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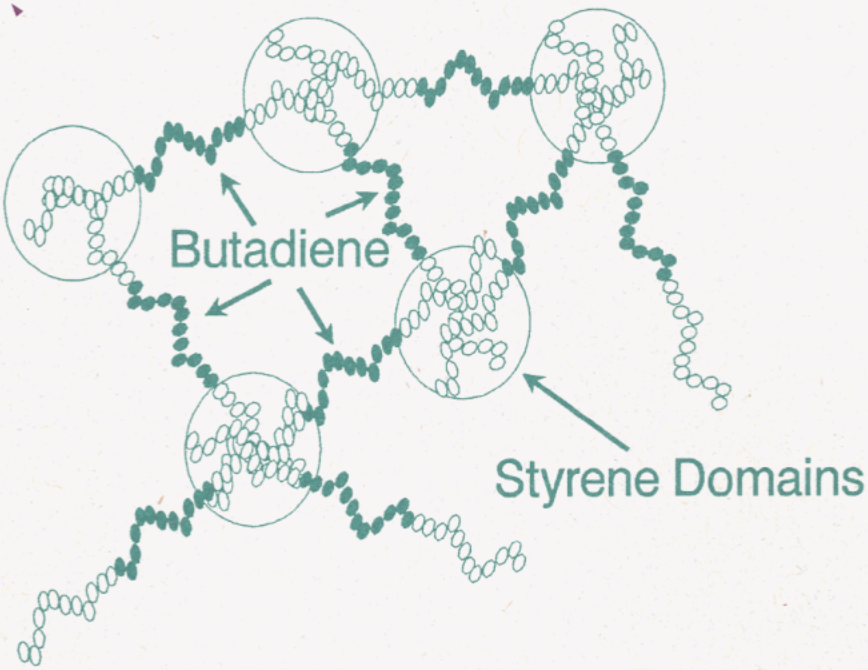

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This report compiles a vast majority of research on polymer modified asphalt cements and mixtures. It covers a general discussion of polymer chemistry and terms typically used by polymer suppliers; asphalt cement chemistry; typical test methods historically used to evaluate modified asphalts; reported results; comparisons of polymer modified asphalt cements and mixtures; proposed binder specifications; and a summary of field trials reported in the literature. Based on this information, the report suggests several experimental designs for use in the completion of the laboratory and field trial phases of this project.

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POLYMER LITERATURE REVIEW

Interim Report

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EXECUTIVE SUMMARY

This literature review represents the initial work on a five-year joint research effort between the University of Minnesota Civil Engineering, and Chemical Engineering and Material Science Departments to investigate improving the temperature susceptibility properties of asphalt cement concrete, on behalf of the Minnesota Department of Transportation and the Federal Highway Administration. The review is separated into six specific topics: polymer chemistry, asphalt cement chemistry, test methods, polymer modified asphalt cements, and specifications and field test sections. A seventh section details suggested laboratory and field experiemental designs based on the information presented in the six previous sections to be used for the remaining research program.

An evaluation of the polymer chemistry literature indicated that key polymer properties that influence thermal and viscoelastic properties are molecular weight and distribution, architecture, and chemistry. Most polymers used in paving applications generally have a narrow molecular weight distribution for any given product; molecular weights for individual products were not typically reported. The two most common polymer structures found were a linear chain and a radial, or star, formation. Types of polymers typically used can be separated into two categories: elastomers and plastomers. Elastomers can stretch and recover their shape but only contribute to tensile strength when the chains are stretched to a great degree. Typical elastomers are natural rubbers, styrene butadiene rubber (synthetic rubber, SBR), styrene-butadiene-styrene (SBS), and Neoprene. Plastomers exhibit quick early strength under load but little ability to strain without brittle failure. Typical plastomers are low density polyethylenes (LDPE) such as Novophalt, ethylene methacrylate (EMA), and ethylene vinyl acetate (EVA) such as Polybilt.

Asphalt cement chemistry is complex and defines how or if a given polymer will interact with the asphalt. Various models have been proposed to describe the asphalt cement composition, however there has been little agreement over the years. Little was found in the literature that links asphalt cement chemistry to estimations of compatibility with polymer modifications. In general two interpretations of "compatibility" of polymers and asphalt cements have been used. The first simply defines it as the ability of the polymer to remain distributed in the asphalt cement without significant evidence of phase separation. The second defines compatibility based on the level of interaction between the polymer and the asphalt cement.

Most of the test methods used to evaluate polymer modified asphalt cements have been historically limited to viscosity measurements with either Cannon Manning vacuum or Asphalt Institute tubes, ring and ball softening point, and penetrations and ductilities at various temperatures. None of these tests can be used to assess the viscoelastic nature inherent in neat asphalt cements, let alone the influence of polymer modification. More recent fundamental rheological tests developed to address this short coming in the traditional tests include dynamic mechanical shear and bending beam rheometers, and direct tension.

Based upon the data presented throughout the literature and a knowledge of the polymer structure of the individual polymer products, it can be seen that a linear structure SBS will produce significantly less of an increase in both viscosity and ring and ball softening point temperatures than a comparable amount of a radial SBS product from the same manufacturer. The interaction between the polymer and the asphalt cement is highly asphalt source specific.

Most testing of polymer modified asphalt concrete mixtures has historically been limited to measurements of resilient or dynamic modulus over a range of temperatures, axial static or dynamic creep at warm temperatures. More recently, both the indirect tensile creep and the thermal stress restrained sample test (TSRST) have been used to evaluate cold temperature responses.

Creep testing has shown that in general, polymer modification has the potential for reducing permanent deformation in asphalt concrete mixtures. Cold temperature TSRST testing has indicated that the cold temperature properties of the mixture are primarily a function of the binder properties only; there was little influence of mixture variables such as aggregate source and air voids on correlations with the mixture fracture temperature and binder limiting stiffness temperatures.

Several binder specifications have been proposed for polymer modified asphalts over the years but they rely heavily upon the tradition binder tests. Several of these specifications are presented in this literature review.

The last section of the review presents suggestions for experimental designs for evaluating:

Polymer structure/source and asphalt grade/source.

Modification with asphalts generally incompatible with SBS products.

Comparison of binder and mixture rheology

Field experiments.

Please note that the figures shown both in the body of the report and in the appendices have been obtained from the original publication cited in the caption. If the reader desires a more complete or clearer view of any figure is needed, please refer to the referenced publication.

CHAPTER ONE

BACKGROUND

Polymer modified asphalt cements have been used in attempts to mitigate both traffic- and environmentally induced pavement distresses. Polymers have been used to reduce rutting caused by traffic loads during warm weather conditions. The most common reasons given for improved rutting resistance are an increase in viscosity due to the additive and/or the formation of an elastomeric network which helps resist traffic-induced stresses. Polymers have also been used to reduce thermal cracking caused by the contraction of the pavement as temperatures decrease. These additives are thought to increase crack resistance because the inclusion of finely dispersed polymer particles impede crack propagation; this mechanism is referred to as crack pinning. Another approach to reducing thermal cracking is to use a softer-than-usual grade of asphalt cement. Polymer additives are then used to mitigate potential warm temperature rutting problems caused by using the lower viscosity asphalt cement. This last approach assumes that the cold temperature properties of the binder are governed by the asphalt cement while the warm temperature properties are primarily a function of the polymer addition (1).

While polymers have been used for more than three decades, their ability to solve pavement distress problems has shown mixed in-service results. Improvements seen in laboratory prepared and evaluated mixtures have not consistently translated into improved pavement performance. Some reasons for these mixed results can be attributed to the modified binder and include an inability to accurately define the function of the polymer within the asphalt, incompatibility of certain polymer and asphalt cement combinations, and no specific method for defining an optimum concentration of polymer. Other reasons for the variable success of polymer modified binders can be the result of mixture problems such as inappropriate aggregate gradation selections, and lack of fundamental laboratory tests which can be related to pavement performance. Construction problems such as blending times, mixing temperatures, and field compaction will also have a large role in the success or failure of a project.

OBJECTIVES

Specifically, the objectives were to identify existing information on:

1. Polymer chemistry and architecture
2. Asphalt chemistry
3. Test methods for evaluating both binder and mixture properties
4. Influence of polymer modified asphalt cement on binder and mixture properties
5. Summary of existing field test sections and information on mix design, construction problems, and field performance.

SCOPE

A computer search of the Transportation Research Information Service (TRIS), and National Technical Information Service (NTIS) databases were conducted as well as a manual literature review of traditional highway research publications such as the proceedings of the Association of Asphalt Paving Technologists (AAPT), Transportation Research Board (TRB) annual publications, and the Canadian Technical Asphalt Association (CTAA). Key words sought in this search includes such topics as polymer modified asphalts and mixtures, asphalt chemistry, rheology, thermal cracking, and permanent deformation.

Since the overall objective of this research study is to improve the cold temperature performance with the use of elastomeric polymer additive, the search concentrated on this class of additives. These materials, tentatively classified as rubbers by the Strategic Highway Research Program (SHRP), include natural and synthetic rubbers (e.g. SBR), block copolymers (e.g. SBS), and recycled tire rubber (i.e., crumb rubber-wet process) (2). While crumb rubber is technically included in the rubber classification, it is a recycled product with properties that are dependent upon the source of tires, processing, etc. There has also been extensive research efforts specifically directed at the use of crumb rubber in recent years, therefore this study was limited to an investigation of virgin polymer additives.

ORGANIZATION OF REPORT

An extensive literature review was conducted in order to summarize the available information prior to the design of both laboratory and field projects using polymer modified binders. This report, which is the result of the literature review, is organized into the following chapters:

Chapter Two: Polymer Chemistry
Chapter Three: Asphalt Cement Chemistry
Chapter Four: Test Methods
Chapter Five: Polymer Modified Asphalt Cements
Chapter Six: Specifications and Field Test Sections
Chapter Seven: Experimental Designs

Chapters Two through Four are intended to provide a wide range of general background information needed in a useful reference document. Chapter Two on Polymer Chemistry was developed to provide the civil engineering community with a general introduction to common polymer terms and properties. Chapter Three on Asphalt Cement Chemistry provides an overview of the more common hypotheses for asphalt cement modelling and chemical composition. This section will also provide important background information for the analysis of polymer-asphalt properties. Chapter Four on Test Methods was developed to provide both civil and chemical engineers with a quick reference source for understanding tests common to one field but foreign to the other.

Chapters Five and Six include the summary of previously reported research results, suggested specifications, and existing field test sections. Chapter Seven presents several experimental designs, both laboratory and field, based on the information presented in the first six chapters.

Appendix A provides a glossary of common polymer and chemistry terms. This appendix is intended to help highway engineers understand the basic terminology used in both research reports and suppliers literature. Appendix B covers terms commonly used in highway research and construction. Appendix C contains both a key word list and annotated bibliographies of all of the literature reviewed for this report. This appendix is intended to provide detailed reference document for those readers desiring more specific information on a given topic.

CHAPTER TWO

GENERAL BACKGROUND

Generically speaking, a polymer is a chain of units called monomers. A chain of beads is commonly used to represent a polymer with each bead representing a repeating unit, or monomer. An indication of the length of polymer chains is typically represented by one of several measurements of molecular weight. The number-average molecular weight, M_n, is just the total weight of the polymer divided by the total number of polymer chains in the sample:

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

where:

N_i = number of chains with i repeating units
M_i = molecular weight of chain with i repeating units, g/mole

The weight-average molecular weight, M_w, is:

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum C_i M_i}{\sum C_i}$$

where:

C_i = the concentration of polymer with i repeating units, g
M_i = the molecular weight of chain with i repeating units, g/mole

In statistical terms, M_n is the first moment of distribution, or mean, and M_w is analogous with the second moment of distribution, or standard deviation. The ratio M_w/M_n is referred to as the polydispersity index and indicates the distribution of molecular weights around M_n. That is, if $M_w/M_n = 1$, then all chains are of identical length and molecular weight (Figure 2.1). As M_w/M_n increases, so does the range of chain length and weight. This ratio is important in explaining the behavior of polymers. When the dispersity is high, the lower molecular weight chains can act as plasticizers which will soften the material (3). Also, these short chains will not contribute as much to tensile strength properties. Excessively long chains will contribute to tensile strength but can also significantly increase viscosity (3). Usually, the narrower the distribution (i.e., the closer the polydispersity index is to 1), the more desirable the polymer properties.

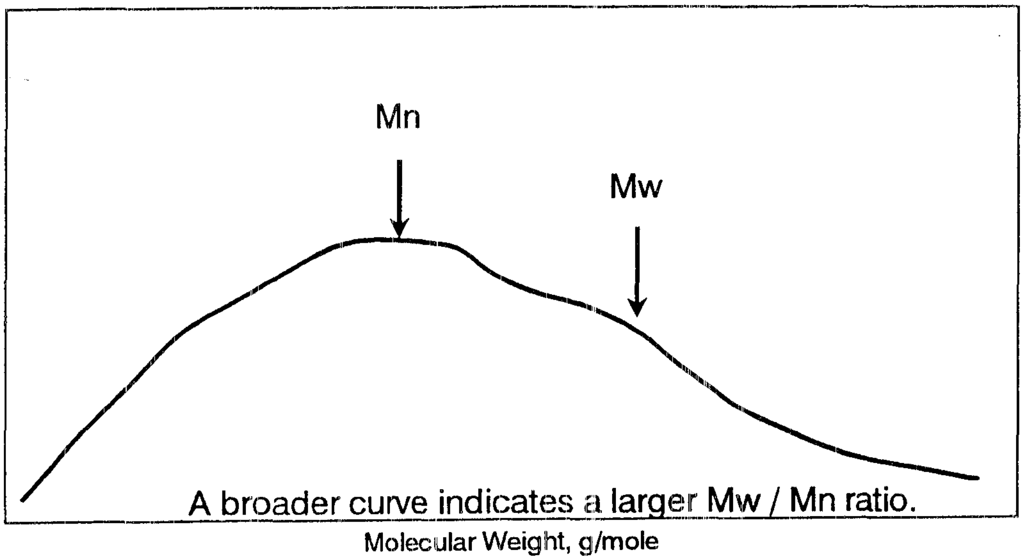


Figure 2.1. Concepts of Molecular Weight Measurements

One commonly reported indication of molecular weight is the melt flow index (MFI). This value is based on a standardized measurement described in ASTM D1238 (4). Briefly, a capillary tube is filled with the polymer and brought to a selected test temperature. A given load is applied to the top of the capillary and the material is allowed to extrude from the bottom over a 10 minute period. The mass of polymer extruded in 10 minutes is the MFI. Therefore, a low

MFI indicates high molecular weight and high viscosity material, and a high MFI indicates low molecular weight and viscosity (5).

