) at 135°C and exhibited a linear fit on a semi-log plot. The viscosity of the binders was a strong function of polymer molecular weight. This is expected because polymer viscosity increases with molecular weight. This effect was most dramatic with larger polymer contents. Overall, the viscosity of the modified binders was relatively low compared to

the other polymers studied. Even a high content of 7% (w/w) easily met the SHRP specification.

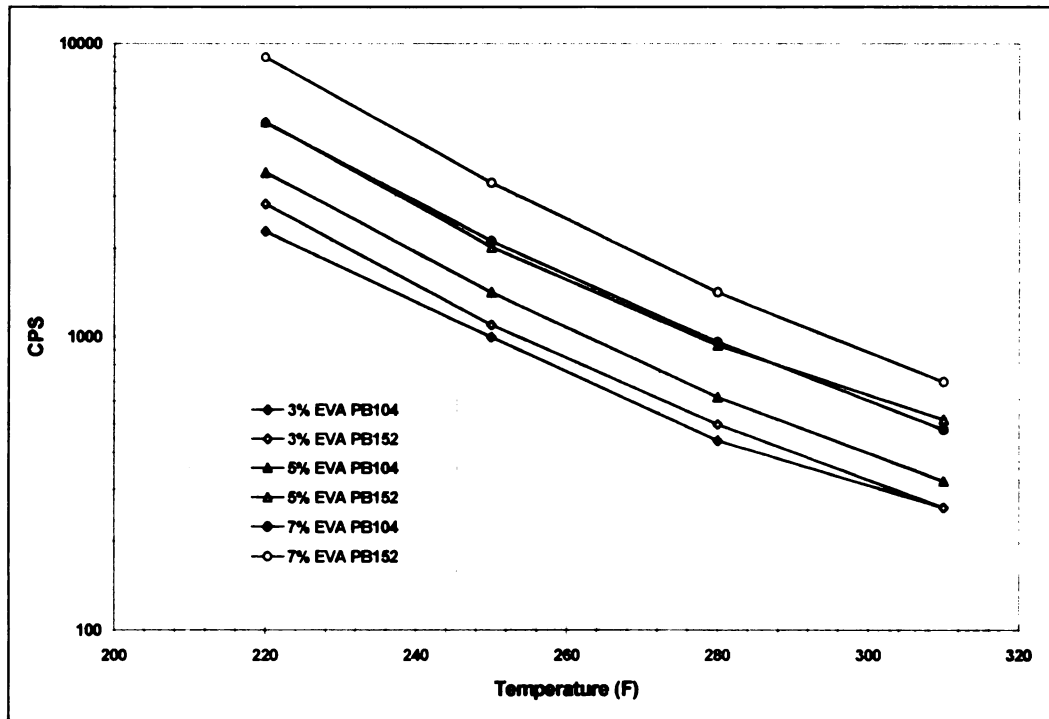


Figure 4.36 - Viscosity of AC-5/EVA binders

4.4.4 - Fourier Transform Infrared Spectroscopy

Fourier-Transform Infrared Spectroscopy (FTIR) has been used to examine AC-5/EVA. It has been determined that there are several defining wavenumbers of interest including 965, 1245, 1375, 1600, and 1740 cm^{-1} . These wavenumbers correspond to the characteristic functional groups in the blends. Ratios of the absorbance intensities of these functional groups can yield useful information when fingerprinting different asphalt grades and binders. The IR characteristic absorption peak for aromatic C-C in asphalt is at wavelength of 1600 cm^{-1} . The IR characteristic absorption peaks for EVA are at

wavelengths of 1740 and 1240 cm^{-1} , which are due to the C=O and C-O bond, respectively. The absolute ratio of the 1740 or 1240 cm^{-1} absorption band to the 1600 cm^{-1} band of an EVA modified asphalt can be used as fingerprinting characteristic tools to determine the polymer content in the binder. Figure 4.37 shows the calibration curves for AC-5/EVA PB104. The calibration curve is valid only for the given asphalt/polymer blend. The system shows a good linear fit for both the 1740/1600 and 1240/1600 ratios. PB152 showed similar results with R^2 values for the 1740/1600 and the 1240/1600 curves of 0.998 and 1.00 respectively. FTIR is a useful tool for determining the polymer content of EVA blends.

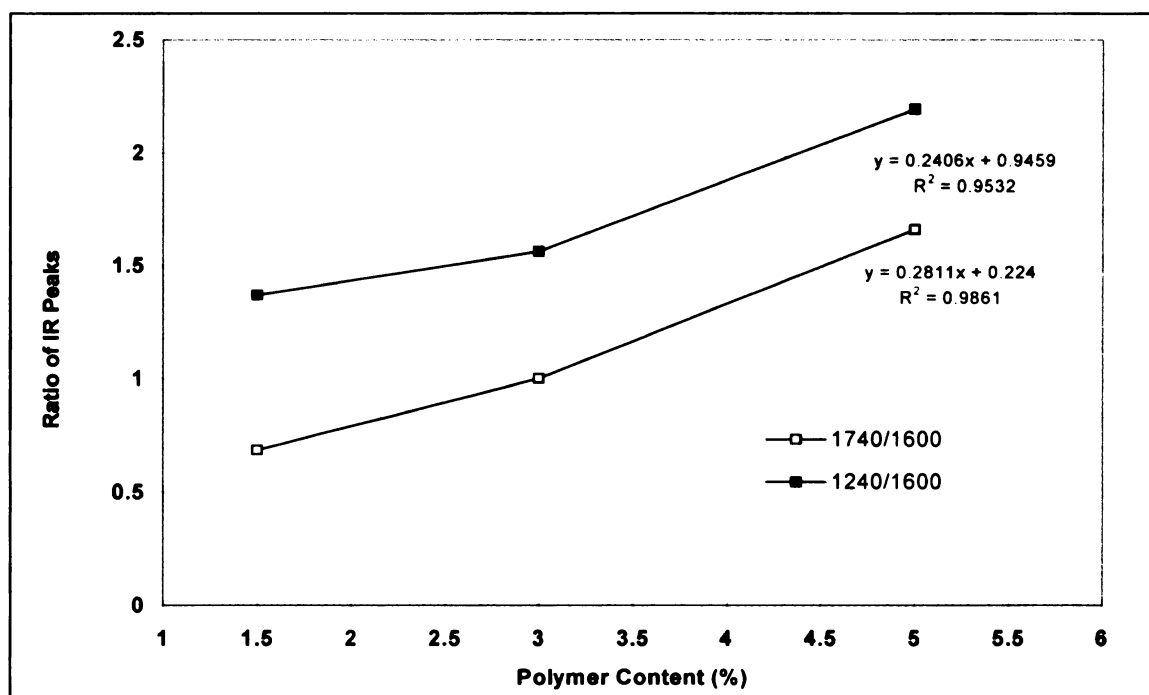


Figure 4.38 - FTIR calibration curves for AC-5/EVA (PB104) blends

4.4.5 - Thermal Mechanical Analysis

The softening points of unmodified and EVA modified AC-5 binders were measured using Thermal Mechanical Analysis. Table 4.19 details the melt temperature and softening point of the AC-5/EVA blends. There is minimal increase with addition of 1.5% (w/w) polymer. At contents of 1.5% (w/w) to 7% (w/w), the increase in the softening point and melting point is relatively linear with an approximate increase of 5°C per percent polymer. This indicates that at contents of 1.5% (w/w) and less, the polymer is too dispersed to affect the softening point. At contents greater than 1.5% (w/w), the polymer acts as a dispersed thermoplastic with the particles becoming more concentrated with increasing molecular weight. TMA data indicates that there is not an internal network forming. If that were the case, a sharp increase in softening point would be seen at the critical content for network formation. When 7% (w/w) EVA was mixed with AC-5, there was an increase of more than 25°C in softening point for both EVA polymers. The increase of the softening point is the largest among the modifiers which were used in this project. This indicates good rutting resistance. There was minimal effect of polymer molecular weight on either softening point or melting point.

Table 4.19 - Melt temperature and softening point of AC-5/EVA blends.

EVA Content	Softening Point (°C) PB104	Softening Point (°C) PB152	Melting Point (°C) PB104	Melting Point (°C) PB152
0% (w/w)	28	28	36	36
1.5% (w/w)	27	30	37	38
3% (w/w)	32	34	44	46
5% (w/w)	45	44	56	57
7% (w/w)	52	56	63	68

Chapter Five

Modeling

The task of modeling the interaction between polymer and asphalt to predict and explain the properties of the blend is daunting. The difficulty stems from two problems encountered in the use of asphalt. The first is that the asphalt is black, making visual inspections of the polymer and asphalt phases difficult. This is partially overcome by the use of fluorescence and scanning electron microscopy. Additional insights can be gained by examining the effect of polymer content on rheological properties. These techniques are used to develop phenomenological models of how the polymer and binder interact. These models are presented in Section 5.1. The second problem is the complex chemical makeup of the asphalt. It is not known how the different asphalt chemical properties affect physical properties in neat asphalt. Without completing this first step, any predictions of how these chemical properties affect the blend physical properties would be at best speculation. An attempt at correlation modeling with neat asphalt is presented in Section 5.2.

5.1 - Phenomenological Modeling

Phenomenological models are presented for SBR and crumb rubber that explain the experimental results and are consistent with the visual evidence gathered by advanced microscopy. These models are not intended for use as quantitative predictive models, rather they are qualitative models which present a theory of how the polymer improves

the blend performance. At best, they are a hypothesis. They should be considered a starting point for further research, rather than a conclusion of this research.

5.1.1 - Styrene-Butadiene Rubber

SBR has been shown to improve the high temperature rheological properties of asphalt binders. The purpose of this section is to investigate and explain the rheological behavior of SBR modified binders. The behavior of SBR modified binders appears to be the result of two independent phenomena: percolation theory and network formation. This is suggested by the rheological properties and supported visually using fluorescence microscopy.

The storage and loss moduli of the SBR modified binders were measured using DSR. Figure 5.1 shows the important rheological properties of the binders at a number of temperatures for various SBR contents. A large dynamic shear modulus is desired for rutting resistance. This can be accomplished by either increasing the total complex modulus (G^*) or increasing the elastic nature of the binder (lowering δ). The addition of SBR reduces the phase angle. This indicates that the binder is becoming more elastic. SBR is much more elastic than asphalt at 60°C. The linear nature of the phase angle reduction suggests that the phase angle can be modeled by a simple parallel model of the form $\delta_{blend} = V_{SBR} \cdot \delta_{SBR} + (1 - V_{SBR}) \cdot \delta_{asphalt}$. The relationship between complex modulus and SBR content is much more complicated. There is virtually no increase at a content of 1% (w/w). At this concentration the SBR acts as a dispersed polymer. The polymer concentration is small enough that it does not significantly affect the rheological properties. At contents greater than 3% (w/w), a continuous network forms throughout

the binder. The result is a relatively linear increase in the complex modulus with increasing SBR content. The network acts as a support structure for the asphalt, resisting deformation. It serves a similar purpose to the reinforcing fibers in a fiber-matrix composite.

There is a sharp increase in all of the modulus values at 2% (w/w). This is likely due to a phenomenon called percolation theory. In simple terms, percolation theory states that there exists a critical content at which a sharp peak is seen in the properties. At this critical content, the dispersed phase, in this case SBR, changes from dispersed behavior to network behavior without actually forming a network. The SBR is still in a dispersed state, however it is present in sufficient quantity that it behaves similar to a network. At contents higher than the critical content, this balance is disrupted and the system acts like a dispersed system with the corresponding drop in modulus values.

This behavior has not been reported in the literature for polymer modified binders. However, similar behavior is seen in other systems. One system of note is a water, oil, surfactant microemulsion. The microemulsion consists of spherical droplets of water surrounded by a monomolecular layer of surfactant dispersed in the continuous oil phase. The microemulsions have a macroscopic conductivity because of the ionic surfactants. At a critical content, the conductivity increases sharply. The conductivity rise is due to the fact that charge carriers are able to move along connected paths in the microemulsion. In the SBR modified binders, the modulus values rise because the SBR has similarly connected paths that allow for support of the binder. This effect is minimized as temperature is increased because the asphalt is practically a liquid and there is nothing for the SBR to support.

Laser scanning microscopy (LSM) was used to investigate the distribution of polymer in the asphalt binder. A Zeiss 10 high performance light microscope operating in fluorescence mode was used in this study. The microscope uses an argon laser emitting 488 nm (blue) light. The microscope operates in scanning mode, rastering the laser back and forth across the surface of the sample. The polymer absorbs the laser light and re-emits it as orange-red length with a wavelength of >520 nm. A filter is used to remove the reflected 488 nm light leaving only the fluorescence light. Features as small as $0.1\text{ }\mu\text{m}$ may be resolved using the confocal LSM.

The progression from dispersed polymer to global network can be visually seen by using a Laser Scanning Confocal Microscope (LSM). In the LSM, the sample is exposed to a blue laser. The polymer fluoresces allowing it to be seen against the dark asphalt background. Figure 5.2 shows the LSM micrographs of 1% (w/w), 3% (w/w), and 5% (w/w) SBR binders. The micrographs have been contrast reversed so that the polymer appears dark while the asphalt appears light.

SBR forms a polymer network phase inside the asphalt. At very low polymer concentrations, the SBR acts as a dispersed polymer and does not significantly affect properties. At 3% (w/w) SBR, a global network has not formed. This supports the percolation theory for the sharp increase at 2% (w/w). Also, the SBR has changed shape from spherical to fibril, which may account for the reduction in modulus values. At higher concentrations, the global network begins to form. The density of this global network increases with increasing polymer content. This causes a gradual increase in the rheological properties consistent with normal network formation phenomena. Figure 5.3 shows a pictorial representation of this phenomenological model.

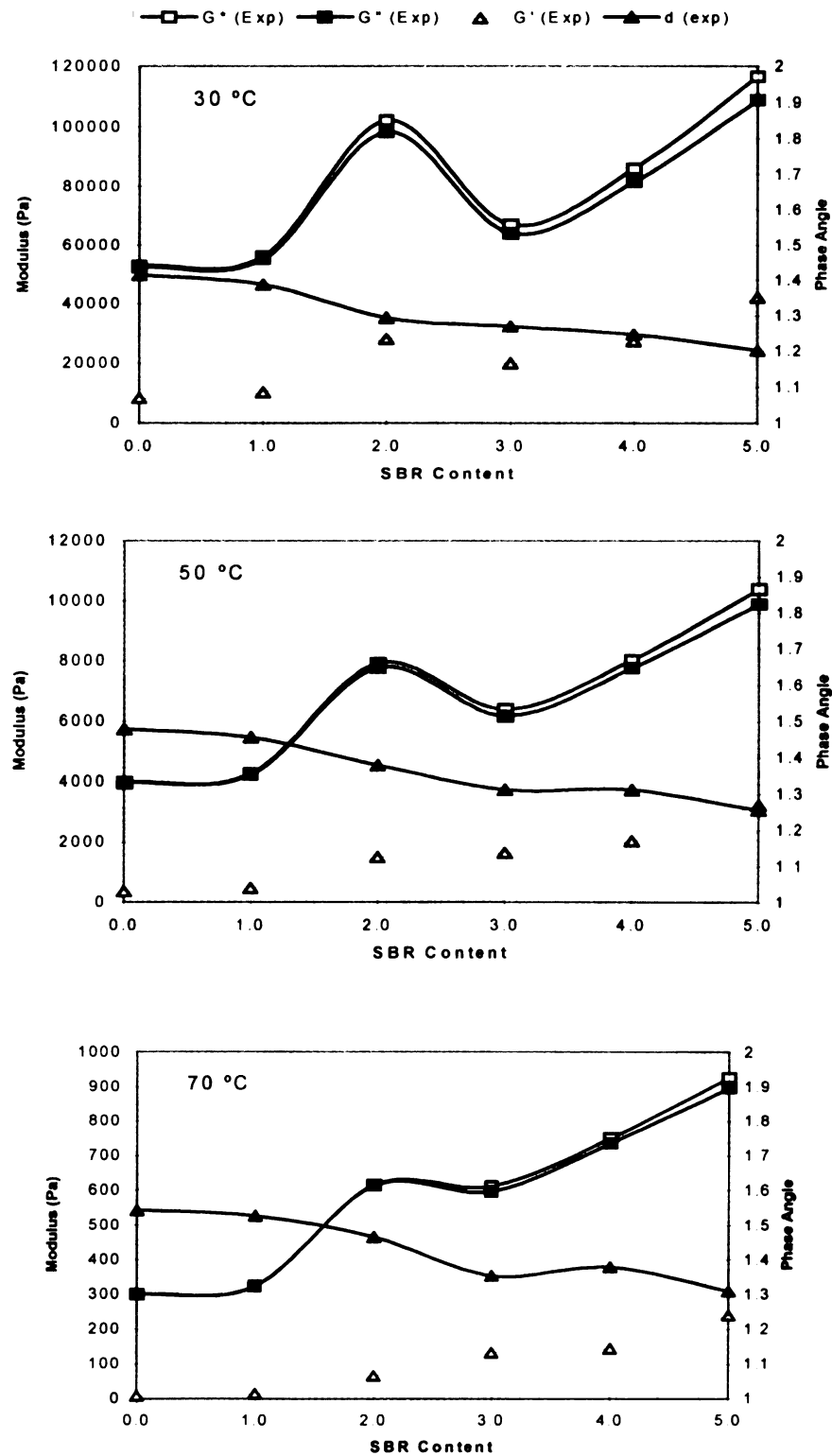
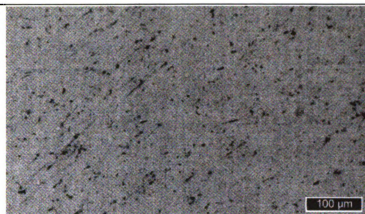
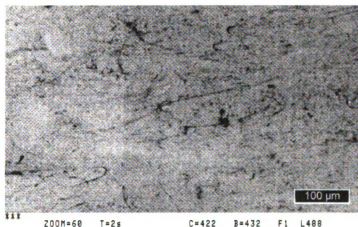


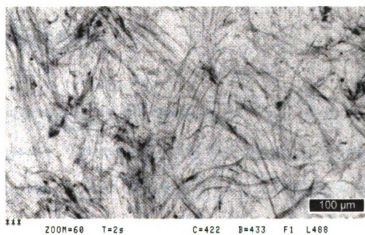
Figure 5.1 - Rheological properties of AC-5/SBR blends



(a) 1% (w/w)



(b) 3% (w/w)



(c) 5% (w/w)

Figure 5.2 - Laser Scanning Microscope micrographs of SBR modified binders

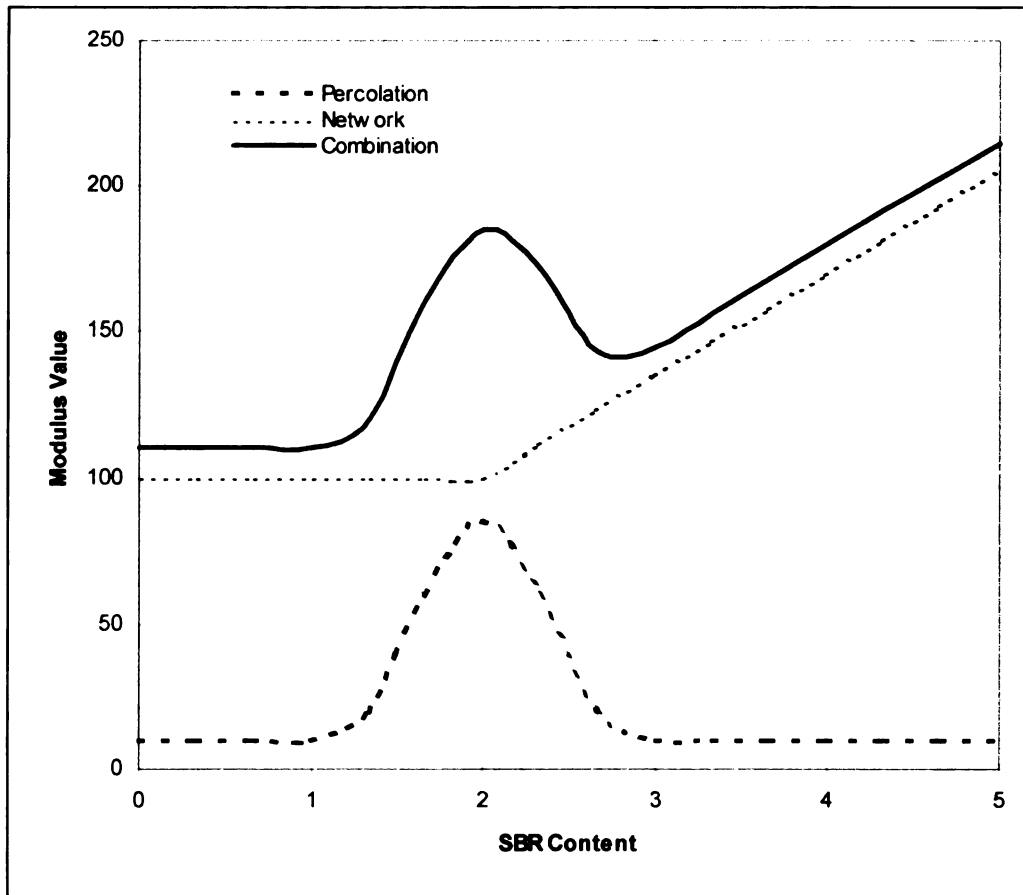


Figure 5.3 - Pictorial representation of SBR behavior model

5.1.2 - Recycled Crumb Rubber

The rheological properties of recycled crumb rubber at various temperatures are presented in Figure 5.4. The modulus values are basically linear when plotted against rubber volume fraction. A rubber density of 60 lb./ft. and an asphalt density of 81 lb./ft. were used to determine volume fraction. Volume fraction was chosen because it is the generally accepted method for two-phase mixing rules. Recycled crumb rubber acts as a

simple dispersed, two-phase system. The rheological properties follow a simple mixing rule of the form:

$$G_M = G_R V_R + G_A (1 - V_R)$$

G_M = mixture property

G_R = rubber property

G_A = asphalt property

V_R = volume fraction rubber

It is likely that G_A is a function of the rubber volume fraction. This is because the rubber tends to absorb some of the oils in the asphalt, increasing the stiffness. This accounts for the deviations from linearity seen in the modulus values, especially at higher temperatures.