Another important characteristic of polymers is their structure. Polymers can be simple straight chains or many variations of linked and crosslinked chains. Figure 2.2 shows examples of typical structures. Both the structure and the chemistry of branches can influence the behavior of polymers. If the ends of a polymer are reactive with either other polymers or components of a surrounding solution, then the more ends (i.e., branching, radial, etc.), the more reaction can occur. Bulky, unreactive branches or grafts can interfere with the function of the reactive portion of the polymer by shielding it from other reactive components. Uniform, unbranched, linear chains may tend to fit together uniformly, forming what is known as a crystalline structure. Crosslinked polymers can be stretched due to swelling from surrounding solutions; the durability of the crosslink depends upon whether it is chemical (e.g. vulcanized tire rubber) or physical (e.g. SBS block copolymers).

The terms random copolymer and block copolymer refer to the chemical composition of the polymer. A random copolymer is some combination, without a specific ordering, of different monomers linked together (Figure 2.2). A block copolymer refers to a block of one homopolymer (i.e., a chain of the same monomers) linked with another block of a different homopolymer. For example, styrene-butadiene-styrene (SBS) is a triblock copolymer consisting of a chain of butadiene polymer with a chain of styrene attached to either end. A styrene-butadiene (SB) rubber is a diblock copolymer and consists of one block of styrene attached to a block of butadiene.

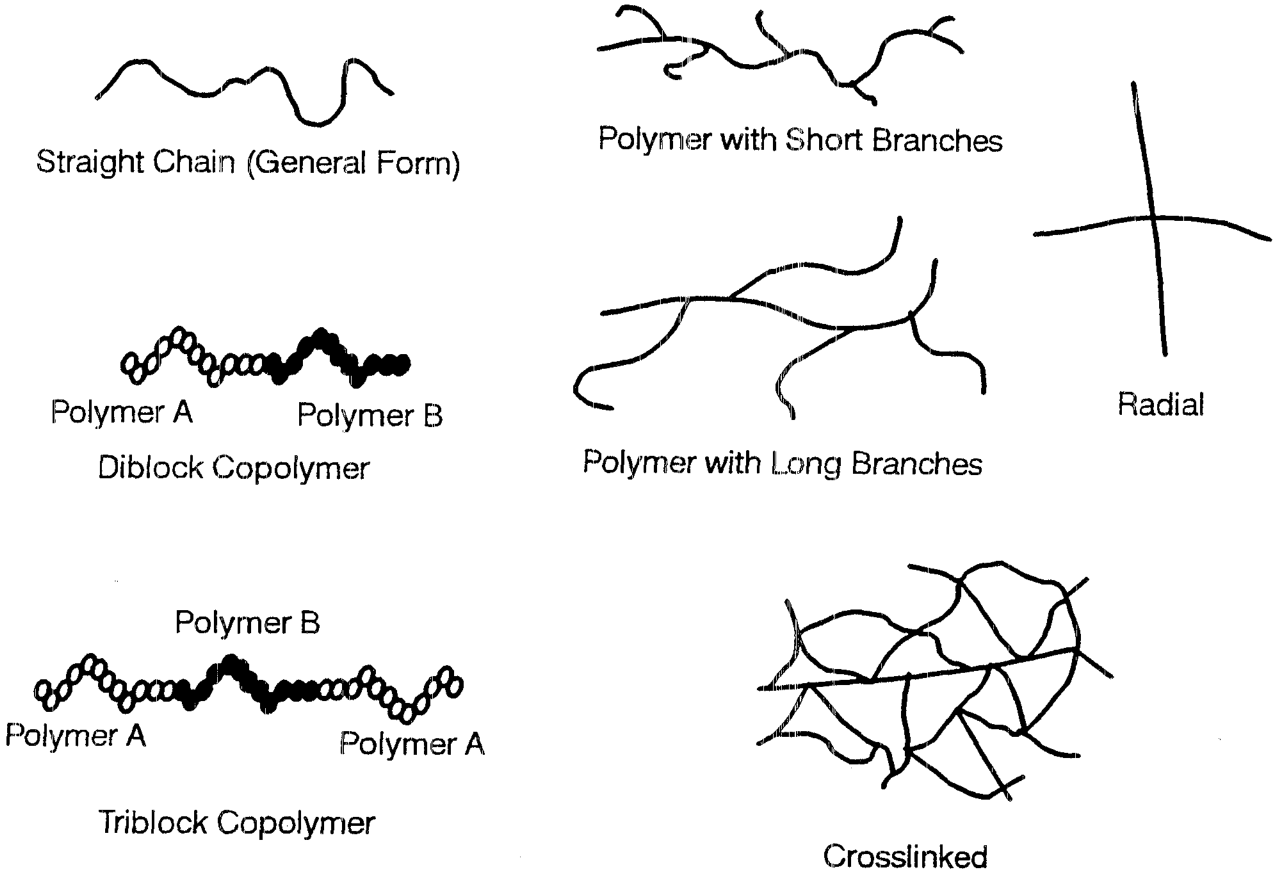


Figure 2.2. Various Types of Polymer Structures.

POLYMERS COMMONLY USED FOR MODIFYING ASPHALT CEMENT

Polymers commonly used in flexible pavement construction can be separated into one of two general categories of polymers: plastomers, and elastomers. Plastomers are materials that exhibit a quick early strength under load but tend to exhibit little ability to strain without brittle failure (6). Any deformation of these materials is permanent; they have little or no elastic component. Elastomers resist permanent deformation by an ability to stretch and recover their original shape once the load is removed. These materials only contribute to the tensile strength when the chains are stretched; their tensile strength increases with the percent elongation (6). It is not uncommon for elastomers to have more than 700 percent elongation before failure.

Over the years, there have been many polymer products used in highway construction. Table 2.1 summarizes some of the more commonly used products along with some general information on their structure and chemistry. All of the products listed under elastomers are considered rubbers, either natural or synthetic (e.g. SBR, SBS, and Neoprene). Plastomers used in highway construction are typically classified as paraffins (e.g. LDPE, EVA).

Not only are there different polymer chemistries within each category, there are also different methods used to manufacture a given type of polymer. Differences in manufacturing processes can have a potential impact on the end product due to trace amounts of chemicals used in the polymerization processes remaining in the finished product. While nothing was found in the literature to indicate these trace chemicals are significant contributors to differences between products, this might be important when comparing different products with the same general chemistry. Another possible source of differences between products of generally similar structure could be the coupling agent used to bond one polymer block to another. However, no information was found on this topic, most likely due to the proprietary nature of this portion of the manufacturing process. Polymer chemistry as well as general information on methods used to manufacture the polymers are discussed in the following sections.

ELASTOMERS

Natural Rubber

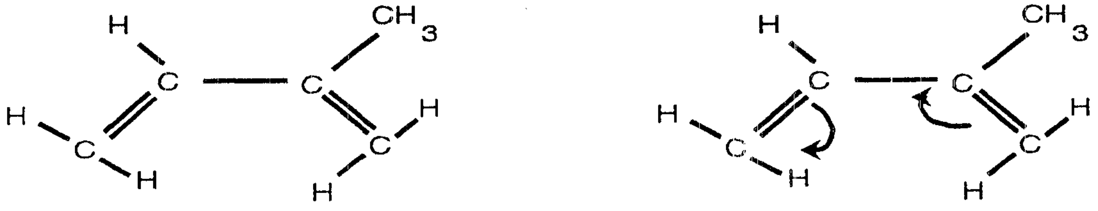
The empirical formula for rubber (C_5H_8) was identified by Faraday as early as 1826. In 1860 Greville Williams further identified rubber as a polymer of isoprene, and in 1910 Pickles presented the now widely accepted the concept of a straight-chain polymer structure for the rubber hydrocarbon (7). It was this initial work that eventually served as the basis for the development of synthetic rubbers.

Table 2.1. Typical Polymers in Use (6).

Trade Name	Manufacturer	Polymer		
		Type	Form	Chemistry
Elastomers				
Butonal	BASF	Block Copolymer	Latex	Styrene-Butadiene (SB)
Downright	Dow	Random Copolymers	Latex	Styrene-Butadiene-Rubber (SBR)
Europrene	EniChem Elastomers Americas, Inc.	Block Copolymer	Crumb or Powder	Styrene-Butadiene-Styrene (SBS)
Finaprene	Fina	Block Copolymer	Crumb	Styrene-Butadiene (SB)
Kraton	Shell	Block Copolymer	Crumb or Powder	Styrene-Butadiene-Styrene (SBS)
Neoprene	DuPont	Homopolymer	Latex	Poly Chloroprene
Polysar	Polysar, Inc.	Random Copolymers	Latex	Styrene-Butadiene-Rubber (SBR)
Styrelf	Elf Aquataine	Block Copolymer	Pre-Blended	Styrene-Butadiene (SB)
Ultrapave	Goodyear	Random Copolymer	Latex	Styrene-Butadiene-Rubber (SBR)
Vector	Dexco	Block Copolymer	Crumb or Powder	Styrene-Butadiene-Styrene (SBS)
Plastomers				
Elvax	DuPont	Copolymer	Crumb or Powder	Ethylene Vinyl Acetate (EVA)
Novophalt	Advanced Asphalt Technologies	Homopolymer	Preblended with AC	Low Density Polyethylene (LDPE)
Polybilt 100 series	Exxon	Copolymer	Crumb or Powder	Ethylene Vinyl Acetate (EVA)
Polybilt 500 series	Exxon	Copolymer	Crumb or Powder	Ethylene Methylacrylate (EMA)
Starflex	Carraux Enterprise International, Inc.	Copolymer	Pellets	Ethylene Vinyl Acetate (EVA)

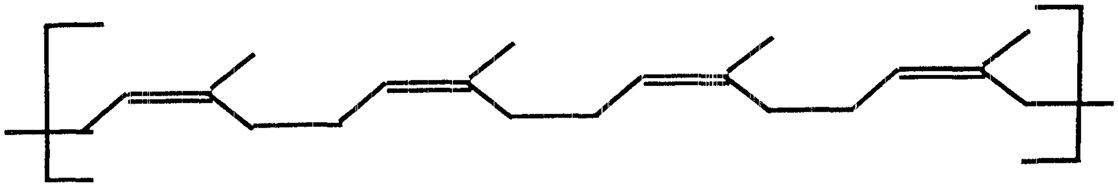
The cis-polyisoprene is the hydrocarbon component in natural rubber and is commonly found in over 2000 species of plants worldwide (Figure 2.3). However, the Hevea brasiliensis is the only commercially economical source of natural rubber. Higher quality natural rubber contains at least 90 percent of the cis-polyisoprene with the remaining portions being comprised of resins, proteins, and sugars. Previous research has shown that at least 99 percent of the cis-polyisoprene is of the cis-1,4 structure; there is no evidence of any 3,4 structure (7, pg 81). It is the cis-1,4 structure that gives rubber a zigzag spring-like formation (Figure 2.3) which is responsible for its elastic properties. That is, the chain can be stretched but when the load is released, the bonds between the atoms "pull" the chain back into its original configuration.

The molecular weight of these hydrocarbons in the raw latex system is at least 1,000,000. Mean molecular weights of solid raw rubber range from 500,000 to 1,000,000. This heterogeneity is commonly attributed to oxygenated groups with carbonyl reactivity (7, pg 81).



Isoprene Unit

Monomer Unit
(Movement of Double Bonds Required)



Structural Representation of Natural Rubber

Figure 2.3. Chemical Structure of Natural Rubber.

The structure of rubber can be broken down by mechanical means, called mastication. The rate of breakdown occurs more rapidly at either high or moderately low temperatures, on either side of 100°C (7, pg 81). Low temperature breakdown occurs because of the interaction of rubber radicals with oxygen which yields oxygen-terminated fragments of lower molecular weight (7). Other radical acceptors should be expected to produce the same result in an inert atmosphere. At higher temperatures, the rubber becomes softer and the rate of mechanical rupture is reduced accordingly. Breakdown, or shortening of the polymer chains, at elevated temperatures then becomes a function of conventional oxidative scission; this increases rapidly with temperature (7). Figure 2.4 shows the efficiency of mechanical breakdown over a range of temperatures. The left hand side (A) is attributable to oxygen stabilization of the free radicals, and the right hand side (B) is the result of oxygen-induced scission. The right hand side of the response can be altered with the inclusion of antioxidants while the left hand side is not sensitive to such additives. Briefly, this means that at least some forms of rubber polymer chains can be easily broken with prolonged mixing at the standard hot mix asphalt (HMA) plant operating temperatures. It also indicates that chains can be mechanically broken at cooler, but typical, in-service pavement temperatures; this could be a consideration when evaluating the durability of a polymer under repeated traffic loadings.

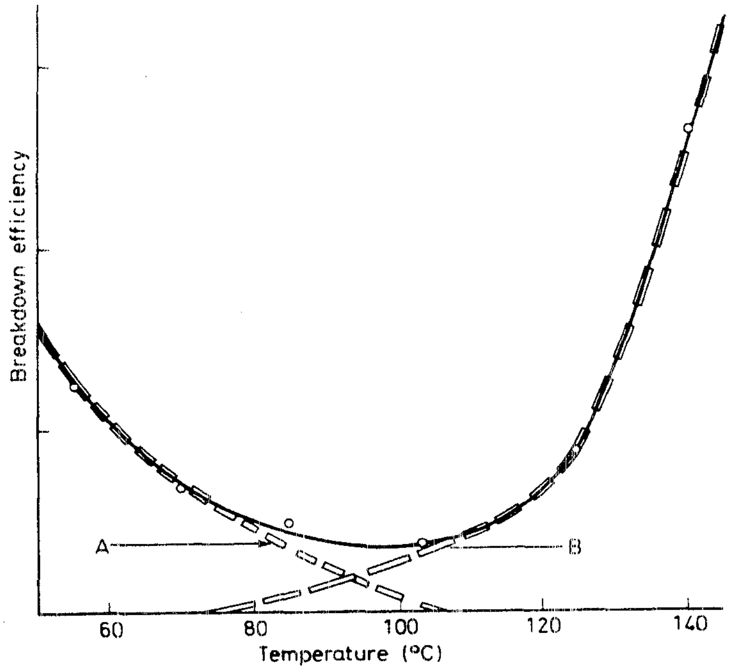


Figure 2.4. Breakdown of Natural Rubber after 30-Minutes of Mastication at Different Temperatures.

Synthetic Rubber (SBR)

Up until World War II, natural rubber (Hevea) was primarily used in the manufacture of all rubber products. Interruption of the natural rubber supply from South America after the bombing of Pearl Harbor led to concentrated efforts to develop comparable, and economically viable synthetic rubber substitutes (8). During this time, the Rubber Director and the Rubber Reserve Co. selected a copolymer of butadiene and styrene, designated as government rubber-styrene (GR-S), as the principle rubber substitute. SBR is a copolymer of styrene, or vinyl benzene, ($CH_2=CH-C_6H_5$) and butadiene ($CH_2=CH-CH=CH_2$).

The popularity of synthetic rubber continued after the war due to both the slow recovery of natural rubber production and new government regulations covering the use of GR-S. During this time both cold rubber, that is GR-S polymerized at 5°C instead of 50°C, and synthetic polyisoprene were competitively developed. The proliferation of new synthetic products became cumbersome and ASTM D-11 developed a practice (ASTM D1418) to describe existing and future synthetic rubbers based on their chemical composition of the polymer (8).

The use of latex instead of the processed (i.e., solid) form of raw rubber began in about 1924 and was used to fabricate primarily dipped products such as rubber gloves. It wasn't until problems with low solids content and unpleasant odors were overcome in the early 1960's that GR-S (later renamed SBR) began to be widely used. Shortly after this time, either natural, SBR, or a combination of the two became interchangeable (7).

Manufacture of SBR by Emulsification

SBRs are manufactured using an emulsification polymerization process that combines 30 percent styrene to 70 percent butadiene (by weight) in de-ionized water at either 4°C (cold SBR grades) or 42°C (hot SBR grades). Styrene contents of the finished polymer are typically around 23.5 percent by weight and are constructed with one styrene which is usually polymerized with six or seven butadienes. Individual monomers are randomly arranged in the chain, with the

Thermoplastic Rubbers (SBS)

These polymers have an ordered block structure of the general triblock form A-B-A. The A component is a thermoplastic polymer block (e.g., polystrene) with a glass transition point above room temperature. The B component is an elastomeric polymer block (e.g. polybutadiene) with a glass transition temperature well below room temperature. Various properties of these thermoplastics can be obtained by selecting A and B from a range of molecular weights. Figure 2.5 shows the conceptual relationship between the properties of the thermoplastic and the molecular weight of the elastomer (B) block developed by Shell in the mid-1960's (7).

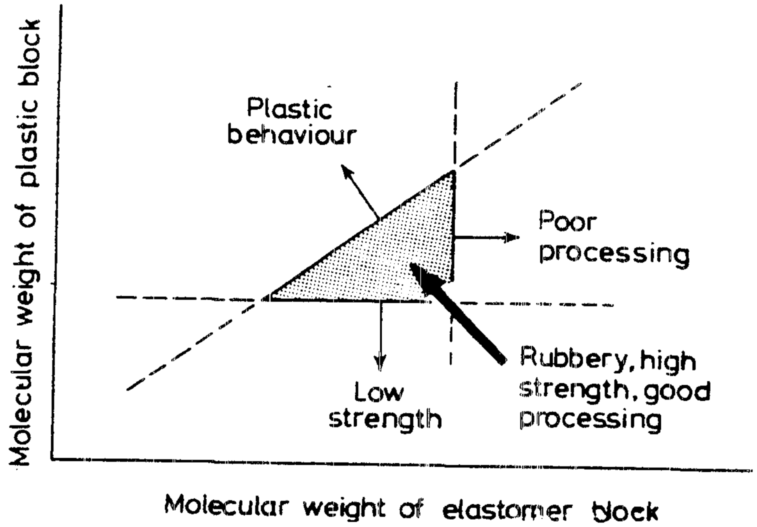


Figure 2.5. Effect of Molecular Weight of Blocks on the Properties of SBS (5).

A physically crosslinked structure developed by these two polymer blocks consists of a large sphere of polystyrene ends (referred to as a domain) linked with elastic-like threads of polybutadiene polymer (referred to as segments) (Figure 2.6). The domains have a dual function: first, they provide sites for multiple physical crosslinking, and secondly, they act as a filler. This structure produces a network that is phase stable and has good strength over a wide range of temperatures, up to the glass transition temperature of the polystrene domain phase. This structure produces a non-vulcanized rubber with physical properties comparable to its vulcanized counter parts.

Comparison of SBR Products'

Table 2.3 compares the information available for selected SBR products. All of the products shown in this table are for SBR in latex form and represent typical information available from either the supplier's literature or from direct inquiries. It can be seen from this table that there is little information readily available with regards to the specific SBR used in any of the products.

Table 2.2. Comparison of SBR Polymers Made with Emulsion and Solution Processes (7).

Property	Solution SBR	Emulsion SBR
Styrene Configuration	Block or Random	Random
Ash, (% wt.)	0.1	0.75
Rubber Hydrocarbon (% wt.)	98+	92
Monomer Incorporation	Controlled	Random
Polydispersity Index	Small	Large
Long Chain Branching	Slight	More Extensive

Table 2.3. Comparison of SBR Products.

Property	Butonal NS 175 (BASF Corp.)	Styrelf 13	Black Max (Husky)	Ultrapave (Goodyear)
Molecular Weight, M_n, g/mole[1]	108,000	Pre-Blended Only information available was for modified asphalts	Pre-Blended Only information available was for modified asphalts	Not Reported
Total Solids in Latex, % by wt.[2]	69			68 - 69 (anionic) 63 - 64 (cationic)
Bound Styrene, %[2]	24			Not Reported
Brookfield Viscosity,[2] #2, 20 rpm, mPa-s	720			1,300 - 1,500 (anionic) 800 - 1,100 (cationic)
Antioxidant[2]	None			Not Reported

1: Information obtained from direct inquiry
2: Information obtained from supplier literature; no temperature noted for Brookfield test.

butadiene fraction usually in the trans configuration (7, pg 84).

The original production of SBR in the mid-1940's resulted in a non-uniform product due to the tendency of this synthetic rubber to produce branched, irregular chains of variable molecular weight as opposed to natural rubber's relatively uniform straight chain configuration. Generally, SBR polymers are amorphous and do not crystalize, even when the vulcanisates are stretched. The uniformity of SBR improved with use of other modifiers such as diisopropyl xanthogen disulphide and TDM. Polymerization at low temperatures also helped form straight-chain polymers (7); originally SBRs were produced 'hot'.

Manufacture of SBR by Solution

The development of stereospecific catalysts directly led to the development of solution SBR. Solution SBR uses a combination of a coordination catalyst with a reductive chemical. Coordination catalysts include chlorides of cobalt, nickel, vanadium, titanium, other transient elements, lithium metal or a lithium alkyl derivative, and oxides of nickel, cobalt, or chromium. Reductive chemicals are usually derivatives based on aluminum, primarily alkylated aluminum chlorides (7).

Polymerization is commonly carried out with an alkyl lithium catalyst in a non-polar solvent. This process produces a polymer with approximately equal amounts of cis and trans configurations and vinyl contents below 10 percent (7). Activation of the catalyst by complexing with ethers produces a more random configuration with approximately 30 percent cis configurations and about 25 percent vinyl content. Table 2.2 shows a general comparison of the polymers obtained by both the emulsion and solution manufacturing process. This table indicates that the structure and molecular size of the SBR can be controlled better with solution polymerization than with the emulsion process.

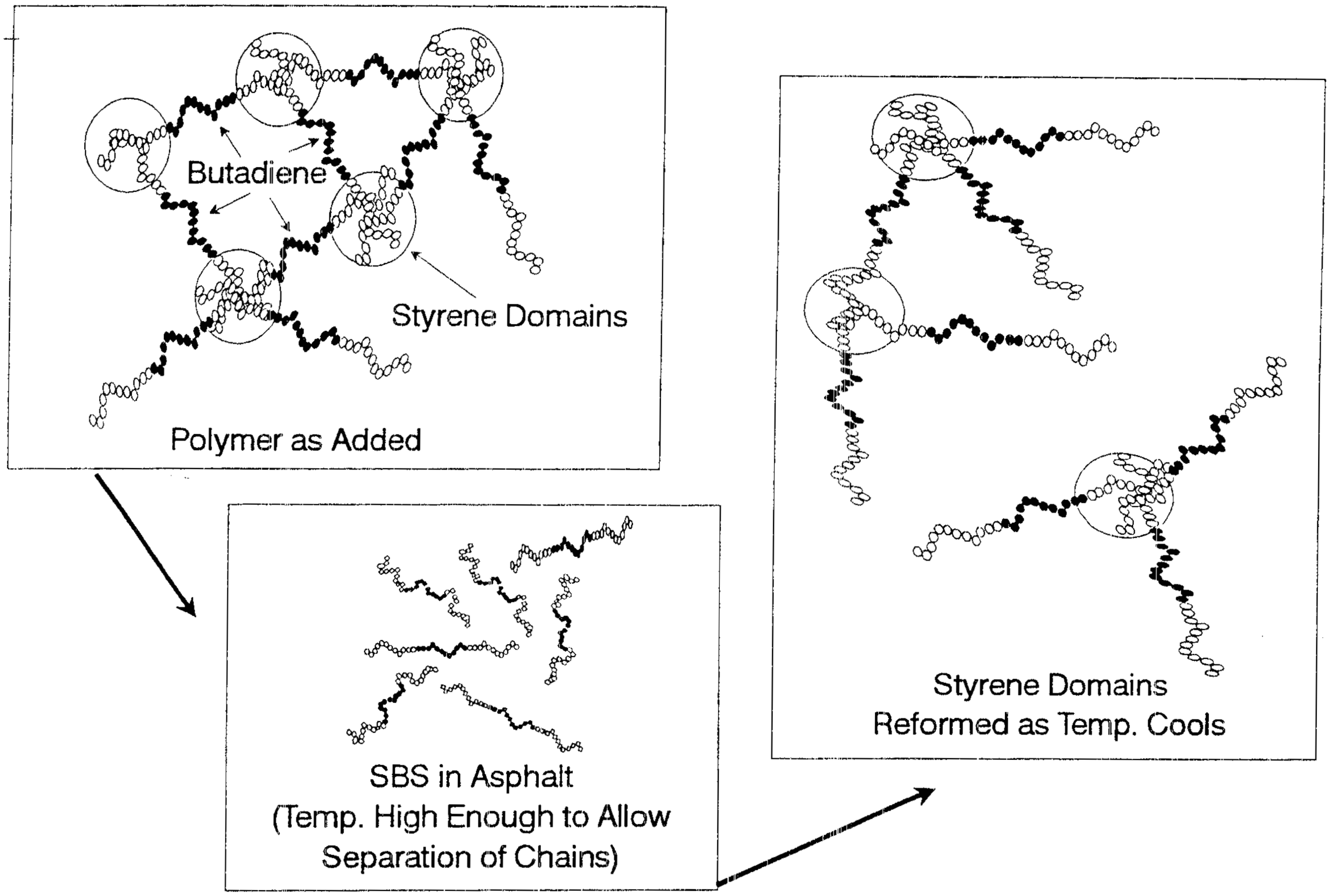


Figure 2.6. Model of SBS Block Copolymer (7).

One important difference between SBS and natural rubbers is that above 150°C thermoplastics can be worked in a molten form whereas natural rubbers will begin to chemically crosslink (7). This temperature-dependent physical crosslinking serves as the basis for using SBS as an asphalt cement modifier. When the SBS is added to the asphalt, the temperature is high enough for the styrene domains to segregate which allows for the dispersion of the individual SBS chains within the asphalt cement. As the temperature cools during laydown and compaction, the thermodynamics of the system force the styrene domains to reform, thus forming an in-place network within the binder. However, a sufficient quantity of polymer chains, referred to as a critical concentration (c*) or overlap concentration, is required for an effective physically crosslinked network. That is, there must be enough individual polymer chains so that the styrene ends are close enough to come into contact with each other (Figure 2.6).

Critical concentrations can be as low as 2 percent by weight for compatible systems and greater than 4 percent for less than optimum combinations of polymers and asphalts (9). The critical concentration, c*, of a modified binder is dependent upon the compatibility between a specific asphalt cement and polymer combination, the percent of polymer added, percent of diblock versus triblock copolymer, mixing temperature, and blending time (9,10). The selection of an asphalt cement which readily dissolves the styrene domains at the mixing temperature will allow the best dispersion of polymer chains within the binder. When a significant quantity of diblocks are present in the polymer instead of triblocks, the physical linking results in the formation of star-like clusters of polymers rather than network formation. This is because the second styrene on the end of the butadiene is missing and the link cannot be completed as shown in Figure 2.6. Research has shown that binder stiffness can be reduced by as much as 50 percent when the percent of SB in an SBS product is increased from 0 to 50 percent (10). Figure 2.7 shows that as the percentage of diblock copolymer is increased, the complex modulus decreases at warmer temperatures.

Although a critical concentration of polymer has benefits, some problems with the formation of a chemical crosslink has been reported when modified binders have been stored at elevated temperatures for several hours. This is due to the formation of a lattice of the polybutadiene phase and although researchers have reported this problem, no hypothesis as to the mechanism for the gelation (i.e., crosslinking) was suggested (11). The results shown in Figure 2.8 indicate that the crosslink density for SBS modified asphalt cement can achieve approximately the same density as for vulcanized rubber (11), however longer times at temperatures greater than 200°C are required to achieve this level of crosslinking. This could be a problem because as gelation progresses, the viscosity of the binder would increase to a point which would prohibit pumping the binder during normal hot mix asphalt (HMA) plant operations.