Scanning electron micrographs validate this theory. It is easy to see in Figure 5.5 that the rubber particles are simply acting as a dispersed particle in the asphalt phase. This lends credibility to the use of a dispersed two-phase mixing rule.

5.2 - Correlation Based Modeling

A great deal of work has been done in an attempt to relate the fundamental chemical properties of asphalt to its physical and rheological properties. The majority of the work has concentrated on correlating molecular size distributions with properties such as penetration, viscosity temperature susceptibility, and penetration viscosity number. While there have been some minor statistical successes, there has been no consistent results.

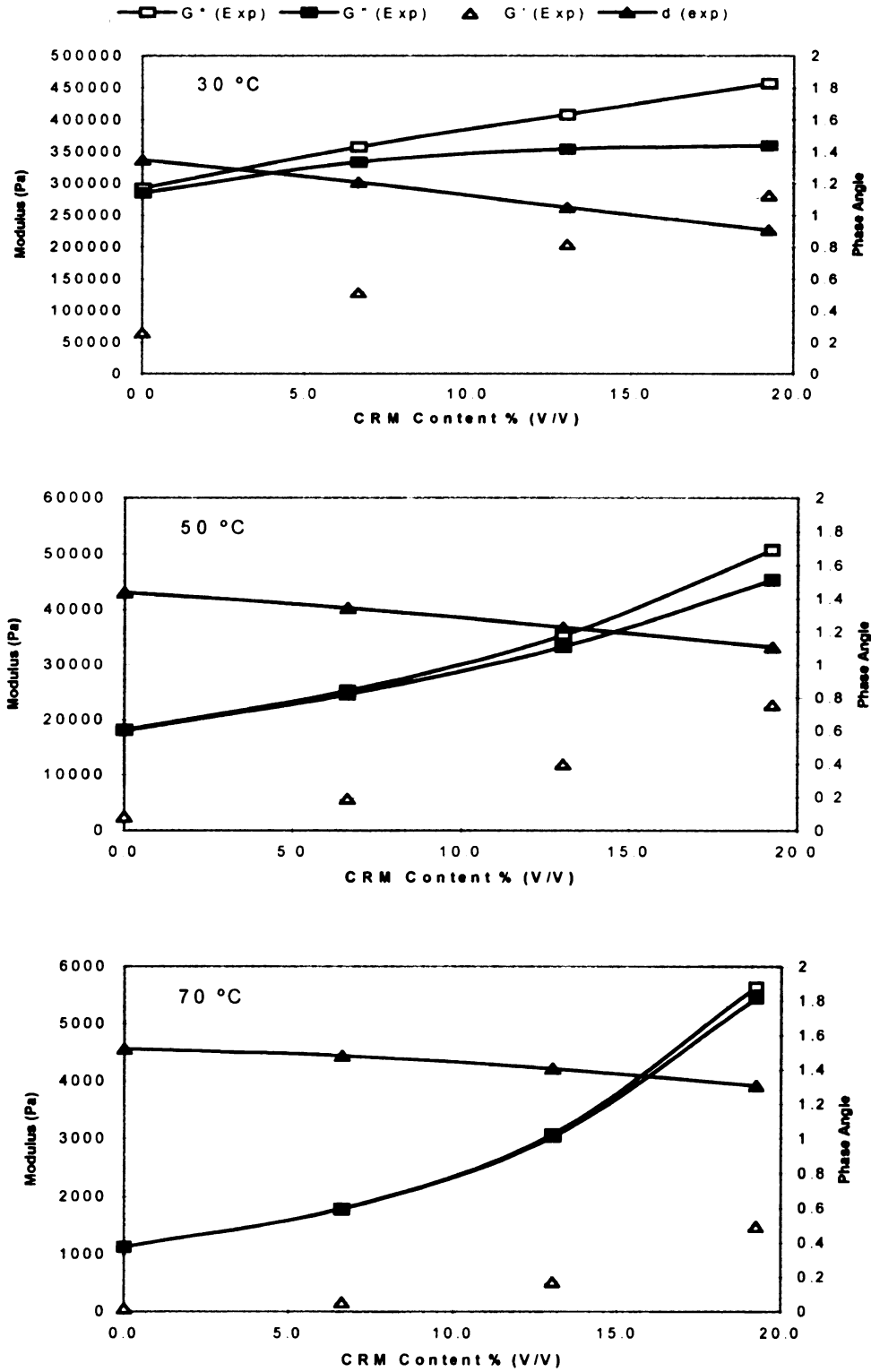


Figure 5.4 - Rheological properties of AC-10/CRM blends



Figure 5.5 - Scanning electron micrograph of 20% (w/w) CRM modified AC-10

The most common method of empirical modeling involves relating physical properties to the molecular size distribution determined using HPGPC³⁸⁻⁴⁸. The molecular size distributions (MSD) are generally divided into arbitrary slices and the percentage of molecules in certain slices is correlated to different physical properties. This is a very simplistic view of asphalt chemistry. Some of the papers reported success in correlating a few properties, but the results tend to be random and are likely a coincidence.

Price and Burati chose to partition the GPC distribution into equal time tenths.³⁸ They correlated the GPC distribution of the asphalt binder to properties of the asphalt pavement. This is one of the few studies that used modified binders. They showed good correlation for specific gravity, indirect tensile strength, and resilient modulus. They showed no correlation for penetration, Marshall stability, Marshall flow, tensile strength at extreme temperatures, or resilient modulus at extreme temperatures. There are a number of problems with this study. The correlations were only good because they incorporated a type factor based on the modifier used which limits its usefulness. The results are based on a modification of a single AC-20. As GPC distributions as well as polymer/asphalt interactions are highly dependent on asphalt source this was a poor choice. Also, the use of THF as the GPC solvent may not be a good choice for SBR and other rubbers.

Bishara, et al had a slightly better study with slightly worse results.³⁹ They studied 20 different virgin asphalts from various sources. The GPC distributions were divided into fifths. They found that MSD correlates well to viscosity for asphalts from the same source, but that it is not applicable to asphalts from different sources. In a later

paper, they also looked at Corbett fractions in addition to MSD.⁴⁹ They found that by including the Corbett fractions the correlations were improved. However, they offered no theoretical basis for including the Corbett fractions.

Garrick looked at the problem backwards.⁴¹ He attempted to predict the MSD from measured physical properties. He created his model from 23 different asphalts from six suppliers. He tested his model using 11 different asphalts. He concluded that although he had limited success, the relationship between MSD and physical properties is dependent on asphalt rheological type.

Jennings, et al. attempted to correlate MSD with pavement rutting and cracking potentials. They found some average correlation to rutting however the study was not without flaws. The major flaw is that binder properties simply do not have as great of an effect on pavement performance, as the authors think. Another minor flaw is that the low molecular size cutoff was determined arbitrarily, which could make the results look better than they are.

The large majority of other papers on this subject had similar flaws. The major flaw with all of these papers is the arbitrary division of the MSD into a number of pieces. In Gaussian distributions, there are only two independent variables: average and standard deviation. A division of a Gaussian distribution into ten partitions still has only two independent variables. Typical asphalt MSD are a little more complicated than a Gaussian distribution, however it is unlikely that there are ten independent variables in an asphalt MSD. An orthogonality analysis on a typical asphalt MSD shows that only three of the sections are of large importance, one is of medium importance, and the rest are almost completely described by the first four³⁸. An attempt was made to correlate MSD

to physical properties without using more independent variables than exist in an MSD. Weight average molecular weight (Mw) and number average molecular weight (Mn) were correlated to a number of properties. In addition, asphaltene content was correlated to those properties as well. Some simple combinations of the above independent variables were also correlated.

5.2.1 - Materials Tested

This study used 19 different asphalts obtained from the Michigan Department of Transportation (MDOT). The samples are from eight different sources and range in viscosity from AC-2.5 to AC-20. The samples had asphaltene contents ranging between 11.8% and 20.4%. The molecular weight range was 586 to 805 for Mn and 1518 to 2284 for Mw.

5.2.2 - Experiments

The majority of the tests were conducted by the MDOT Materials and Technology laboratory. The following properties were measured by MDOT:

- Penetration (4°C)
- Penetration (25°C)
- Specific Gravity
- Flash Point
- Ductility
- Absolute Viscosity (140°F)
- Kinematic Viscosity (140°F, 225°F, 250°F, 275°F)

- TFOT and PAV aging
- Aged Penetration (4°C)
- Aged Penetration (25°C)
- Aged Absolute Viscosity (140°F)

All chemical tests and some physical tests were conducted at Michigan State University. These tests include:

- Fourier Transform Infrared Spectroscopy
- Gel Permeation Chromatography
- Asphaltene/Resin Compatibility
- Asphaltene Extraction
- Softening Point/Melting Point by TMA
- Rheological Properties

A number of standard asphalt indexes used to predict temperature susceptibility were determined. These include:

- Penetration Viscosity Number (PVN) - lower PVN indicates greater temperature susceptibility
- Viscosity Temperature Susceptibility (VTS) - larger VTS indicates greater temperature susceptibility
- Penetration Ratio (PR) - lower PR indicates greater temperature susceptibility

Two other indexes that are used to predict aging effects were investigated. These are:

- Aging Index - measure of the change in viscosity and penetration due to aging. Higher numbers indicate less aging effects.
- Viscosity Ratio - measure of the change in viscosity due to aging. Higher numbers indicate greater aging.