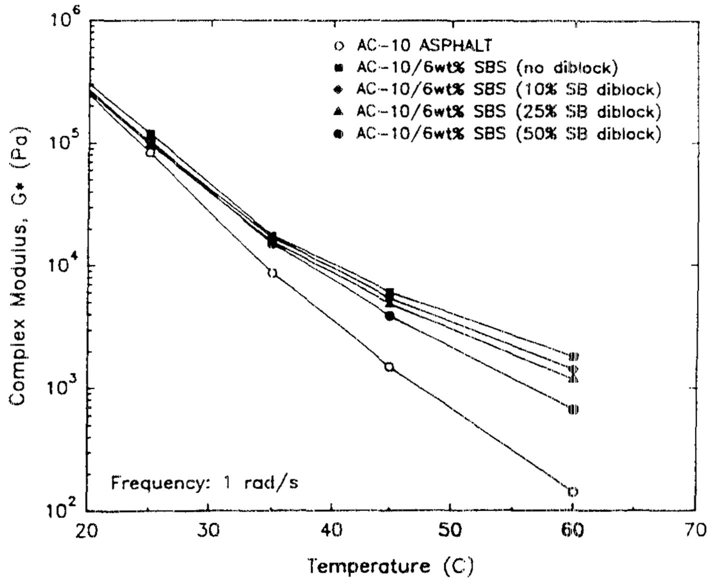


Figure 2.7. Influence of Diblock Concentration on Polymer Properties (10)

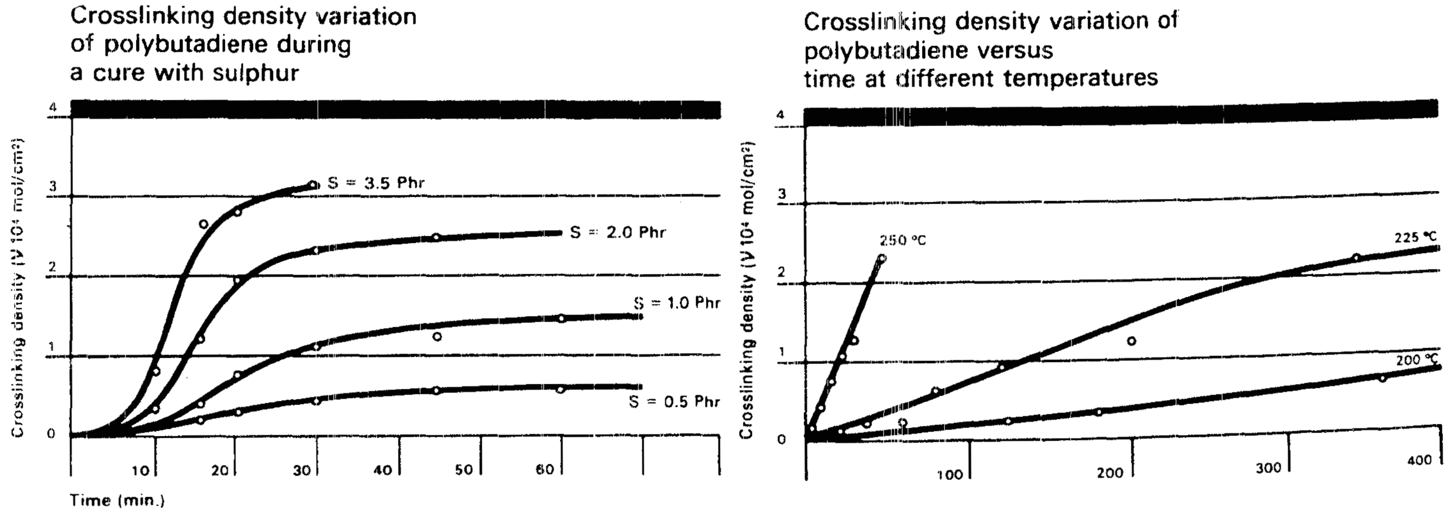


Figure 2.8. Comparison of Crosslink Density for SBS Held at High Temperatures and Vulcanized Rubber.

A combination of polymers (i.e., styrene and butadiene) with different glass transition points produces unique modulus versus temperature relationships. Figure 2.9 shows that the phase shift angles determined from dynamic shear tests have a minimum peak, corresponding to a relatively steady dynamic modulus, over a temperature range of -25 through 40°C for the pure SBS polymer (7). Outside of this range, there are significant increases in the phase shift angle, accompanied by rapid changes in the dynamic moduli. The two distinct maximums in the phase angle shift are due to the inherent material properties of each of the polymer blocks. Each peak is a function of the specific homopolymer properties.

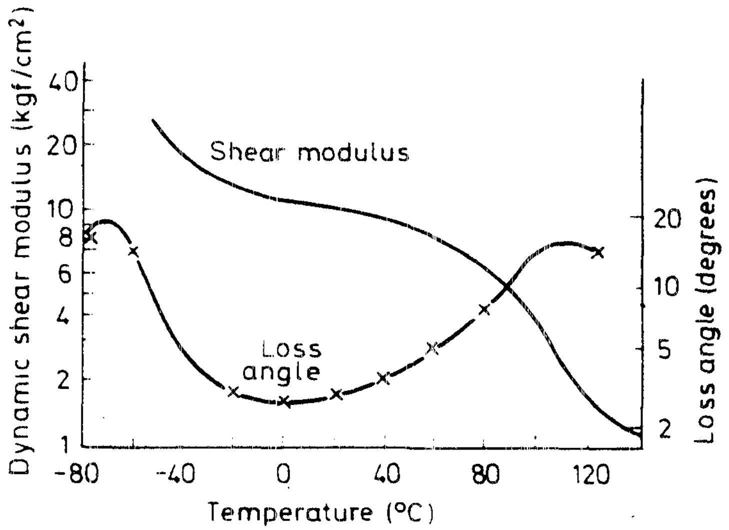


Figure 2.9. Dynamic Shear Modulus and Loss Angle of a Typical SBS Polymer (7).

Other additives that can be used to alter the properties of the polymer include naphtenic or mineral oils, and antioxidants. Processing oils such as naphthenic types can improve the flow properties, reduce hardness, and tensile strength. Light oils such as mineral oil can be used to extend the volume of the final rubber product and are typically added to high molecular weight rubbers in an amount of approximately 50 percent. While the use of extender oils can enhance the properties of the polymer, it can sometimes lead to accelerated oxidation degradation (i.e., a breaking of the polymer chains which is seen as a reduction in molecular weight) of an SBS polymer (12,13). One hypothesis for this phenomenon is that polymers mixed with napthenic oils are more readily dispersed within the asphalt thus more of the oxygen-reactive double bonds are exposed (13).

While it is commonly accepted that oxidation degradation can be reduced with the use of antioxidants, the chemical nature of most of these products is proprietary and will therefore, not be discussed. However, polymer degradation can also be reduced by saturating the SBS double bonds. The effectiveness of this antioxidant strategy has been confirmed by several researchers. Collins and Bouldin indicated that saturated SBS [styrene ethylene-butadiene styrene (SEBS)] modified binders recovered from field test sections from 3 to 4 years old showed no polymer degradation (i.e., decrease in polymer molecular weight) while the corresponding unsaturated SBS modified sections showed between 10 and 15 percent degradation (12).

Linde and Johansson used size exclusion chromatography (SEC) to show that the molecular weight of the asphalt cement increased with high temperature storage, regardless of the type of polymer added to the asphalt (13). Figure 2.10 shows examples of these results; the x-axis of this figure indicates the time it takes for molecules to exit the chromatography column and the y-axis is an arbitrary scale indicating the quantity of molecules exiting at a given time interval. The shift in the left hand side of all of the curves shown in Figure 2.10 indicate that molecular size of the asphalt portion increases after aging (i.e., faster exit times equal larger molecular sizes). The peaks on the right hand side of all of the unaged curves reflect the molecular size of the polymer molecules. After aging, the polymer peaks for the SBS polymer indicate a degradation of the polymer due to aging, that is, the polymer molecules show a reduction in size. There is virtually no change in the peak for the SEBS after aging indicating that this polymer does not appear to be susceptible to aging-induced degradation.

Figure 2.10 also shows that the asphalt portion of the curves for the SBS modified asphalts are similar while the same portion of the curve for the SEBS modified asphalt has shifted to the left. This may mean that the type of polymer influences the molecular associations within the asphalt cement, which can result in an apparent change in the molecular size of the asphalt molecules. The result of this phenomena, if real and not a result of testing variation, could indicate that the properties of a polymer modified asphalt cement are not just a function of the polymer additive but will also include the polymer influence on the internal structure of the asphalt cement. This concept will be explored more thoroughly in the following sections.

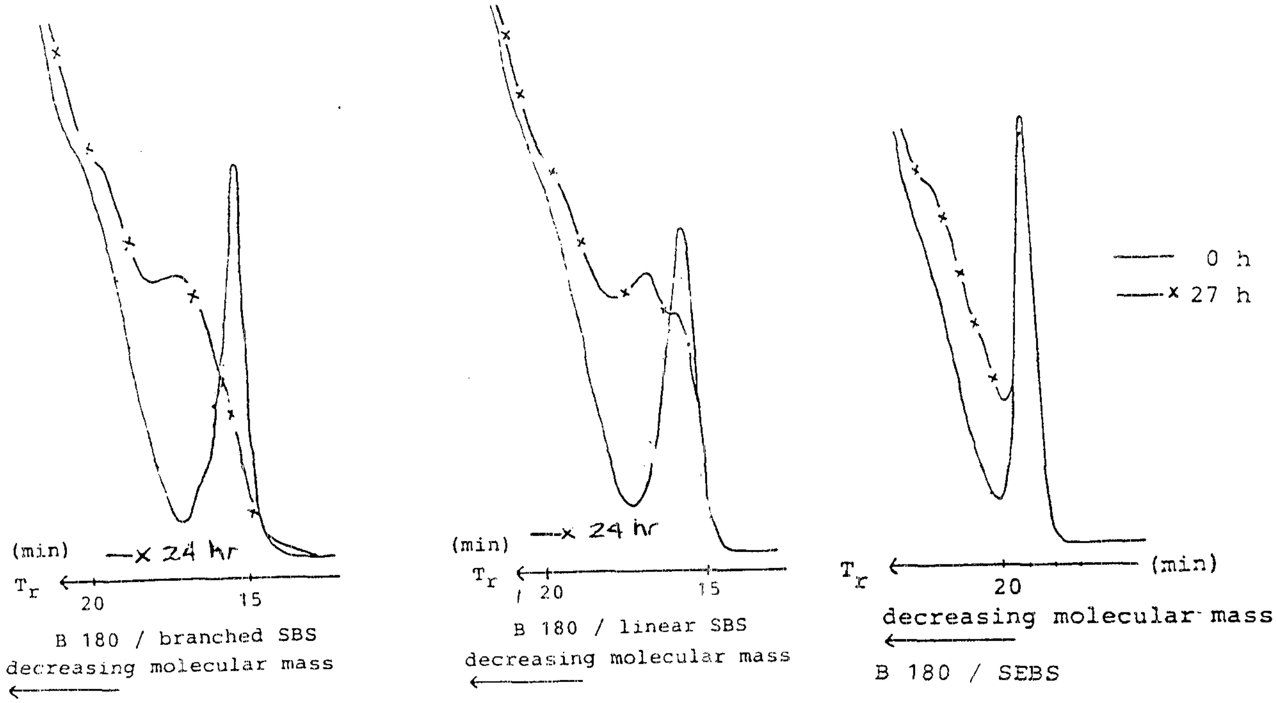


Figure 2.10. SEC Results for SBS and SEBS Modified Binders After Laboratory Aging (13).

Comparison of SBS Products

Table 2.4 shows a comparison of selected SBS products that have been used to modify asphalts. The first impression when extracting product information from the supplier literature was that all values were based on standardized tests. While this turns out to be a generally correct assumption, there is a broad range of test methods and conditions from which to choose when running any given test. For example, the melt flow index as reported by Shell was determined at 200°C with a load of 5 kg, and at 200°C/10 kg and 190°C/5 kg for the Dexco and Enichem products, respectively. The tensile strengths were determined at a loading rate of 250 mm/min (10 in/min) for Shell, at either 50 or 500 mm/min for Dexco (rate was not specified in the literature and the test method permits a choice), and unspecified for Enichem. Therefore, the only comparisons that can be made are for different products from the same supplier. Based on the information in Table 2.4:

1. Inclusion of an extender oil with the Shell SBS polymer reduces the tensile strength of the polymer by about half and increases the percent elongation at failure by about 80 percent.
2. The Kraton SEBS has approximately the same tensile strength as either the linear or radial SBS, however the percent elongation is lower by about 55 percent.

Table 2.4. Comparison of SBS Products.

Property	Kraton (Shell)				Vector (Dexco)		E Sol T (Enichem)	
	D1101	D1184	G1652	D4141	2518	2411	6302	T 161C
Polymer	SBS	$(SB)_n$[1]	SEBS	SBS	SBS	SBS	SBS	SBS
Structure	Linear	Radial	Linear	Linear	Linear	Radial	Linear	Radial
Styrene/Butadiene, % Wt.	31/69	30/70	29/71	31/69	29.5/70.5 32.5/67.5	30/70	30/70	30/70
Tensile Strength, psi	4,600	4,000	4,500	2,250	NA	4,000	2,870	2,600
Melt Flow Index	<1	<1	10	11	2.5 - 8.5	NA	NA	NA
% Elongation	880	880	500	1,300	NA	725	750	700
Oil Content	0	0	0	29	0	0	0	0
Molecular Wt.	NA	NA	NA	NA	NA	NA	100,000	193,000

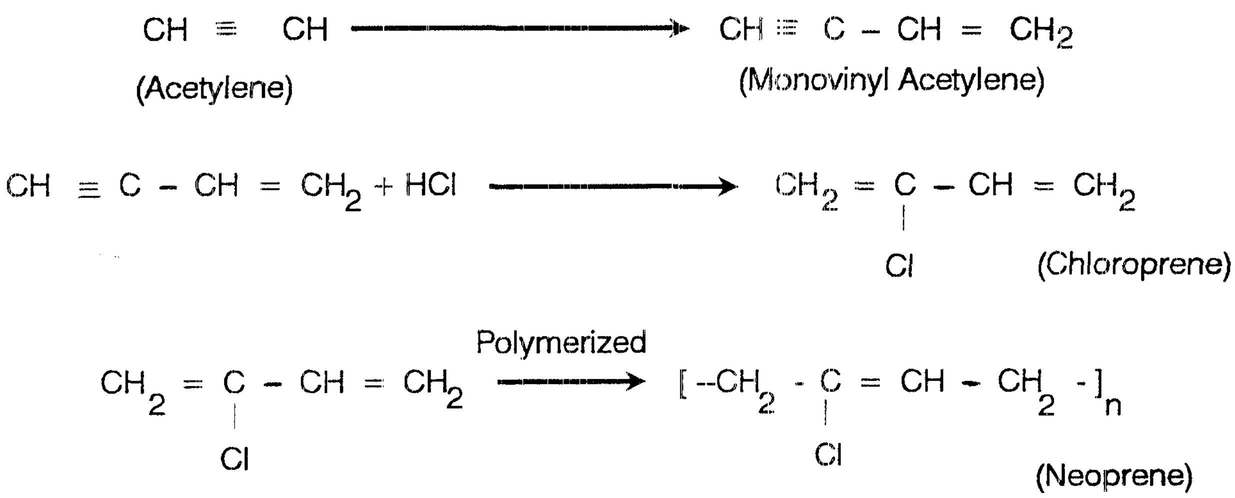
NA: Information Not Available

1: The $(SB)_n$ structure refers to each arm of the radial polymer; the final product is considered an SBS.