5.2.3 - One Variable Correlations

The first attempt at correlation was to plot all of the important properties against Mw, Mn, and asphaltene fraction. Asphaltene/Resin compatibility was not used because the variation in the compatibility index values is very small, likely due to the subjective nature of the test. The following pages include the plots of viscosity, penetration, PVN, VTS, aging index, viscosity ratio, penetration ratio, softening point, and melting point plotted against the three variables. It is very clear that there are no direct correlations between any of the pairs of variables. The best correlation has an R^2 value of only 0.66

5.2.4 - Multivariable Correlation

It may be possible to correlate physical properties to a combination of chemical properties. Molecular weight, asphaltene content, polarity, and asphaltene/resin compatibility all seem to play an important role in determining the physical properties of asphalt. A simple visual examination of the raw data generated in this section shows clearly that asphaltene content alone cannot explain the variation in properties with respect to molecular weight. The compatibility index used in this study is problematic. Because the tests require determination of the initiation of flocculation in a dark solution it is dependent on the experimenter's judgment of when flocculation begins. A new procedure, utilizing light scattering or some other technique for determining the presence of solids in the solution, would make the compatibility measurement much more accurate. An increase in accuracy is required before compatibility can be a useful measurement tool. A possible measure of polarity is to look at ratio's of polar Corbett fractions to non-

polar Corbett fractions. This is a time consuming process which makes rapid classification of asphalt impossible. While a multivariable correlation may give good statistical results, the reality is that asphalt is so complex that a few simple measure will probably not be able to fully describe the wide range of physical and thermodynamic properties. Performance based binder specifications, however flawed, are infinitely more practical than chemical based specifications.

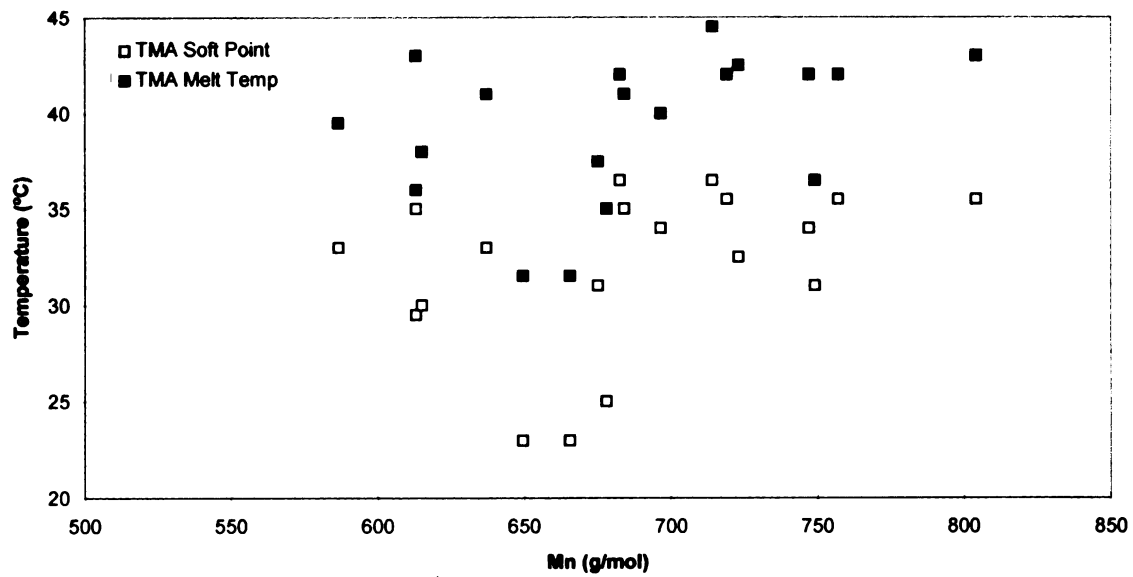


Figure 5.6 - Softening and melt temperature versus Mn.

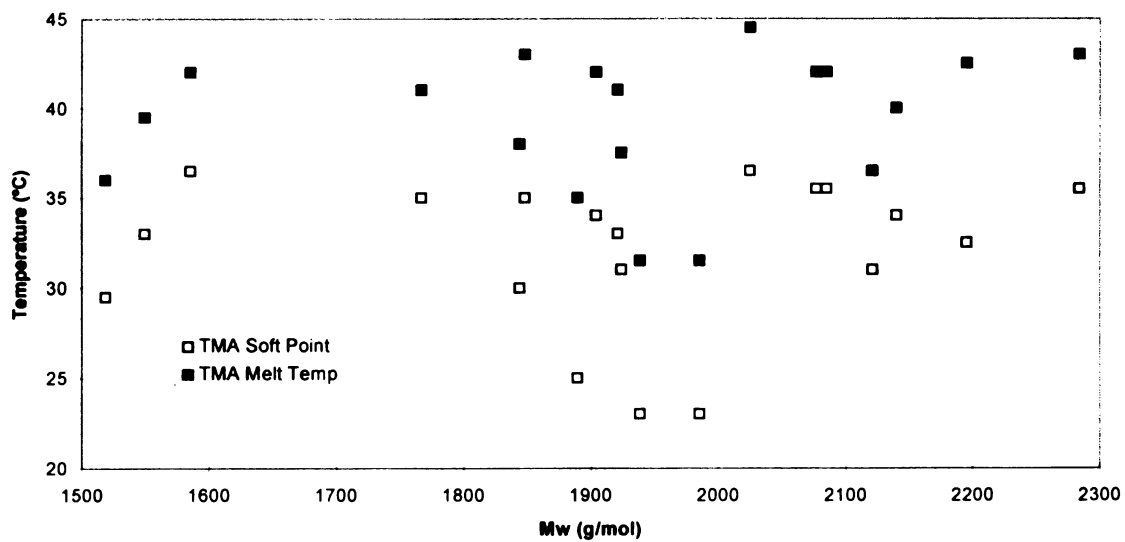


Figure 5.7 - Softening and melt temperature versus Mw.

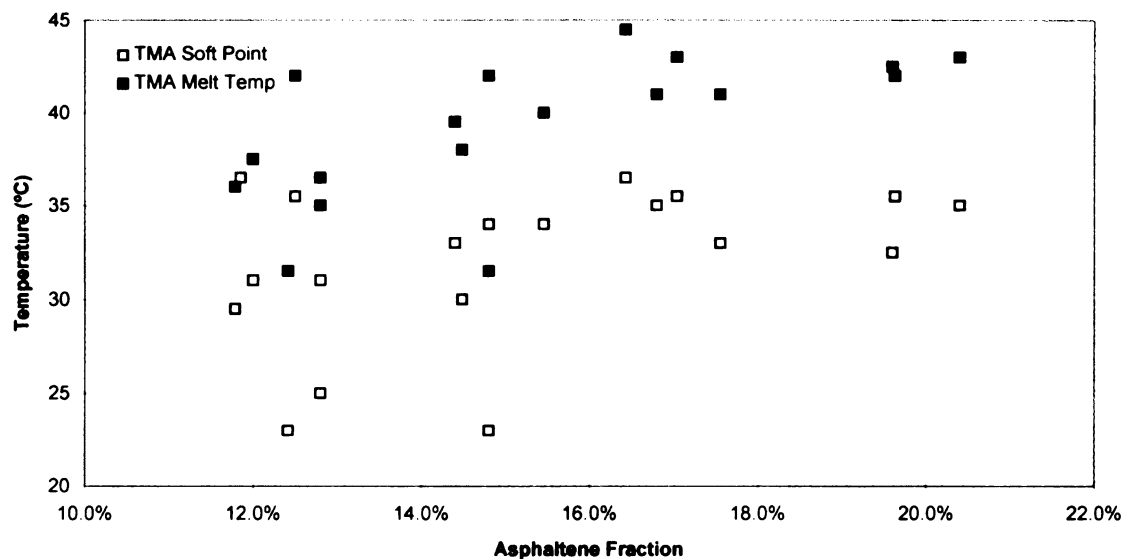


Figure 5.8 - Softening and melt temperature versus asphaltene fraction.

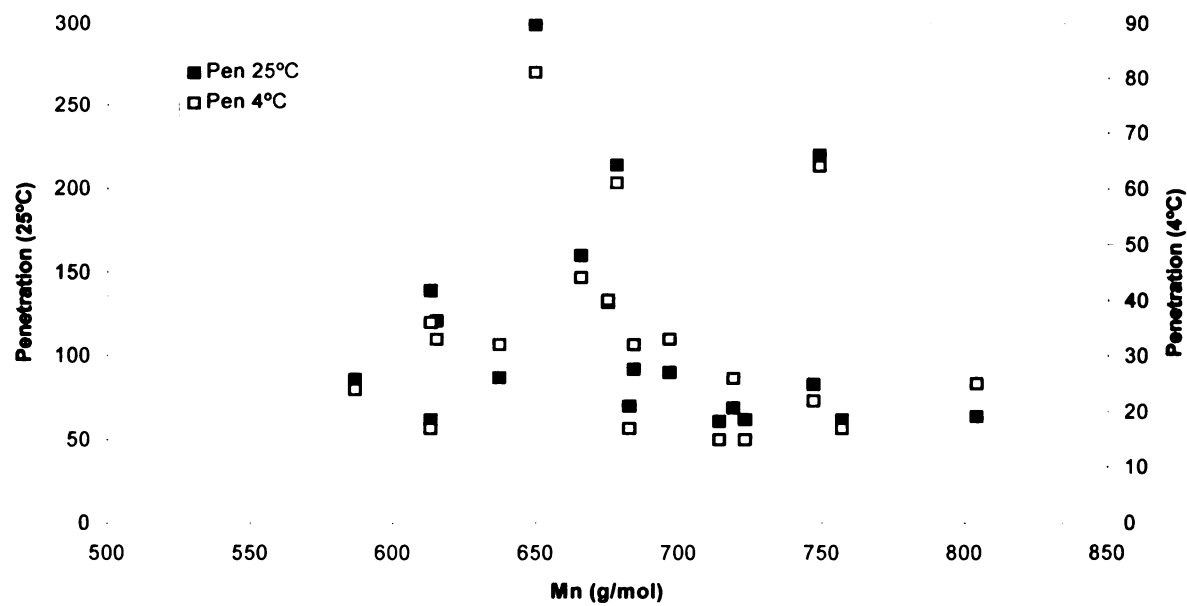


Figure 5.9 – Penetration versus Mn.