Neoprene

Neoprene, the generic name for polymers produced from chloroprene and produced by the Du Pont Company, is supplied in latex form. This is a colloidal dispersion of chloroprene polymers prepared by emulsion polymerization (14). The raw materials that form the basis for the production of neoprene are acetylene and hydrogen chloride (15). Acetylene is dimerized into a monovinyl acetylene in the presence of an aqueous catalyst (cuprous chloride). The monovinyl acetylene is then reacted with hydrogen chloride to form another monomer. This monomer was officially named "chloroprene" by the Du Pont Company in 1933 (15). Historically, an emulsion polymerization process is used in the presence of sulfur with a catalyst (potassium persulfate). Polymerization is then halted at the desired specific gravity by the introduction of thiuram disulfide.

The neoprene structure is extremely regular although its tendency to crystallize can be controlled by altering the polymerization temperature. The final polymer is comprised of a linear sequence of trans-3-chloro-2-butylene units which are derived from the trans 1,4 addition polymerization of chloroprene. (Figure 2.11) (15).



$$CH \equiv CH \longrightarrow CH \equiv C-CH=CH_2$$

$$CH \equiv C-CH=CH_2 + HCl \longrightarrow CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CH_2$$

$$CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CH_2 \xrightarrow{\text{Polymerized}} [-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_2-]_n$$

Figure 2.11. Chemical Process for the Manufacture of Neoprene (14).

The most common product used for asphalt cement modification is the Neoprene latex 735A which contains a low modulus, slow crystallizing polychloroprene homopolymer made in an anionic colloidal system (16). Basic information on the product lists the solids content of the latex at 45 percent by weight, a pH at 25°C (77°F) of 12, and an average particle size as 0.12 microns.

PLASTOMERS

Polyethylenes are alkane chains of $-[CH_2-CH_2]_n-$ and are essentially a high molecular weight paraffin (17, pg 188). The simple, regular shape of the polyethylene monomers takes on a crystalline structure in the bulk state. Traditionally, a crystal structure refers to a single continuous structure grown from one nucleus (17, pg. 43). The crystalline structure developed by polyethylene could more accurately be referred to as a polycyrstalline in which the structure is comprised of groups of single crystals grown from many nuclei (17, pg. 43). Polymer molecules of this nature develop by the long chains folding back and forth upon themselves at intervals of about 100Å; this action forms lamellae which are the final structure of a crystalline polymer (3,17).

The degree of crystallinity greatly influences the properties of the polymer. Polymers with high levels of structuring show high tensile strengths but little ability to deform before failure. Less structuring results in an increased ability of the material to flow. Polyethylenes, as is typical of paraffinic materials, are also relatively unreactive with most solvents.

All plastic additives used in flexible pavement construction are either polyethylenes or modified polyethylenes. Modifiers incorporated as copolymers are used to disrupt the crystalline nature of the unmodified polyethylene. This results in a more elastic, amorphous additive.

The function of these polymers within the asphalt is not to form a network but to provide plastic inclusions within the matrix (18,19). At cold temperatures, these inclusions are intended to directly improve the binder's resistance to thermal cracking by inhibiting the propagation of cracks. At warm temperatures, the particle inclusions should increase the viscosity of the binder and therefore the mixture's resistance to rutting.

Low Density Polyethylenes (LDPE)

Low and high density polyethylenes are generally defined as those having a specific gravity of about 0.915 to 0.94 and approximately 0.96, respectively. Since the lower densities represent less molecular packing, and hence less structuring, the low density polyethylenes are more suited to use in flexible pavement construction applications.

Novophalt has been the most commonly used LDPE product in flexible highway construction applications. Novophalt not only refers to a polymer modifier but the process of modifying the asphalt as well. Special proprietary processes have been developed by the company in order to overcome the natural tendency for the LDPE to separate out of the asphalt. Since this product is supplied as a modified binder rather than as a polymer additive, no information was available on the specific properties of the polymer.

Ethylene Vinyl Acetate (EVA)

EVA is a copolymer of ethylene and vinyl acetate. The inclusion of the vinyl acetate is used to decrease the crystallinity of the ethylene structure and to help make the plastomer more compatible with the asphalt cements (17,18 pg. 240). Copolymers with about 30 percent vinyl acetate are classified as flexible resins that are soluble in toluene and benzene (19). When the vinyl acetate percentage is increased to 45 percent, the resulting product is rubbery and may be vulcanized (i.e., crosslinked) with peroxides (19).

The Elvax 150W produced by the Du Pont Company was the most prevalent EVA asphalt modifier reported in the literature. The "W" behind the product designation indicates that the polymer contains an anti-blocking additive to reduce structuring of the polymer; no chemical information was available. The properties of the Elvax 150W were reported as: a melt flow index of 43 g/10 min (no testing conditions specified), 33 percent by weight of polymer was vinyl acetate, a tensile strength of 6.9 to 8.3 MPa (1,000 to 1,200 psi) at a loading rate of 500 mm/min (20 in/min.), and a percent elongation at failure of 900 to 1,100 percent (20).

Ethylene Acrylates

This general category includes ethylene methacrylate (EMA), and ethylene acrylate which are both formed from polyethylene polymerization processes using acrylic acid. Both of these modified polyethylenes are designed to reduce the crystalline structure, thus improving the ductile properties of the polyethylene. Little specific product information was available in the literature.

SUMMARY

The key points of this section are:

1. Polymers can have a wide range of polydispersity and structure. These characteristics can influence the stiffness of the polymer (e.g., crystalline polymers have stiff, non-ductile properties), and the ability of the polymer to form cross links within the asphalt cement (e.g., diblocks can only form "star" shapes while triblocks can form networks).

2. Elastomer chains can be mechanically broken when mixed with asphalt cements above about 135°C (275°F). This indicates there is a potential for degradation of polymers during normal hot mix operations.

3. Elastomer chains could eventually start to crosslink in asphalt cement when stored above about 200°C (°F). If a modified asphalt cement were stored at elevated temperatures for an extended period of time, this could lead to an unfavorable reaction in the storage tank (i.e., the material might not be able to be pumped).

4. The mechanism for improving the properties of asphalt cement with the inclusion of elastomeric polymer additives is based the assumption that the styrene domains disassociate at mixing temperatures and then reform as the mix cools, thus forming an elastic network within the asphalt cement. The actual occurrence of this mechanism has not been well established.

5. Products between manufacturers cannot be easily compared due to a wide range of test methods used to determine the polymer properties.

CHAPTER THREE

In order to understand how polymers interact with asphalt cements, it is important to first understand the chemical nature of asphalt cement. While the exact nature of asphalt chemistry has yet to be defined, several conceptual models have been presented that generally explain the behavior of asphalt cements. This section will present a brief background covering the development of the models, and key asphalt cement parameters.

CONCEPTUAL MODELS FOR ASPHALT CEMENT

Colloidal Model

Asphalt cement was originally considered to be colloid by Nellensteyn in 1924 (21). While the current definition of a colloid is a dispersion of discrete particles ranging in size from 1 to 1,000 nm in a continuous phase, original concepts of colloidal systems were much less well-defined with respect to the size of discrete particles (5,21). Both the current definition of colloids and the early asphalt models consider the boundaries between the particles and the continuous phase to be discrete.

Nellensteyn referred to the discrete particles as asphaltenes which were defined as non-volatile, highly polar, friable particles precipitated from crude oils in the presence of added *n*-alkanes. Since asphaltenes are not volatile, they are not removed during the petroleum refining processes. This means that asphaltenes should be concentrated in asphalt cements since asphalts are the residuals (i.e., resids) left after refining has been completed. This fraction of the asphalt cement was found to have viscosities much greater than the composite system and to contain heteroatoms of nitrogen, sulfur, oxygen, and various metals. Asphaltenes were considered to be dispersed in a continuous maltene, or petrolene, phase which was defined as the low viscosity components remaining after the asphaltenes have been removed. The viscosity of the whole asphalt cement was assumed to reflect the various percentages of asphaltenes and maltenes.

Early research by Mack (1932) and Labout (1950) tended to confirm this model by reporting that asphaltenes formed agglomerations within the maltene phase (21). The size of the agglomerations were apparently controlled by the aromaticity of the maltenes. High aromaticity led to well dispersed asphaltenes and was referred to as a sol-type asphalt cement. These materials exhibited high temperature susceptibilities, high ductilities, low complex flows, and low rates of age hardening. Low aromaticity of the maltenes resulted in larger agglomerations of asphaltenes and was referred to as a gel-type asphalt cement. These materials showed physical properties with low temperature susceptibility, low ductilities, significant signs of thixotropy, and significant elastic components, and rapid age hardening.

Other researchers used new technology in attempts to either confirm or refute the colloidal model concept. Herzog, et al. (1988) and Sengelt et al. (1990) used X-ray absorption spectroscopy to show that large structural units of molecules existed in asphalt (21). Ravey et al. (1988) used small angle X-ray scattering techniques to show individual asphaltene particles were fairly uniform between crude sources with a disk-like shape having a diameter between 1 and 10 nm and a thickness of about 1 nm.

Various measures of molecular weights were also used to identify the role of asphaltenes within the asphalt cement. Speigth (1984) showed that results from an ultra centrifugation indicated very large molecular weight components were present in asphalt (21). A comparison of these results with vapor pressure osmometry (VPO) showed that the molecular weights, M_n, varied substantially; the magnitude of the variations were solvent dependent. The molecular weights for aspaltenes in polar solvents such as nitrobenzene were much lower than in non-polar solvents such as toluene. Boduszynski (1991) used mass spectrometry to conclude that lower boiling point fractions had lower molecular weights than higher boiling point fractions (21,22). However, the high boiling point fractions showed lower molecular weights with mass spectrometry than with VPO; the researchers interpreted these results as evidence of asphaltene association phenomena.

Variations on the Colloidal Model

In 1940, Pfieffer and Saal expanded the basic discrete two-component colloidal system to assume that the dispersed phase was composed of an aromatic core surrounded by layers of increasing less aromatic molecules dispersed in a relatively aliphatic solvent phase (21). Pfieffer and Saal assumed a continuum from low to high aromaticity with asphaltenes having the lowest aromaticity followed by the less aromatic portions of the maltenes and then the naphtenic and aliphatic components (i.e., the high aromaticity portions of the maltenes).

In 1988, Park and Mansoori compared two models: 1) the steric colloidal model, and 2) the continuous thermodynamic model (21). The steric colloidal model assumed the existence of asphaltenes, whose associations were stabilized by resins. This model assumed that absorbed resins on the surface of the asphaltenes act as repellant forces, which then prevent associations between asphalt molecules. When *n*-alkanes are added, the resins are desorbed which results in the precipitation of the asphaltenes. This model is similar to the Pfieffer and Saal model in that no discrete boundary between two phases was assumed.

The continuous thermodynamic model is more of a solution model than a colloidal model. This model considers the crude oils to be solutions of organic materials of widely varying molecular weights and polarities, the mutual solubility of the system being dependent upon the ranges of polarity and molecular weights. When the system stability is disrupted by the addition of *n*-alkanes, associations are encouraged which eventually lead to the flocculation of the portion of the asphalt referred to by other researchers as asphaltenes. In this model, a homogenous solution goes to a colloidal system when the chemical balance of the system is disturbed.

Solution Models

In 1994, Little et al. used various rheo-optical methods to compare the traditional colloidal or micelle models with the hypothesis that asphalt cement was a solution in which the asphaltenes were dissolved in the oil-resin phase. Small angle X-ray scattering (SAXS) was used to show a lack of large colloidal structures and suggest the dominance of linear type structures instead. These findings were assumed to refute the colloidal model concepts.

Infrared spectral analysis (IR) results were used to represent the length of the methylene chain structure, which was assumed to be the dominate linear structure, as the ratio of the peak values for methylene (CH_2) to methyl (CH_3) (Figure 3.1) (23). This was used as method of evaluating the representative length of the methylene chains in asphalt cement. The authors used this ratio as a representation for molecular weight in the reptation model that relates the zero shear viscosity, η_o, to molecular weight by:

$$\eta_0 = MW^{3.4}$$

Their results plotted as the log of the zero shear viscosity versus the log of the $(CH_2)/(CH_3)$ ratio indicated that the slope of this relationship was 4.2 instead of 3.4 (Figure 3.2) (23). The authors used this relationship to conclude that asphalt cements cannot be considered truly polymeric solutions.

Although not specifically stated in the authors' paper, this representation for molecular weight appears to be equivalent to M_n since it does not seem to account for the range of molecular dispersity in the asphalt cement. However, previous research in the polymer field has indicated that when there is a large polydispersity index, as should be expected in asphalt cements, the appropriate molecular weight for the reptation model should be at least M_w and preferably the third moment molecular weight, M_z (24, 25). Conversely, if the moment of the molecular weight is not increased to reflect a large dispersity, then an increase in the slope of the reptation model should be expected (24, 25). Based on this information, this reviewer disagrees with the authors' conclusions and believes the test results support considering asphalt cements polymeric solutions.

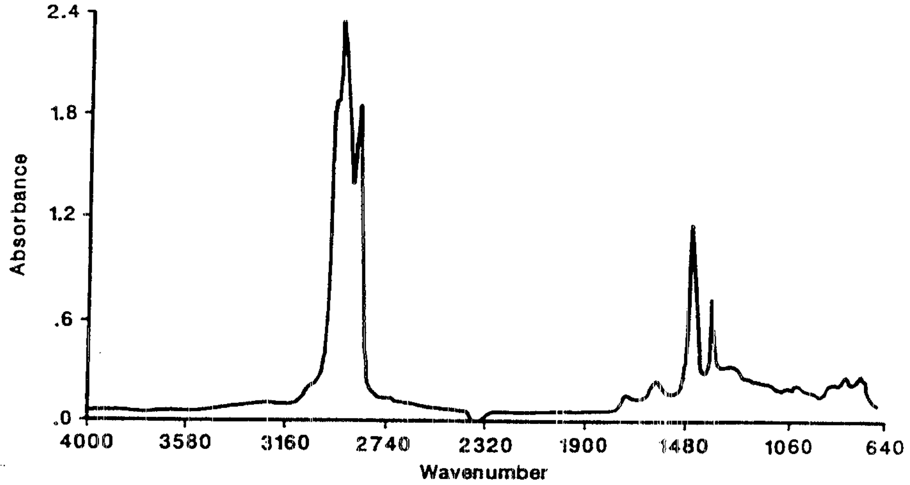


Figure 3.1. Typical IR Results Used by Little, et al. to Represent Molecular Weight (23).