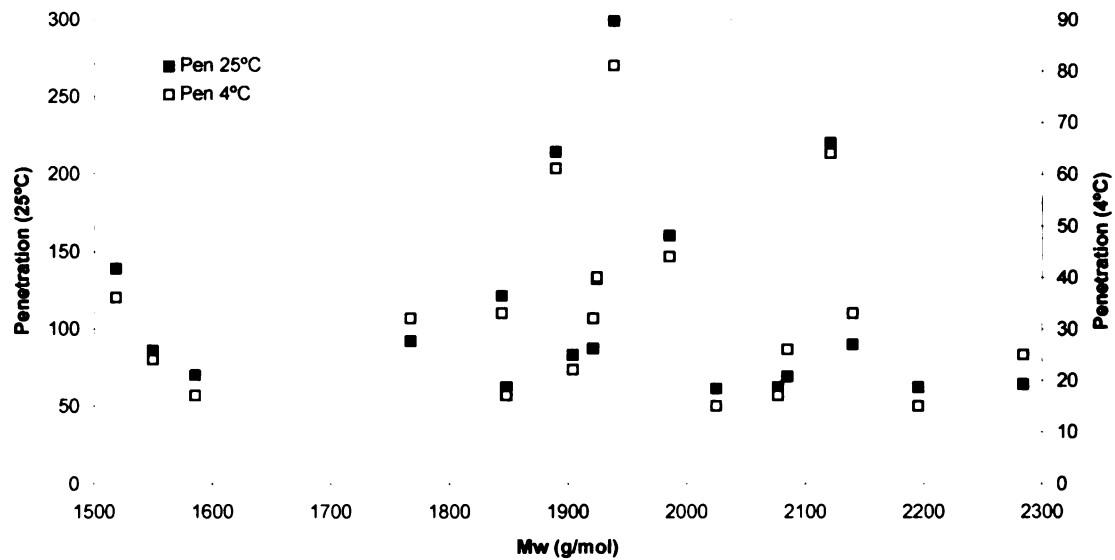


Figure 5.10 – Penetration versus Mw.

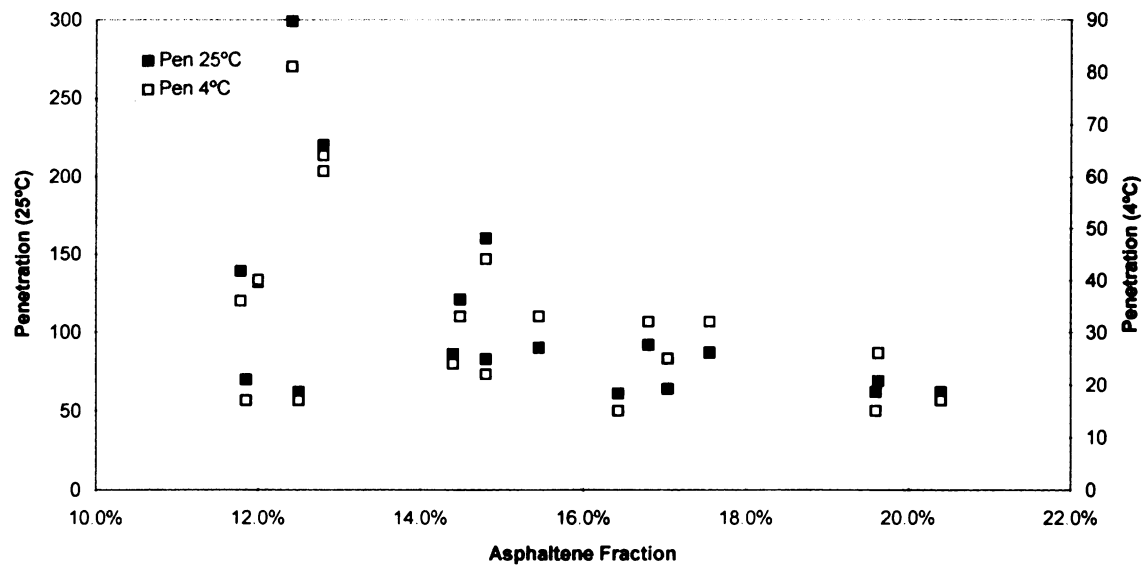


Figure 5.11 – Penetration versus asphaltene fraction.

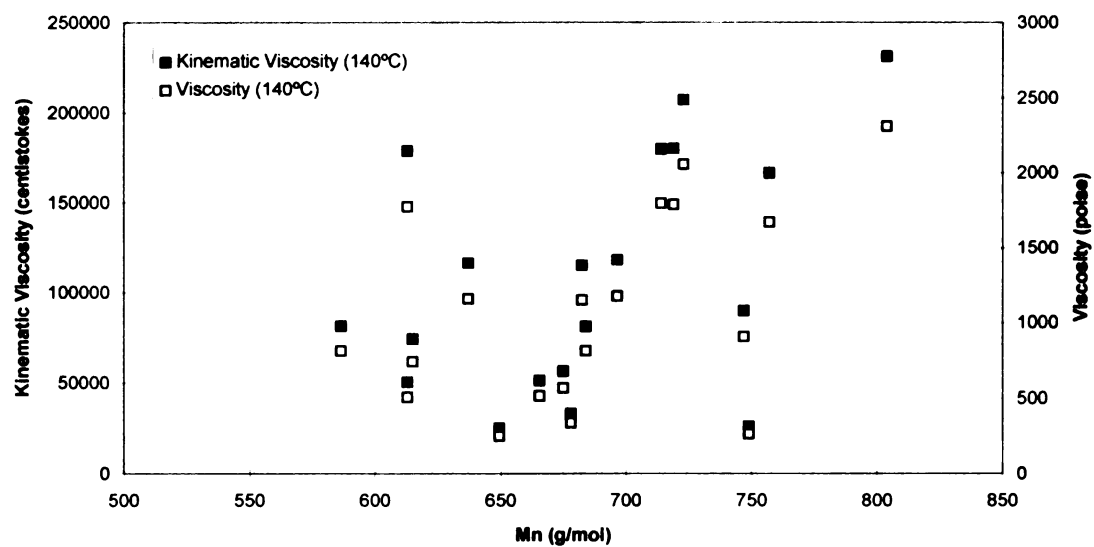


Figure 5.12 – Viscosity versus Mn.

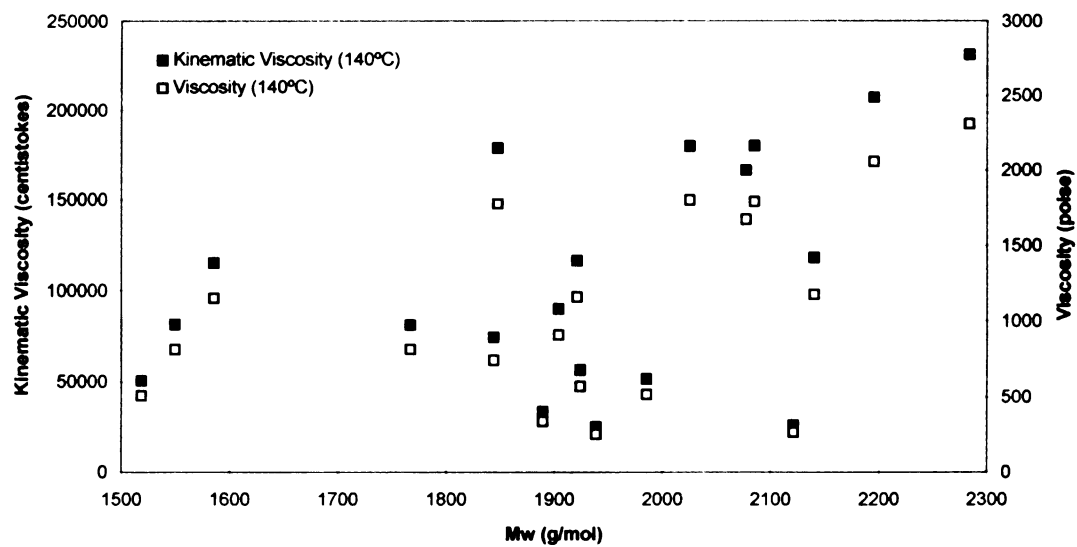


Figure 5.13 – Viscosity versus Mw.

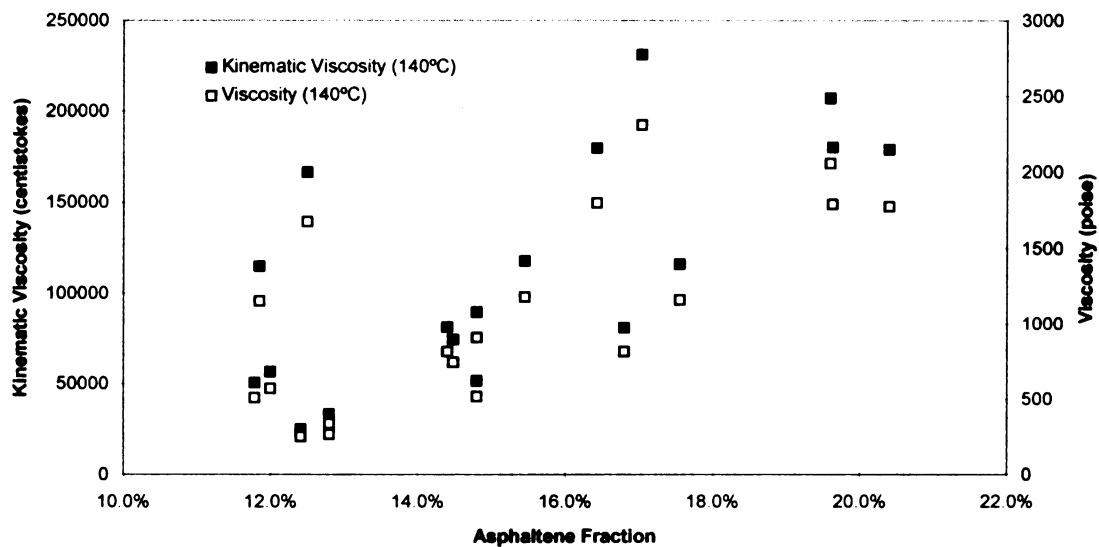


Figure 5.14 – Viscosity versus asphaltene fraction.

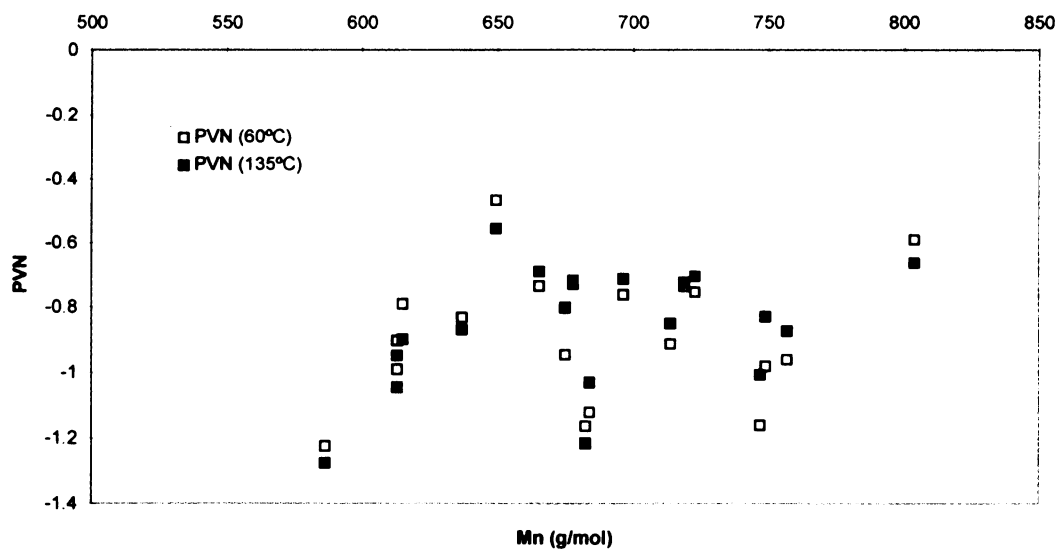


Figure 5.15 – PVN versus Mn.

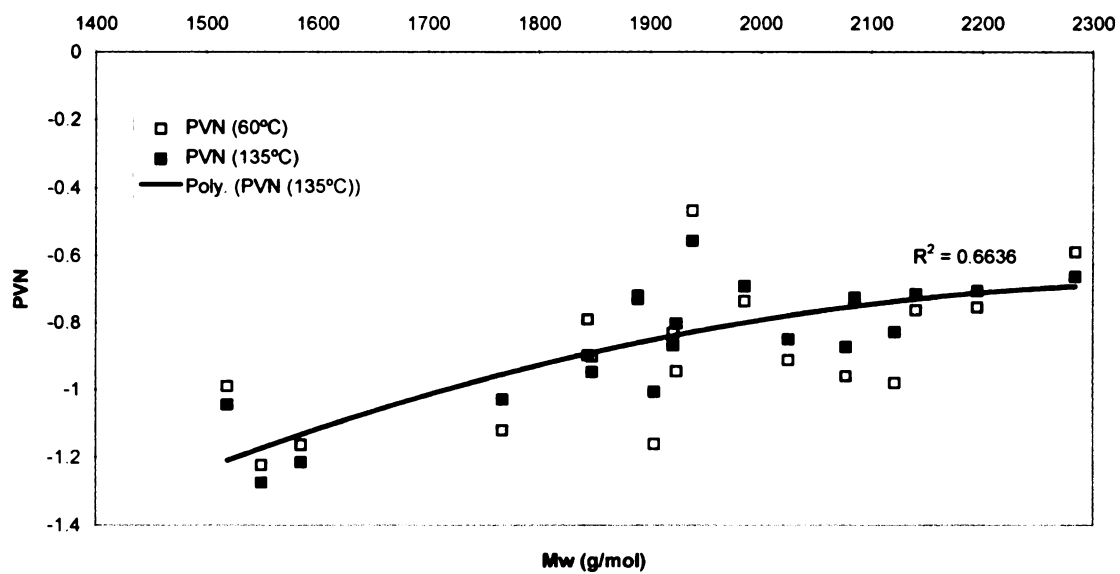


Figure 5.16 – PVN versus M_w .

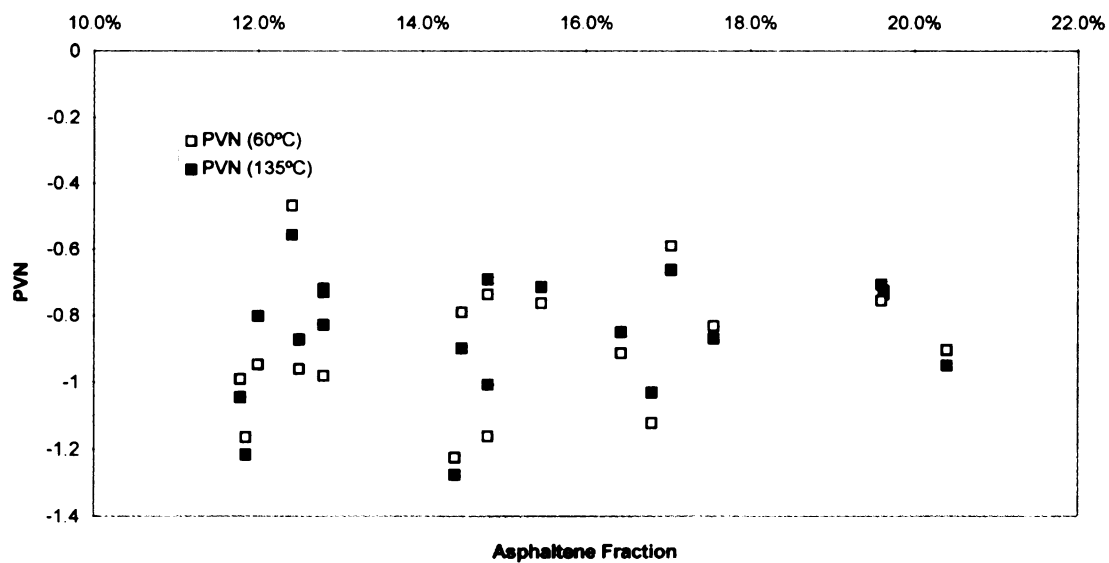


Figure 5.17 – PVN versus asphaltene fraction.

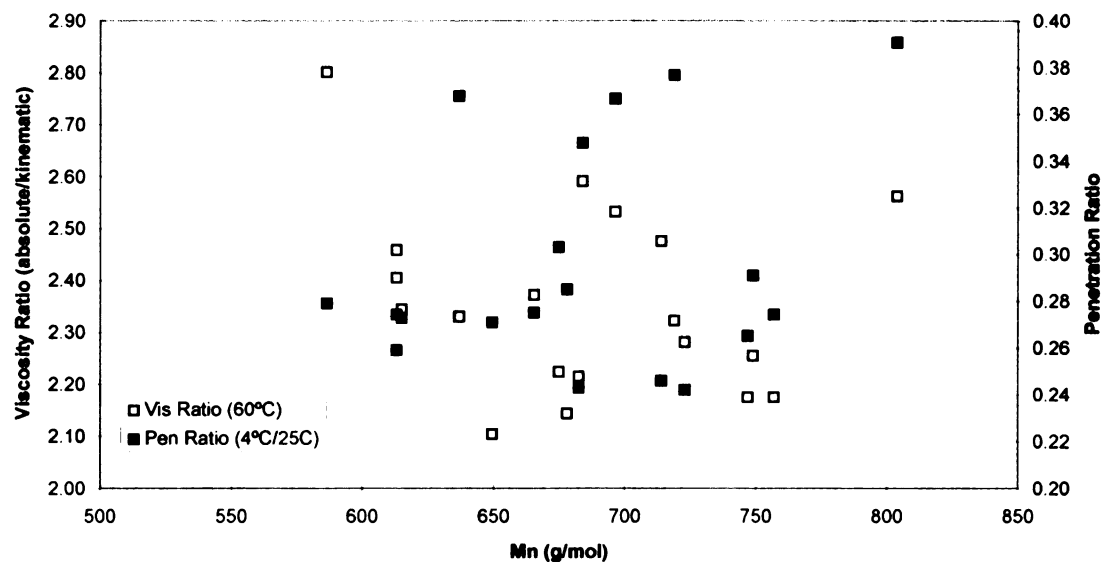


Figure 5.18 – Viscosity and penetration ratios versus M_n .

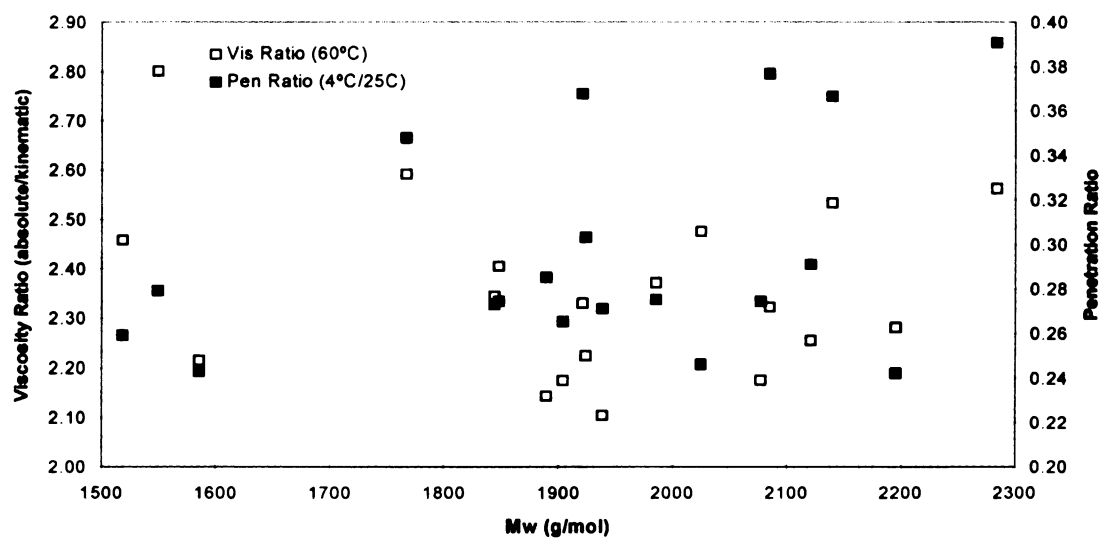


Figure 5.19 – Viscosity and penetration ratios versus M_w .

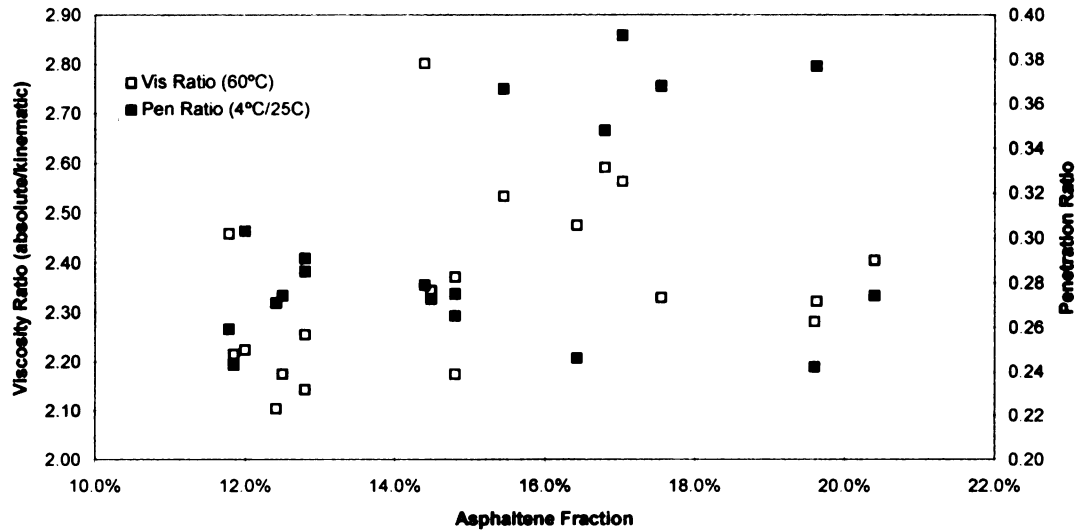


Figure 5.20 – Viscosity and penetration ratios versus asphaltene fraction.