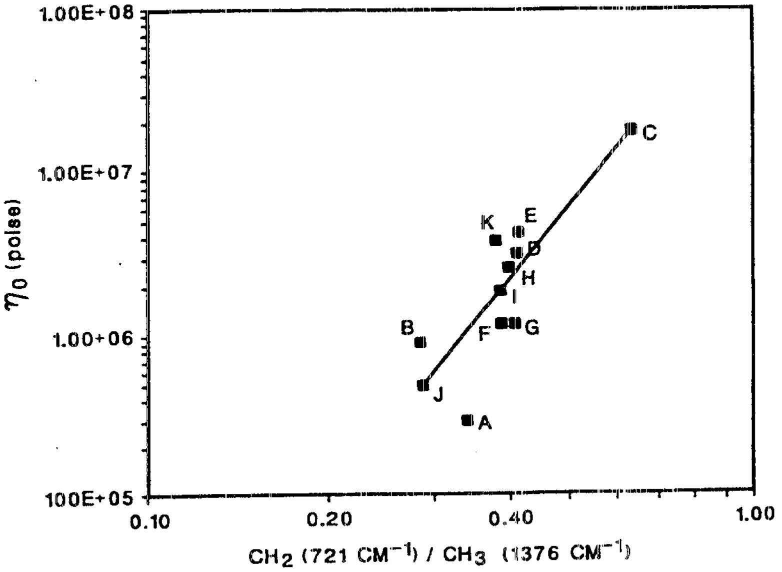


Figure 3.2. Relationship Between Representative Length of Methylene Chains and the Zero Shear Viscosity (23).

Strategic Highway Research Program (SHRP) Model

In 1994, Robertson et al. used the above information to formulate the original model for the SHRP effort. The original model, named the microstructural model, is essentially an extension of the colloidal model. In this model, the solvent phase consists of relatively aliphatic non-polar molecules low in heteromatoms except for sulfide, thiophenic sulfur, ether, and ester oxygen. The dispersed phase, which forms the microstructure, was assumed to be comprised of the more polar, aromatic asphaltene-like molecules. These molecules should be polyfunctional and capable of forming associations through hydrogen bonding, dipole interactions, and pi-pi bonds.

Robertson et al. hypothesized that if a colloidal model was indeed applicable to asphalt cements, then one of the models from other areas of colloidal science should be applicable. These researchers listed five of the most likely models (lyophobic sols, gels, micellar solutions, microemulsions, and liquid crystals) and then promptly eliminated each of these for one reason or another. The lyophobic sol model assumes that dispersed particles which comprise only 1 to 2 percent of the total colloidal volume have little or no affinity for solvents. This model would not be applicable to asphalt cements as the percentage of the asphaltene fraction has been shown to be well above 2 percent in paving grade asphalt cements. The gel model assumes that a three-dimensional network with rubbery properties is present; this is not the case for unmodified asphalt cements. The micellar solution model was eliminated because it was questionable if micelles could solely account for the level of structuring seen in asphalt cements. The microemulsion model was eliminated because it could not sufficiently account for steric hardening. The liquid crystals model assumes that there is a long range ordering of rod or disk shaped molecules as a result of polar interactions, but no tendencies for a long-range ordering of molecules in asphalt cement have been shown.

All of these investigations led to the hypothesis that since none of the colloidal models fit the behavior of asphalt cements, the only reasonable assumption for a model was that asphalt cement was a "relatively homogenous and randomly distributed collection of molecules differing in polarity and molecular size" (21). While not specifically stated, this appears to be just a rewording of the continuous thermodynamic model proposed by Park and Mansoori in 1988.

The final model, supported by rheological results (discussed in the following chapters) was named the dispersed polar fluid (DPF) model and describes asphalt cement as a continuous, three-dimensional association of polar molecules dispersed in a fluid of non-polar or relatively low-polarity molecules (23). Polar functional groups attached to the hydrocarbon molecules consist of sulfur, nitrogen, and oxygen heteroatoms and should behave either as acids or bases and be capable of forming dipolar, intermolecular bonds of varying strengths. It was assumed that the viscoelastic properties of the asphalt cement should be a result of these bonds being continually formed and broken when the system is stressed.

METHODS OF MEASURING ASPHALT COMPONENTS

Since most asphalt cement models have concentrated on the colloidal concept with asphaltenes being the major contributor to viscosity, most research has historically dealt with methods of quantifying the percentages of asphaltenes and maltenes. The two oldest tests for measuring these parameters are the Rostler-Sternberg chemical precipitation and Corbett selective adsorption/desorption methods. Newer methods for separating asphalt cements include ion exchange chromatography (IEC) and size exclusion chromatography (SEC). One method, mapping solubility profiles of the asphalt, was found that classifies components of the whole asphalt without separation.

Rostler-Sternberg

The Rostler-Sternberg method separates the whole asphalt cement into five fractions: asphaltenes (A), nitrogen base resins (N), first acidifins (A_1), second acidifins (A_2), and paraffins (P) (26). The asphaltenes are the highly polar fraction of the asphalt cement that are precipitated out with the addition of an *n*-alkane solvent (usually *n*-heptane or *n*-pentane). The nitrogen base resins, N, are the most reactive component and contain essentially all of the nitrogen-containing compounds (26). The first acidifins, A_1, are the unsaturated resinous hydrocarbons; the second, A_2, acidifins are only slightly unsaturated. The paraffins, P, are saturated hydrocarbons and considered an unreactive component in asphalt. The Rostler parameter is a ratio of the mostly unsaturated to the more saturated components:

$$Rostler\ Parameter = \frac{A_1 + N}{A_2 + P}$$

This parameter was used to separate the 400 asphalts obtained in the mid 1950's for the Bureau of Public Roads reference library into the five groups shown in Table 3.1 (26):

Table 3.1 Classification of Asphalt Cements by the Rostler Parameter.

Group Number	Range of Rostler Parameter
Group I	minimum (0.54) to 1.00
Group II	1.01 to 1.20
Group III	1.21 to 1.50
Group IV	1.51 to 1.70
Group V	1.71 to maximum (2.24)

A variation of the Rostler parameter is the Gotolski parameter: (26):

$$Gotolski = \frac{A_1 + A_2 + N}{A + P}$$

This is a ratio of the asphalt components that inhibit structuring to those that form a structure. Research showed that the Rostler parameter was more closely related to temperature susceptibility with either high or low values indicating poor performing binders. The Gotolski parameter was related more to changes in the asphalt cement due to aging with high values indicating poor performance.

Corbett

The Corbett method initially separates the asphalt into two general components: asphaltenes (A) and maltenes. The maltenes are further separated into three fractions: saturates (SAT), naphthene aromatics (NA), and polar aromatics (PA). The saturates in the Corbett analysis are similar to the paraffins in the Rostler. The naphthene aromatics are considered softening agents in the asphalt cement and a contributor to the change in binder properties during aging. The polar aromatics are related to both ductility and changes due to aging. As with the Rostler parameter, a ratio of these components was used to provide some information as to the binder performance. The Gaestel index (21):

$$GI = \frac{A + SAT}{PA + NA}$$

is a ratio of the structuring components of asphalt cement to the components thought to inhibit structuring which is just the inverse of the Golotski index for the Rostler parameter. A higher GI should be indicative of a more defined structure within the asphalt cement. This ratio appears to be similar to the Gotolski parameter. Therefore lower values of the Gaestel index should indicate a poorer performance due to aging.

The GI is a specific form of the more general colloidal instability index, I_c:

$$I_c = \frac{Asphaltenes + Saturates}{Resins + Aromatic\ oils}$$

which has been used to identify asphalt cements that are compatible with polymer additives. Values of I_c of less than about 0.15 indicate good compatibility between asphalt cements and polymers (27, 28). This low of a number indicates that the structure-inhibiting components are the dominant components of the asphalt. If the polymer absorbs some of these fractions during blending with the asphalt cement, the higher initial percentage might possibly still be sufficient to prevent floculllation of the asphaltenes. A second possibility is that the polymer merely needs a certain amount of this fraction in order to effectively swell and blend within the asphalt cement.

Variations of the Corbett fractionation process have also been used to establish ranges of key properties for each fraction. Marvillet found that between 23 to 33.7 percent of the whole asphalts were comprised of maltenes with molecular weights of 720 g/mole for both M_n and M_w (29). Whole asphalts were between 45.5 and 56 percent soft asphaltenes with M_n and M_w of about 855 and 930 g/mole, respectively. The hard asphaltenes were between 14.3 to 22.2 percent of the total asphalt with M_n and M_w of 3,340 to 3,350 g/mole and 9,390 to 14,800 g/mole, respectively. These values indicated that the hard asphaltenes will have the largest range of molecular sizes. That is, the M_w/M_n ratio is the greatest for this fraction; this indicates a wider distribution of molecular sizes.

Based on cone and plate rheometry, the non-volatile maltene portion had a strong shear rate dependency with viscosities at least 3 orders of magnitude lower than the whole asphalt. The soft asphaltenes were not shear rate dependent at high temperatures, however, as the test temperature decreased the shear rate dependency increased. The viscosities for this fraction were only about 1 order of magnitude lower than those for the whole asphalt cement. No information was presented for the hard asphaltenes, however since this was the only fraction not represented, it can be assumed that the viscosity for this fraction was significantly higher than that for the whole asphalt. This conclusion is based on the fact that the viscosities of the other two fractions are both significantly less than the whole asphalt, leaving the hard asphaltene fraction to make up the difference.

Ion Exchange Chromatography (IEC)

IEC, like the Rostler or Corbett approaches, is a method of separating the asphalt cement into various fractions. IEC fractions are: strong acids (SA), strong bases (SB), weak acids (WA), weak bases (WB), and neutrals. The strong acids represent the more aromatic, higher molecular weight portions. The neutrals represent the less aromatic, fluid portion of the asphalt cement. These two fractions represent the extremes within the asphalt cement.

Whole asphalt cements had percentages of both strong acids and bases combined ranging from 10 to 31 percent; the neutrals were more than 50 percent of all asphalts (30). Typical solubility parameter, δ, ranges of whole asphalt cements were between 9.03 and 9.35 $(cal/cm^3)^{1/2}$ while ranges for the strong acids and neutrals were 10.82 to 11.67 and 8.99 to 9.44 $(cal/cm^3)^{1/2}$, respectively. Solubility parameters are an indication of how stable the mixture of components will be; the closer the solubilities, the more stable the mixture. The M_n molecular weight for whole asphalts ranged from 700 to 1,300 g/mole; M_n was between 1,080 to 3,040, and 510 to 1,140 g/mole for the strong acids and neutrals, respectively. While this method has been used to separate asphalts for analysis, Youcheff found that properties for the fractions did not necessarily reflect the properties of the whole asphalt cement (30). He took this as an indication that separating asphalt cement into components disrupted the natural molecular associations and hence the natural structure of the asphalt cement.

Size Exclusion Chromatography (SEC)

SEC is essentially a sieve analysis for asphalt cement molecules. Briefly, a small sample of asphalt is dissolved in a solvent and then the solution is filtered through a column packed with materials with different size pores. As the solution flows through the column, the largest particles flow out first as they have only a few paths for flow available to them. The smaller the particles, the longer their path to the exit. This is because the smaller the asphalt cement particles have a greater percentage of pores in the packing material that they can fit through. This increases their path length and hence the time to exit. The size of the particles in the effluent is monitored with some means of determining the concentration of solute in the effluent, and then the concentrations are plotted against time. Because the size of the molecules in the effluent will reflect molecular associations and the type of solvent used to dissolve the asphalt will influence these associations, results are only comparative for materials tested under the same conditions.

SHRP research by Jennings et al. used a High Performance Gel Permeation Chromatography (HP-GPC) column method with tetrahydrofuran as the solvent to determine the molecular size distributions for a wide range of asphalt cements (31). The concentration of the solute was measured with a range of ultraviolet wave lengths. Figure 3.3 shows that the shape of the curve varies with the wave length of the detector. The sum of the areas for all of the curves (i.e., chromatograms) shown in Figure 3.3 was termed the conjugated volume, CV_t; a larger value indicated more associations, or higher aromaticity, in the asphalt. A ratio of the area from the 340 nm to the 280 nm curves was termed the total conjugated index, CI_t, and assumed to represent smaller chromophores. Based on the shape of these curves, Jennings et al. separated asphalt cements into four groups (Table 3.2).

Table 3.2. Grouping of Asphalts Based on SEC (After Ref. 31).

Group	Approx. Initial Elution Time, Min.	Approx. Peak Width, Min.	Time of Primary Peak, Min.[2]	CV_t	CI_t
Group 1	14 -15.2	15.5 - 18.0	20.5 - 21.5	23.8[3] - 28.3	0.243 - 0.340
Group 2	12.1 - 13.2	18.0 - 19.5	20.5 - 22.0	22.6 - 28.6	0.274 - 0.352
Group 3[1]	12.2	19.0	24.5	20.6	0.245
Group 4	12.2 - 13.3	16.8 - 18.3	20.0 - 22.0	22.7 - 23.5	0.245 - 0.345

1: Only one asphalt cement was included in this group.
2: Estimated from graphs.
3: One anomaly of 17.7 was noted.