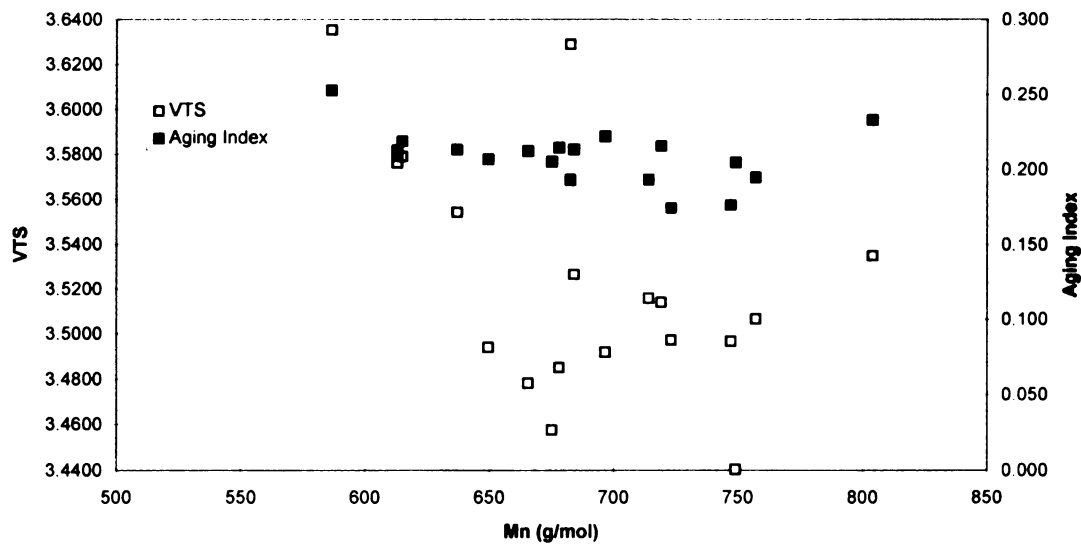


Figure 5.21 – VTS and aging index versus Mn.

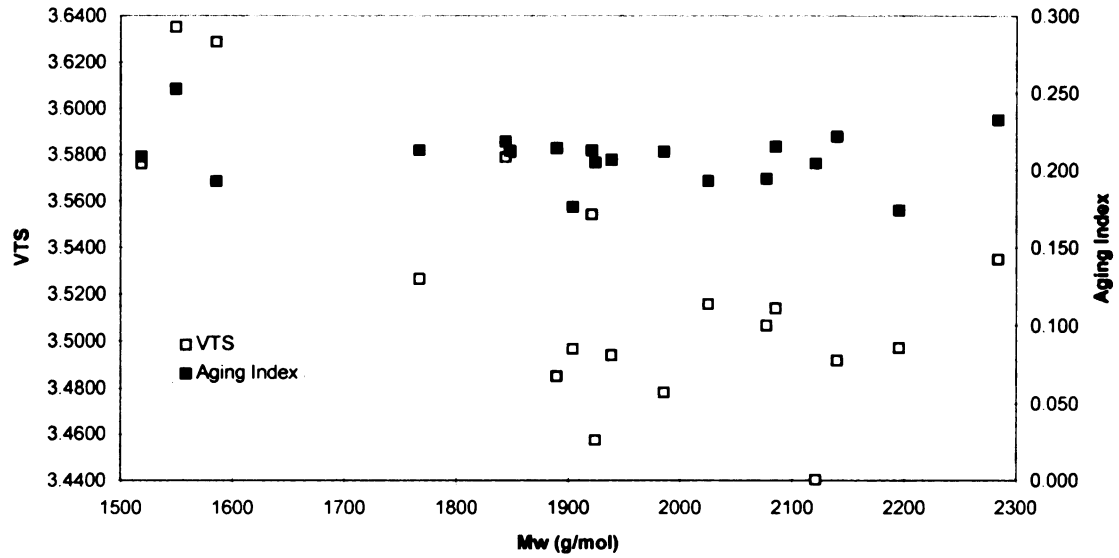


Figure 5.22 – VTS and aging index versus M_w .

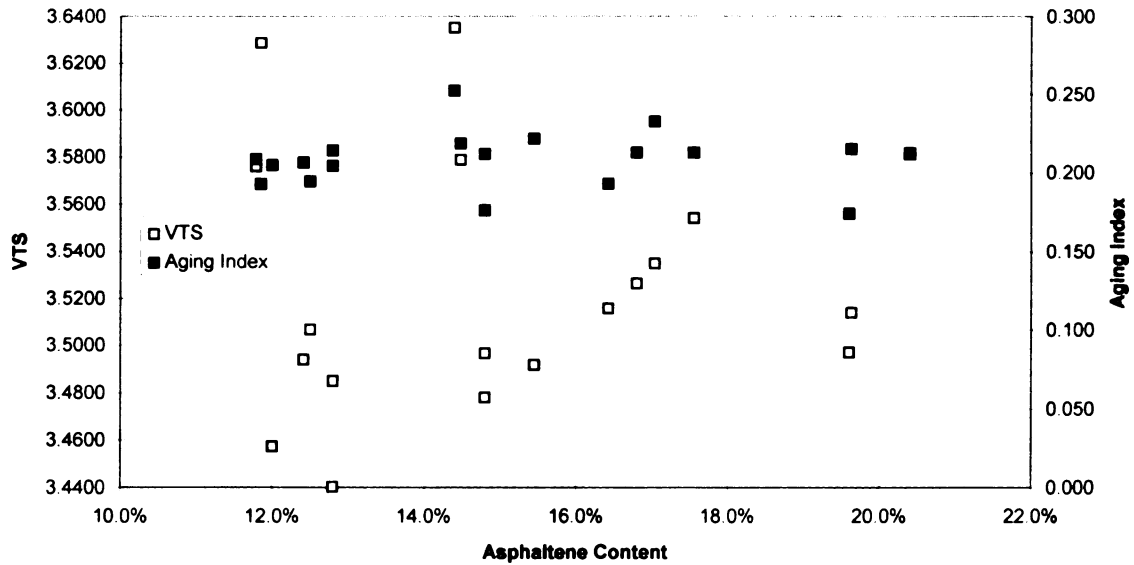


Figure 5.23 – VTS and aging index versus asphaltene content.

Chapter Six

Applicability of SHRP Performance Grading to Modified Binders

The SHRP performance grading system was created using unmodified asphalt binders. The binder properties were correlated to pavement performance to determine the specification values. This section addresses the applicability of those specification values to polymer modified asphalts and recommends changes in the SHRP protocol where necessary.

6.1 - Flash Point Test

The flash point specification calls for a minimum flash temperature of 230°C. Because this specification is a safety measure, there is no reason it should not apply to modified binders.

6.2 - Viscosity Test

The viscosity test calls for a maximum rotational viscosity of 3 Pa·s at 135°C. This specification ensures that the asphalt can be pumped and handled at the hot mix facility. Polymer modified asphalt is processed using conventional paving equipment. For this reason, the viscosity specification should not be changed for polymer modified binders.

6.3 - Rutting Resistance

Rutting resistance is measured by dynamic shear rheometry on the unaged and RTFO aged asphalt binder. While aggregate properties and aggregate-binder interfacial properties are important in preventing rutting, the binder itself plays a significant role. This is seen by the use of harder asphalts in hot climates to prevent rutting. An AC-0.5 will likely rut in Arizona regardless of the aggregate and mixture properties. Rutting is a result of repeated loading cycles. Some of the deformation is recovered while the rest is dissipated as permanent deformation and heat. To prevent rutting, this dissipated work should be minimized. This work is inversely proportional to the dynamic shear modulus ($G^*/\sin\delta$). Therefore a larger dynamic shear modulus is desired to prevent rutting. Modification of binders should increase the rutting resistance of most asphalts. However, the specification should not be altered because the same specification limits are applicable to both unmodified and modified binders.

6.4 - Excessive Aging

Excessive aging is measured by determining the mass loss of an asphalt after aging. The specification calls for a maximum mass loss of one percent. This specification should be eliminated. It does not adequately represent the aging chemistry. Mass is lost through volatilization and is gained through oxidation. Unless the ability to measure these two processes independently was developed, overall mass loss is a misleading measurement.

6.5 - Fatigue Cracking

Fatigue cracking resistance is a function of complex modulus and phase angle. Unlike rutting resistance, which calls for a stiff binder, fatigue cracking calls for a soft, elastic binder. The specification requires a maximum $G^*\sin\delta$ of 5000 kPa. This value should not be changed for modified asphalts because the assumptions built in to the specification are equally valid for modified and unmodified binders.

6.6 - Low Temperature Cracking

Low temperature cracking is measured using a bending beam rheometer. The specification calls for a minimum m-value of 0.300 and a maximum stiffness of 300 MPa. There is some question as to whether these values are sufficient for specifying low temperature cracking properties for modified binders.

When the temperature drops, the asphalt concrete shrinks. Tensile stresses accumulate in the pavement because friction against the lower pavement layers inhibits movement. When these stresses exceed the tensile strength of the material, low temperature cracks form. The two properties chosen by SHRP to characterize low temperature performance are m-value and stiffness. Stiffness is a measurement of the amount of stress that occurs for a given strain. The m-value is a measurement of the ability of the asphalt to relax tensile stresses through flow mechanisms. To prevent cracking, the accumulation of stresses needs to be prevented. This can be done two ways. A low stiffness indicates the amount of stress will be reduced for a given strain. A large m-value means indicates that the stresses will be dissipated faster. The ideal binder will have a low stiffness to minimize stress and a high m-value to dissipate the stress quickly.

The SHRP stiffness specification of 300 MPa was selected based on previous studies that correlated thermal cracking with stiffness. There are some problems inherent in this process, namely the fact that stiffness is not the only factor that controls thermal cracking. However, this study has shown that m-value, not stiffness, is the limiting factor. Therefore the stiffness specification value was not scrutinized as closely.

The SHRP specification for the m-value of a minimum of 0.300 was selected based on the experience of the Expert Task Group and on various asphalts tested during the SHRP development. There is much debate about what the specification value should be. The correlation to performance data is not as good for m-value as it is for stiffness. There is very little correlation between m-value and stiffness, however, which suggests that both properties need to be controlled.

There are some fundamental assumptions that are made when using these two values to predict thermal cracking. The first is that the cracks are caused by tensile stress exceeding tensile strength. This seems reasonable. Accepting this assumption leads to the conclusion that there are four variables which are involved in thermal cracking. Three variables are used to characterize the accumulation of tensile stress due to thermal contraction. Coefficient of thermal expansion (CTE) determines the strain occurring for a given temperature change. Stiffness determines the stress that occurs as a result of that strain. M-value determines the ability of the material to relax that stress. The three variables together determine the tensile stress that occurs. These three variables, with tensile strength, determine thermal cracking potential. The SHRP specification assumes that CTE and tensile strength of all asphalts will be approximately equal. This makes m-

value and stiffness the only two parameters that need to be characterized. These assumptions do not hold for polymer modified binders.

Polymer modification may alter the CTE and tensile strength of the binders. It is likely that the CTE will remain relatively unchanged while the tensile strength will increase. SBR has a cubical linear expansion coefficient of $37 \times 10^{-5} \text{ ft}/^\circ\text{F}$ while a generic asphalt has a coefficient of $35 \times 10^{-5} \text{ ft}/^\circ\text{F}$.⁵⁰ For a mixture of these two materials, the CTE would be expected to remain constant. Other modifiers have a CTE of the same order of magnitude, although they are not as close to that of asphalt as SBR. There may be some small changes in the CTE of the blend compared to the virgin asphalt, however the effect should be minor. An increase in tensile strength will allow for greater stress accumulation before cracking. This means that modified pavements with a larger tensile strength and a stiffness or m-value slightly off specification will likely perform better than a normal asphalt that barely meets the specifications. The specification, as written, only considers direct tension if the stiffness is 300 - 600 MPa and the m-value is greater than 0.300. The specification should be changed to incorporate tensile strength measurements. A likely solution would be to first measure the tensile strength. The tensile strength would then determine the cut-off values for stiffness and m-value. A separate study should be done to determine the effect of tensile strength on low temperature pavement performance in order to determine the cut-off values. The specification, as written, is likely over conservative. That is, a pavement which meets the specification should perform as specified, and likely will perform better than specified. More work needs to be done to determine the applicability of the SHRP low temperature tests for modified binders.

Chapter Seven

Conclusions

This study shows that polymer modified asphalt can be used to extend the temperature range over which asphalt pavements show good performance. This is accomplished by using a soft asphalt to give good low temperature performance and modifying it with polymer to extend the high temperature performance. Each of the modifiers studied to date showed some different characteristics which are addressed below.

7.1 - Styrene Butadiene Rubber

Styrene butadiene rubber is one of the most common polymers used for modification. An SBR content of 3% (w/w) improves the high temperature performance one grade, while a content of 5% (w/w) improves it by two grades. There is minimal improvement with contents of less than 3% (w/w). At low contents, SBR acts as a dispersed polymer while at higher contents a network forms inside the asphalt. This network lends support to the asphalt at high temperatures improving rutting resistance. In each case, the low temperature grade remained the same as the base asphalt used for modification. There was some slight improvement in the low temperature creep stiffness of the SBR modified binders, however the SHRP performance grading scale is too coarse to register this improvement. The viscosity of SBR modified binders was sufficiently low at contents less than 6% (w/w) to be processed using standard equipment. FTIR was an excellent tool for determining polymer content in SBR modified samples. The sharp peak

at 965 cm^{-1} in the SBR is a good indicator of polymer in modified binders. GPC was not as useful. Due to the low solubility of SBR in THF, GPC results consistently underestimated polymer content. The molecular weight of the SBR modifier plays an important role in the properties of the modified binder. There is little change in initial softening point with molecular weight, however there is significant variation in final melt temperature. Dynamic shear modulus shows a range of about one performance grade from the low molecular weight SBR to the high molecular weight SBR. No such effects were seen in low temperature properties. This is because the low temperature properties are mainly governed by the base asphalt and not the polymer. All in all, SBR appears to be a promising modifier.

7.2 - Elvaloy® AM

Elvaloy® AM is a reacting polymer which bonds to the asphalt. Rather than forming a one-phase Elvaloy® AM/Asphalt network, it is believed that the Elvaloy® AM simply attaches to some of the functional groups in the asphaltenes creating larger asphaltene micelles. This is seen clearly in the GPC curves which show a large increase in the high molecular weight region of the asphalt.

The high temperature performance grade was the highest of any modifier used in this study. An improvement of one grade over the control sample was seen with addition of 2% (w/w) Elvaloy® AM. One of the reasons for the large increase in performance grade compared to the virgin asphalt is the high temperature and long time required for blending the asphalt and the modifier. These extreme mixing conditions cause severe oxidation which leads to stiffer binders and better high temperature properties. Because

this is a reactive process, the mixing procedure is very sensitive to thermal gradients and three dimensional flow patterns. Direct scale up to batch sizes of 300 g from 150 g resulted in significant differences in properties. Because of the difficulty in producing consistent samples, any Elvaloy® AM pavement work needs to be monitored closely.

Elvaloy® AM modified samples had very high viscosity. Samples with 2% (w/w) and greater Elvaloy® AM had viscosity that did not meet the SHRP specification for handling. Because 2% (w/w) is the optimum content, this means that to get the most benefit from of Elvaloy® AM, different processing equipment may need to be developed.

The low temperature properties of Elvaloy® AM were poor. This degradation is likely caused by the excessive oxidation of the binders during processing. The low temperature SHRP performance grade was one to two grades worse than that of the base asphalt. There was no improvement shown with increasing Elvaloy® AM content.

FTIR was a somewhat useful tool for Elvaloy® AM detection. The characteristic peak for Elvaloy® AM is a C=O peak at 1740 cm^{-1} . This peak overlaps slightly with asphalt which forms C=O bonds during oxidation. The calibration curves showed good linear results with Elvaloy® AM content, however the presence of a peak at 1740 cm^{-1} is not a definitive indicator of polymer.

Thermomechanical analysis shows that Elvaloy® AM improves the softening point of the asphalt significantly. Unlike the rheological properties, which showed most of the improvement came from oxidation, the softening properties show significant improvement both from oxidation and the polymer. For example, the optimum 2% (w/w) Elvaloy® AM modified AC-5 shows an improvement in melt temperature of 18°C due to

oxidation and an additional 7°C due to polymer. Similar results are seen at all contents and with all three asphalts tested.

Elvaloy® AM appears to show some benefits, however there are some significant drawbacks. The largest drawback is the degradation of low temperature binder properties due to the severe mixing procedure. Another drawback is the difficulty encountered in scale up of the mixing procedure. Without a good scale-up procedure, the lab results are not very meaningful to a real world pavement application. Other polymers such as SBS and SBR are better candidates for asphalt modification.

7.3 - Recycled Crumb Rubber

There is a great deal of interest in using recycled crumb rubber in asphalt. This is driven by the environmental problem of disposing of used tires. Because the goal of CRM modification is not necessarily improvement of the pavement, but rather as a dumping ground for old tires, the basis for success is simply maintaining the performance of the base asphalt upon CRM modification.

Only the high temperature properties of CRM modified pavements have been studied. The mixing procedure is a low temperature, low time procedure which should result in minimal oxidation of the asphalt. The use of ultrafine CRM aids in dispersion in the asphalt, however, CRM particles do not dissolve completely and are still visible in the final mixture. Dynamic shear rheometry shows that addition of CRM results in an improvement of the high temperature performance grade by one grade for every 5% (w/w) CRM. Viscosity tests show that up to 15% (w/w) CRM can be added to the binders while maintaining a processable viscosity. Studies on the long term (24 hr.) high

temperature storage of the CRM binders indicate that the presence of CRM either masks or retards the aging process. The increase in softening point after storage is less for the CRM modified binders than it is for the control.

CRM looks to be a promising modifier, resulting in significant increases in the high temperature binder performance. This result is very preliminary. Before any recommendations can be made, the low temperature performance needs to be investigated. There are also issues such as how the macroscopic CRM particles will effect the binder-aggregate adhesion and how CRM will affect the long term aging of the asphalt. There is also the issue of recyclability of the CRM pavement that will probably become impossible due to the large CRM contents required for modification.

7.4 - Ethylene Vinyl Acetate

EVA appears to be a promising modifier which doesn't suffer from some of the problems of the other modifiers. It dissolves well in asphalt at the same conditions as SBS blending. It improves the high temperature performance one grade with 3% (w/w) polymer and two grades with 5% (w/w). The viscosity remains low enough to process 7% (w/w) EVA modified binders. It has a characteristic IR peak at 1240 cm^{-1} that makes polymer detection easy. It shows softening and melt properties that are better than those of SBR. It does not suffer from the phase separation problems that plague polyethylene.

Two different molecular weight EVA polymers were studied. There was minimal differences in the high temperature properties of the two polymers. For this study, both were blended with asphalt using the same procedure. However, in reality, the low MW polymer can be blended at lower temperatures for shorter times. This can improve the

low temperature properties of the modified binder. While these results are still preliminary, it appears that EVA is an excellent choice for asphalt modification.

7.5 - Recommendations for Further Study

This study attempts to present a comprehensive investigation of polymer modified asphalt. As good as it was, there are still many areas than need to be investigated.

One of the main areas that should be investigated is the effect of asphalt source on the properties of the modified asphalt. This study used four different asphalt grades from the same supplier. In order to generalize these results, the modifiers need to be tested with asphalts from different sources. It will be more beneficial to use the same asphalt grade from different suppliers than using different asphalt grades from the same supplier. The majority of the differences in properties between modified AC-2.5 and modified AC-20 are due simply to the differences in the base asphalt properties.

Another area to investigate is to develop a better model of how the asphalt and modifier interact to yield the properties seen in the blend. A first step is to determine what variables are important in determining neat asphalt properties. This study investigated molecular weight and asphaltene content. While it is still believed that these play an important role, the inability to correlate properties using only these factors indicates that other variables are also important. Two possible factors are asphalt polarity and asphaltene/resin compatibility. Asphalt polarity can likely be determined by looking at different ratios of Corbett fractions. Asphaltene/resin compatibility is currently measured by looking for the onset of flocculation. Because asphalt forms dark solutions,

a more quantitative method than visual inspection is required to determine the actual onset.

Another view of modeling was presented in Chapter 6, namely phenomenological modeling. The complex chemical nature of asphalt make it unlikely that good predictive models can be developed for the physical properties based on chemistry alone. This is complicated further by the addition of modifiers. One way to deal with this is to concentrate more on what is happening rather than why it is happening. For example, with SBR modification, the two main phenomena are network formation and percolation effects. The rheological properties seen in SBR blends is a result of the interaction of these two phenomena. Similar models should be developed for the other modifiers.

If the pavement performance studies of Elvaloy® AM modified binders show improvement, further work needs to be done to better understand the mixing procedure. This could include kinetics studies, studies of thermal gradients in the mixing vessel, etc.

The final area of work is to synthesize the data collected by the author with data collected by the microstructure group and the engineering properties group to get a better understanding of how, on a fundamental level, polymer modification improves pavement performance. This is especially important when considering low temperature cracking behavior. The binder properties have only shown slight improvement in low temperature behavior as measured by SHRP. One thing that SHRP ignores is the crack propagation behavior and how it is affected by modification. Another is the failure mode of the asphalt at low temperatures. These factors need to be considered when evaluating the use of modified binders to prevent low temperature failure.

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