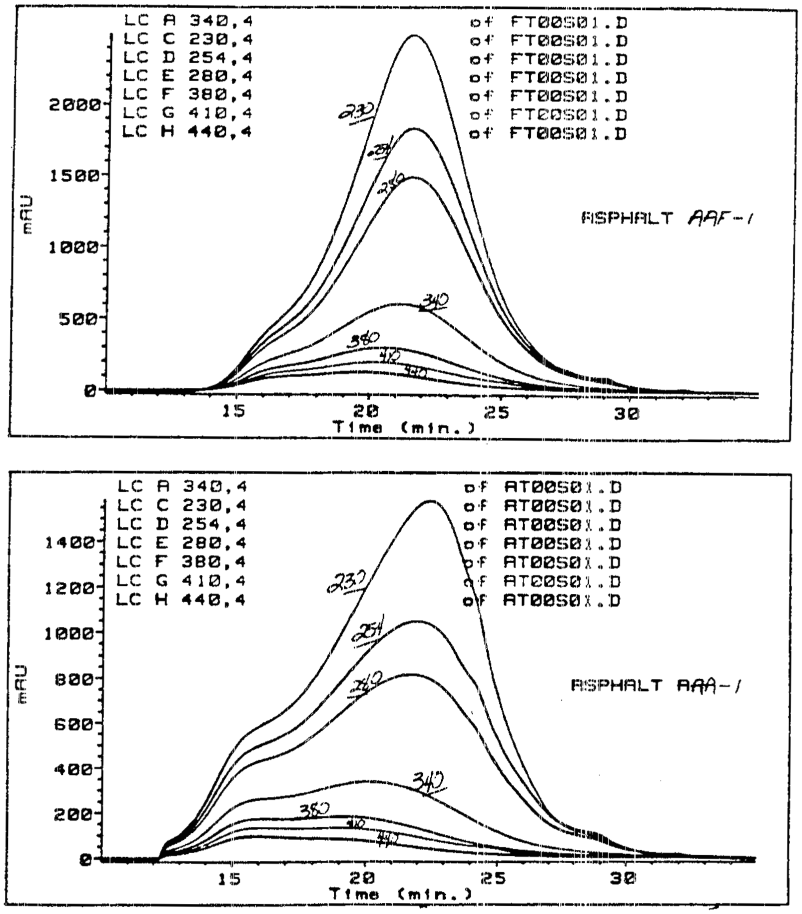
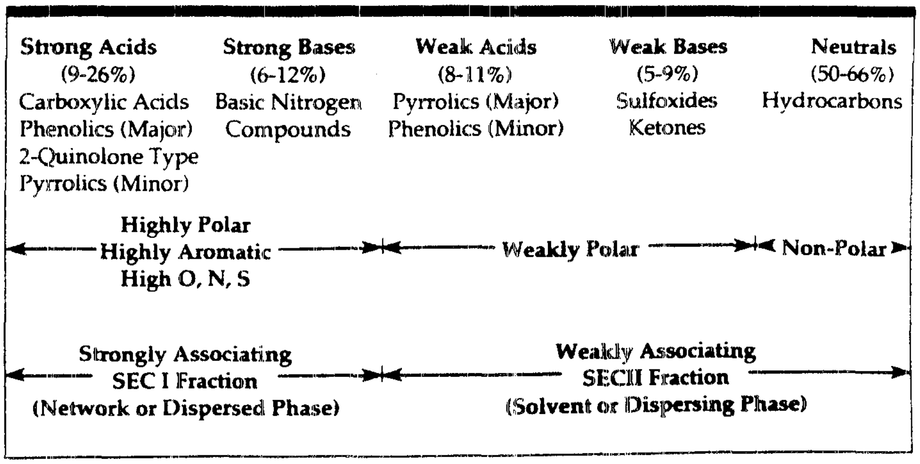


Figure 3.3. Typical SEC Results (31).

Asphalts in Group 1 show narrow peak width distributions and an overall smaller molecular size as indicated by the longer initial elution times. The major difference between Group 1 and Group 2 is the presence of larger molecules (shorter initial elution times) and the presence of a strong secondary shoulder in the Group 2 asphalts (Figure 3.3). The presence of this secondary peak was assumed to indicate a second grouping of associated molecules. The presence (or absence) of this peak cannot be detected by the parameters shown in Table 3.3; a visual assessment of the actual data is required. Group 3 has wide distribution of molecular sizes as seen by the low CV_t, but the peak value occurs at approximately 24 minutes; this would reflect a very small molecular size. Group 4 has relatively large molecules as seen by the shorter elution times as well as a narrow peak width range.

Youcheff also used SEC with toluene solvent to determine the characteristics of IEC fractions, however he only separated the SEC chromatograph into two regions: SEC I and SEC II. The SEC I region represents molecules that are eluted first; the cut off between SEC I and SEC II was defined as the onset of fluorescence under 350 nm light. Materials in the SEC I region are generally friable with high aromaticity, and higher molecular weights; this would be analogous with the historical definitions of asphaltenes. The percentage of strong acids and strong bases found in IEC separation were roughly equivalent to the percentage of SEC I (approximately 10 to 31 percent of the whole asphalt cement). The SEC II fraction, on the other hand, is fluid at room temperature, less polar, less aromatic, and have much lower solubility parameters; this would be analogous to the historical definitions of maltenes. Figure 3.4 shows the relationship between IEC, SEC, and asphalt components (30).



Strong Acids	**Strong Bases**	**Weak Acids**	**Weak Bases**	**Neutrals**
(9-26%)	(6-12%)	(8-11%)	(5-9%)	(50-66%)
Carboxylic Acids Phenolics (Major) 2-Quinolone Type Pyrrolics (Minor)	Basic Nitrogen Compounds	Pyrrolics (Major) Phenolics (Minor)	Sulfoxides Ketones	Hydrocarbons

Highly Polar
Highly Aromatic ←→ **Weakly Polar** ←→ **Non-Polar**
High O, N, S

Strongly Associating
SEC I Fraction ←→ **Weakly Associating**
SECII Fraction
(Network or Dispersed Phase) **(Solvent or Dispersing Phase)**

Figure 3.4 Relationship Between IEC, SEC, and Asphalt Components (30).

Solubility Profile

Only one method of characterizing the whole asphalt cement was found. In 1984, Hagen et al. used the energy density for hydrogen bonding or associative interactions per molar volume, δ_r^2, and the sum of the London dispersion forces and dipole-dipole polar interactions per molar volume, δ_V^2 to map the solubility profiles of asphalt cements. The solubility of the material is the plot by (δ_r, δ_V) coordinates of the solvents in which the asphalt is soluble and the corresponding degree of solubility. The relationship between key parameters are given by:

$$\textit{Total Energy} = \Delta E = \Delta E_D + \Delta E_P + \Delta E_h$$

$$\textit{Energy Densities per Molar Volume} = \frac{\Delta E}{V} = \frac{\Delta E_D}{V} + \frac{\Delta E_P}{V} + \frac{\Delta E_h}{V}$$

where

ΔE_D = energy density due to London dispersion forces
ΔE_P = energy density due to dipole-dipole interactions
ΔE_h = energy density due to hydrogen bonding

or:

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_h^2$$

where

$\delta_r^{\ 2} = \delta_h^2 =$ energy density per molar volume of hydrogen bonding or associative interactions, $(\text{cal/cm}^3)^{1/2}$

$\delta_V^2 = \delta_D^2 + \delta_P^2 =$ energy density per molar volume due to London dispersion forces (i.e., non-polar interactions) and the dipole-dipole polar interactions, $(\text{cal/cm}^3)^{1/2}$.

The authors identified key asphalt components as information shown in Figure 3.5 and then separated the information into four general regions (Figure 3.6) with the cyclic saturates, napthene-aromatics, acid derivatives, and phenolic derivatives represented by regions 1 through 4, respectively (32).

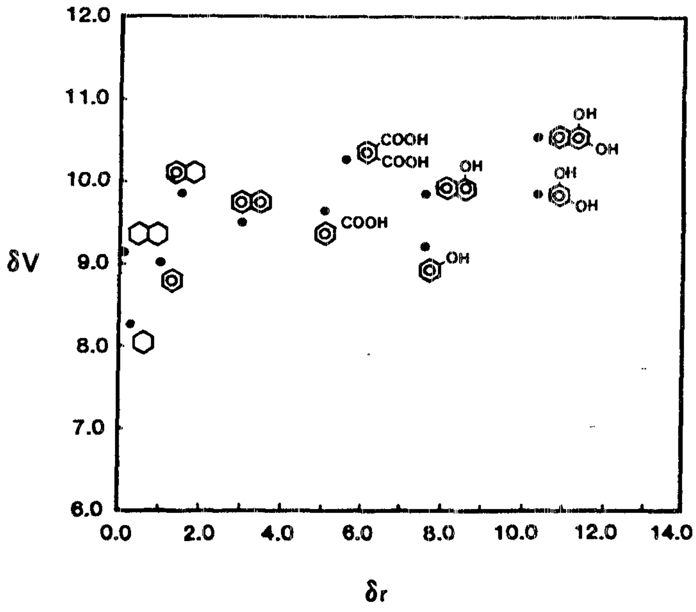


Figure 3.5. Selected Values of Solubility Parameters Applicable to Asphalt Cement Components (32).

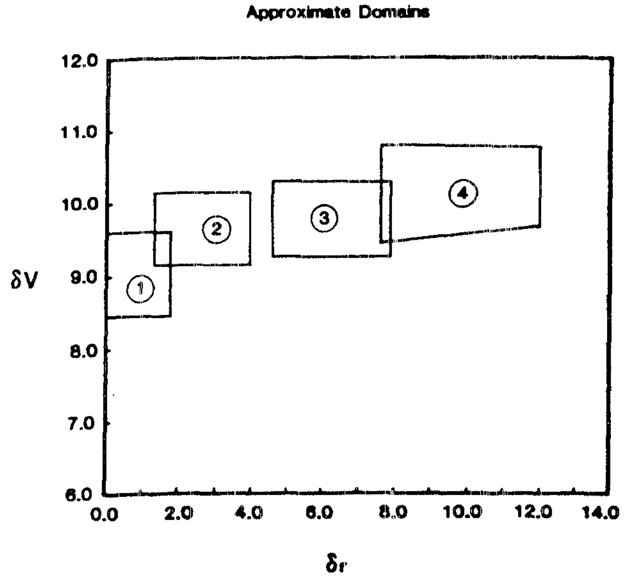


Figure 3.6. General Regions of Solubility Parameters Based on Changes in Asphalt Due to Aging (32).

Selected asphalts were evaluated using a range of 22 solvents and a numerical methods solution of an equation representing an elliptical cone to produce a solubility map of an AC 3 and an AC 4 (Figure 3.7) (32). The numbers shown in this figure represent the percent of the asphalt that was soluble in a solvent with given solubility parameter coordinates.

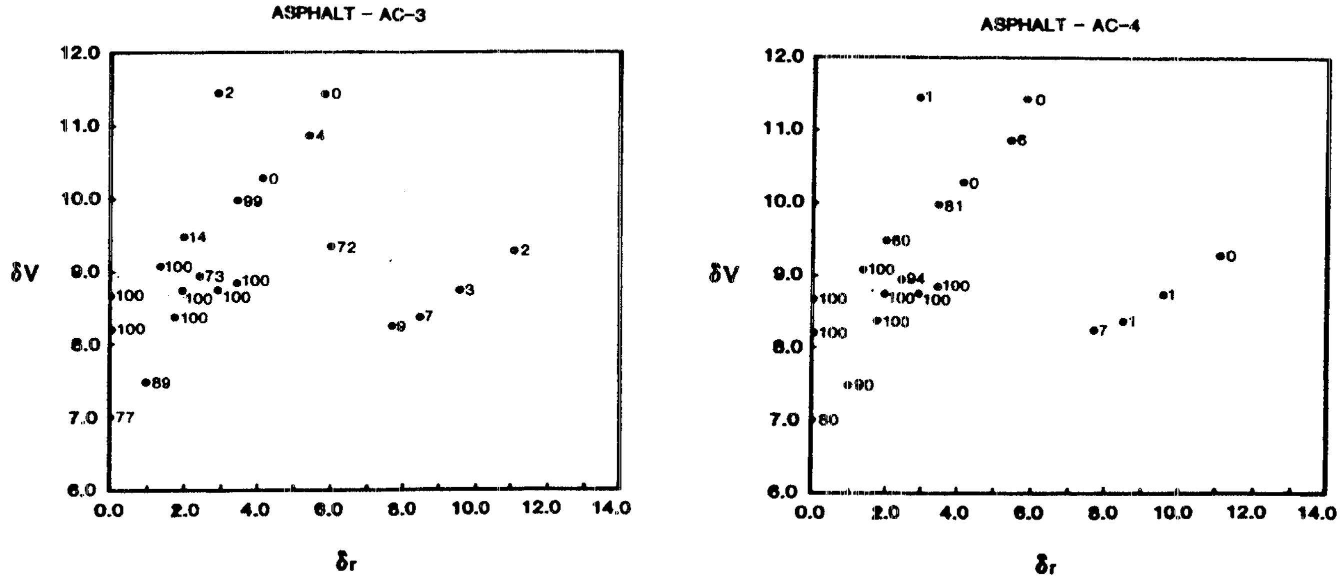


Figure 3.7. Solubility Map for Two Asphalts (31a).

Information on asphalt cement solubility parameters is important because compatible solubilities between the asphalt and the polymer defines the percent of polymer swell, level of polymer dissolution, and the morphological structure of the polymer within the asphalt matrix.

SUMMARY

The key points presented in this chapter were:

1. The most current asphalt cement model represents it as a dispersed polar fluid.

2. Rostler and Corbett fractionations are methods of separating the asphalt based on the polarity of the fractions. The Rostler parameters called the paraffins and asphaltenes represent components that would like to form a structure within the asphalt cement. The first acidifins, second acidifins, and nitrogen bases are components which inhibit the formation of a structure within the asphalt cement. These compare with the asphaltenes and saturates (structure forming), and the polar and napthene aromatics (structure inhibiting) as determined by the Corbett analysis.

3. Ratios of the separated components are then used as a single parameter for characterizing a particular asphalt cement. Common ratios include the Rostler (unsaturated / saturated), Gotolski (structure inhibiting / structure forming), and Gaestel (structure forming / structure inhibiting).

3\. SEC is a method of separating asphalt based on the apparent molecular size of the components. The apparent size is dependent upon the polarity of the solvent used to dissolve the asphalt. The SEC analysis has been divided into two regions with the SEC I region representing the structure forming components and SEC II representing the structure inhibiting components.

4. Solubility profiles map the ranges of solubility parameters of the whole asphalt. No separation of the asphalt components is needed.

CHAPTER FOUR

Many researchers over the years have attempted to correlate key binder properties to either laboratory-developed mixture test results or actual field performance. This section will identify binder and mixture test methods that either have or should have potential as field performance indicators. The theory, assumptions, and their applicability to modified binders will be discussed for selected test methods. A discussion of traditional tests such as penetration, ductility, and softening point will not be included in this section.

In general, both binder and mixture test methods can be separated into three general categories: 1) temperature susceptibility, 2) permanent deformation characteristics, and 3) low temperature behavior. Table 4.1 summarizes applicable test methods that can be quickly implemented and evaluated. Tests such as the SHRP simple shear and constrained beam tests were eliminated as not having fully developed testing protocol and/or the equipment was not readily accessible.

Table 4.1. Key Binder and Mixture Test Methods.

Category	Binder Tests	Mixture Tests
Temperature Susceptibility	Dynamic Mechanical Testing (Frequency Sweeps, Different Temperatures)	Resilient or Dynamic Modulus at Different Temperatures
Permanent Deformation	Viscosity: Vacuum Viscometers Dynamic Shear Viscosity Ring and Ball Softening Point Yield Stress from Dynamic Shear Testing	Axial Creep Testing: Static Repeated Load
Low Temperature Behavior	Development of Glass Transition Temperature, T_g: Dynamic Mechanical (Torsional) Testing Dilatometry Bending Beam Rheometry Direct Tension Fraas Brittle Point	Indirect Tensile Creep

TEMPERATURE SUSCEPTIBILITY

Dynamic Mechanical Rheometry (Binder Testing)

Dynamic mechanical rheometry subjects a specimen to a constant angular stress or strain and measures the corresponding strain or stress response. These measurements are then used to calculate such fundamental properties as the complex, loss, and storage moduli, and the loss tangent. Figure 4.1 shows the specimen configurations most commonly used for evaluating asphalt cements. The parallel plate configuration, referred to by SHRP as the dynamic shear rheometer, is used to determine properties at intermediate (0 to 36°C) to warm (46 to 70°C) temperatures; the diameter of the plate size is increased for warmer test temperatures. The torsion bar configuration is used to determine properties at cold temperatures (typically below 0°C). The results from all three configurations are combined to produce a master curve based on a full range of anticipated in-service temperatures.

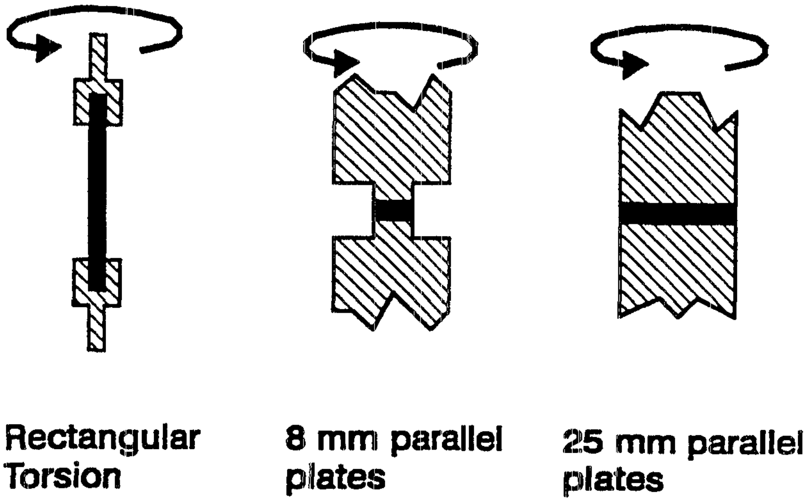


Figure 4.1. The Most Common Configurations Used for Dynamic Mechanical Rheometry for Asphalt Cements (33).

Dynamic Shear Rheometer (DSR)

The working equations for dynamic shear testing are (34):

$$\textit{Shear Strain} = \gamma = \frac{\theta R}{h}$$

$$\textit{Shear Rate} = \dot{\gamma}_R = \frac{\omega R}{h}$$

$$\textit{Shear Stress} = \tau = \frac{M}{2\pi R^3}\left[3 + \frac{dln\ M}{dln\ \dot{\gamma}_R}\right]$$

where

γ = shear strain at the edge of the plate

θ = angle of rotation

R = plate diameter, cm

h = gap height, cm

ω = angular frequency, rad/sec

M = torque, g-cm.

dln M/dl γ_R = 1 within the linear viscoelastic region

The complex modulus, G*, is then just:

$$G* = \frac{\tau}{\gamma}$$

The loss modulus, G", and the storage modulus, G', are components of the complex modulus:

$$G'' = G^* \sin\delta \; ; \qquad G' = G^* \cos\delta$$

where δ is the phase angle between the peak stress and the peak strain response.

Selected points from the dynamic shear frequency sweep data have been included in the new SHRP binder specification for characterizing the original, rolling thin film oven aged, and pressure aging vessel (PAV) aged binders. Specific procedures for using this test method have been developed by the American Association of State Highway Transportation Officials (AASHTO) (provisional test method TP-5) (35). A thorough review of the sample preparation, and test method procedures detailed in this method was conducted at the University of Minnesota and has been reported in a separate document (36).

Dynamic Torsion Bar Rheometry

The working equations for the torsion bar configuration are (34):

$$Stress = \tau = 1000\, M\, G_c \left[\frac{3 + 1.8\frac{T}{W}}{WT^2}\right]$$

$$Strain\ Rate = \dot{\gamma} = \omega\, \frac{T}{L}\left[1 - 0.378\left(\frac{T}{W}\right)^2\right]$$

where

M = Torque, g-cm

G_c = conversion constant: 980.7 if dynes/gm or 98.07 if Pa

T = thickness of bar, mm

W = width of bar, mm

L = length of bar, mm

ω = angular frequency

The complex, loss, and storage modulus are calculated as described in the preceding section.

SHRP Modeling of Master Curves

SHRP researchers have used the concept of a master curve developed from DSR data to identify four isolated parameters hypothetically common to all asphalt cements (Figure 4.2) (33). These parameters were used to develop equations for modeling the overall response of the binder. The four parameters, used in the development of a linear viscoelastic (LVE) model, were: the rheological index, R, the glassy complex modulus, G_g, the steady-state viscosity, η_o, and the crossover frequency, ω_c.

The rheological index, R, was defined as the log of the glassy complex modulus minus the log of the shear modulus at the crossover frequency. The SHRP researchers considered this a shape factor that described the width of the upper portion of the master curve and the temperature susceptibility of the binder. As R increases, the temperature susceptibility of the asphalt cement should decrease. The glassy modulus, G_g was defined as the maximum modulus that any binder could obtain at either very fast frequencies or very cold temperatures and was shown to be approximately 1 GPa for all unmodified binders. The steady state shear viscosity was interpreted as the slope of the master curve at low frequencies (Figure 4.2). The crossover frequency, ω_c, was described as the point at which the loss modulus is equal to the storage modulus. Based on this definition, R is a measure of the region of the master curve that dominated by the storage modulus properties.

The LVE model developed for calculating the full range of rheological behavior was:

$$G^*(\omega) = G_g \left[1 + \left(\frac{\omega_c}{\omega}\right)^{\frac{(\log 2)}{R}}\right]^{-\frac{R}{\log 2}}$$

where:

$G^*(\omega)$ = complex modulus at a given angular frequency (rad/sec), Pa

G_g = glassy complex modulus, typically assumed to be 1 GPa

There was some difficulty in interpreting the correct form for the above equation. In one version, the last exponent is shown without the minus sign (21, pg. 73), another report shows there is no last exponent but subtracts R/log2 (33, pg. 28) from the remainder of the equation. The original paper referenced by both of these reports shows the last exponent as (no minus sign) r/log 2. After evaluating the supporting literature, it is assumed that the equation shown above was the intended outcome of all of the reports.

The phase angle is calculated by:

$$\delta(\omega) = \frac{90}{1 + \left(\frac{\omega}{\omega_c}\right)^{\frac{\log 2}{R}}}$$

where

$\delta\ (\omega)$ = phase angle corresponding to $G^*(\omega)$, degrees

ω_c = crossover frequency, rad/sec

R = rheological index

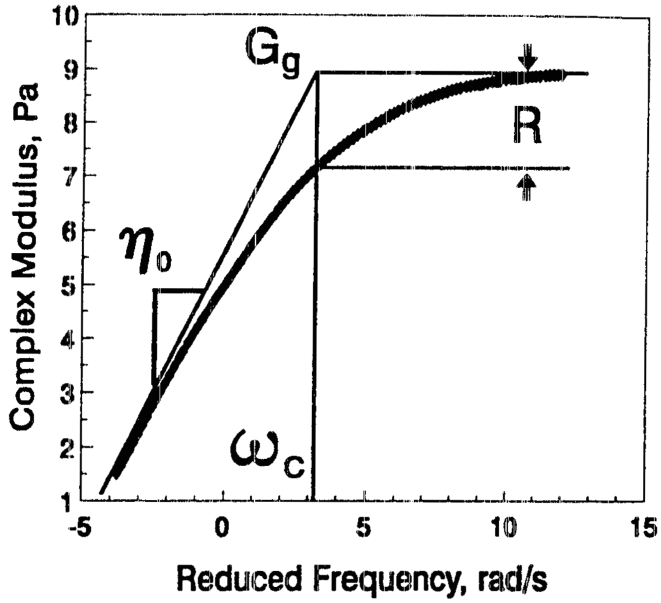


Figure 4.2. Definition of Rheological Model Used for SHRP Prediction Models (33).

A series of four plots (Figure 4.3) from dynamic shear data were used to experimentally obtain G_g, η_o, ω_c, and R. When the complex modulus is plotted against the phase angle, G_g is the value of G* as the phase angle approaches 0 (Figure 4.3.a) (33). The value for η_o is the intercept of the plot of complex viscosity versus $(1 - \delta/90^{o})^{1.5}$ (Figure 4.3.b). The rheological parameter, R, is found by plotting log (log G_g/G*) versus log (G"/G'). This parameter is then the antilog of the log (log G_g/G*) value at log (G"/G') = 0 (Figure 4.3.c). When the reduced frequency is plotted versus the log (G"/G'), the crossover frequency is that at which log (G"/G') = 0 (Figure 4.3.d). Since the steady state viscosity and the crossover frequency are dependent on the reference temperature, a standard reference temperature was selected as the defining temperature, T_d,which is approximately to the glass transition temperature.

Researchers reported good agreement between the model and test data over a wide range of temperatures and frequencies that extended well into the glassy region. However they noted poor correlations as viscous flow was approached at either high temperatures or longer loading times. Results were improved by setting R equal to 0.81 in the area of viscous flow. This led to separating the master curve into two sections referred to as the primary (i.e., LVE model) and secondary regions. These regions are separated based on a calculated transition phase range, δ_v, or a transition frequency, ω_v:

$$\delta_v = 90 \left(\frac{\eta_{ss}\omega_c}{G_g}\right)^{\frac{\log 2}{R-0.81}}$$

$$\omega_v = \omega_c \left[\frac{90 - \delta_v}{\delta_v}\right]^{\frac{R}{\log 2}}$$

where

η_{ss} = steady state viscosity, Pa-s

ω_c = crossover frequency, rad/sec

G_g = glassy complex modulus, Pa

R = rheological index

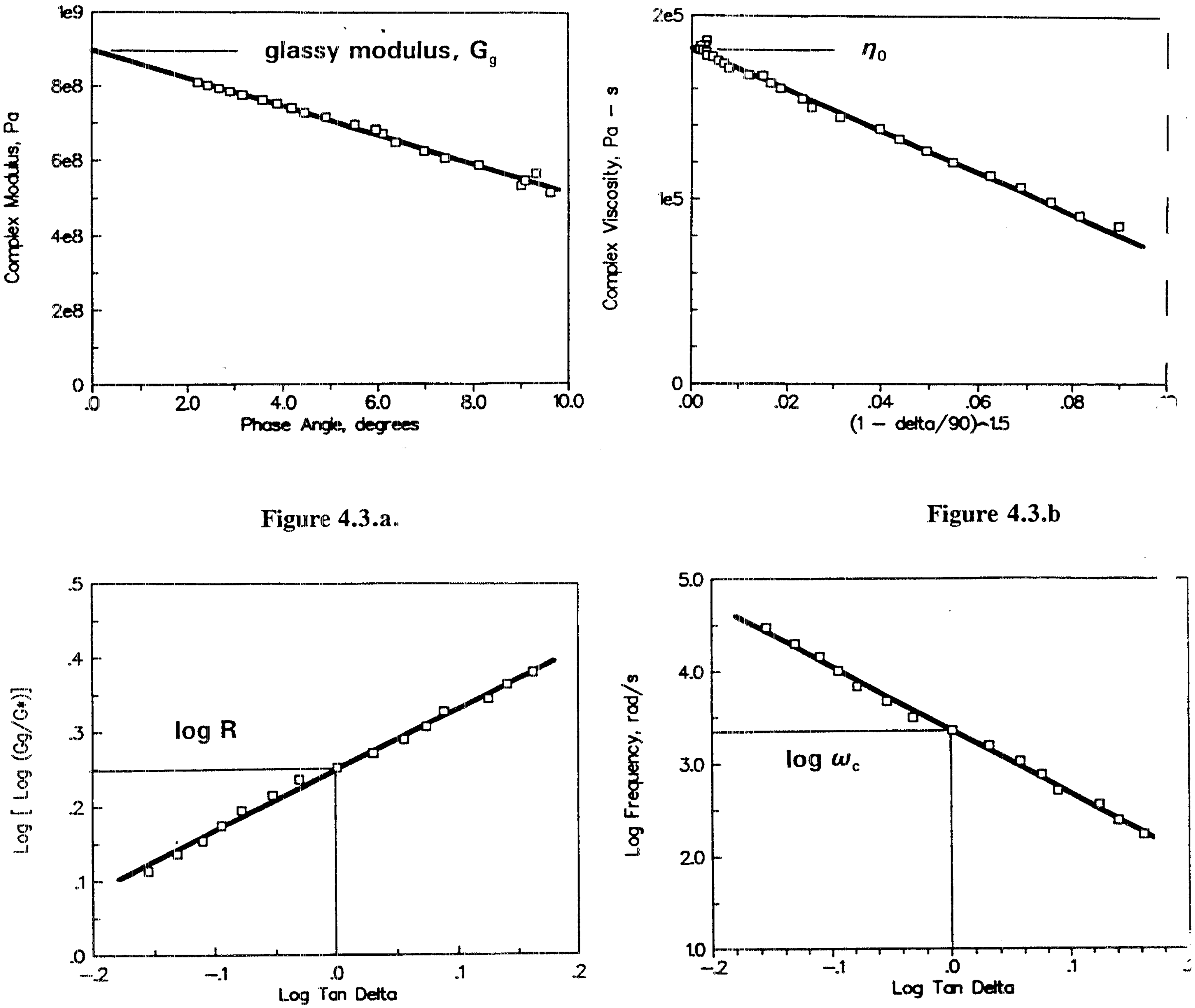


Figure 4.3.a.

Figure 4.3.b

Figure 4.3.c.

Figure 4.3.d

Figure 4.3. Graphs Needed to Determine LVE Model Parameters (33).

For phase angles less than δ_v or transition frequencies above ω_v, the LVE equations apply; otherwise, the following equations are used to calculate the modulus and frequency:

$$G_{gv} = G_g \left[\frac{90}{90 - \delta_v}\right]^{0.81 - \frac{R}{\log 2}}$$

$$\omega_{cv} = \omega_c \left[\frac{90 - \delta_v}{\delta_v}\right]^{\frac{R}{\log 2} - 0.81}$$

where

G_{gv} = *limiting modulus in the viscous flow region*, Pa

ω_{cv} = location parameter for the viscous flow region, rad/sec

Robertson et al. have empirically related several of these LVE parameters to key asphalt chemistry components. Their research found the following relationships:

$$R = -0.49 + 0.0018M_n + 1.90GI; \quad r^2 = 0.81$$

$$\omega_c = -0.79 - .055A; \quad r^2 = 0.47$$

where

M_n = number average molecular weight as determined from VPO with toluene, g/mole

GI = Gaestel index

A = asphaltene content (*n*-heptane), weight percent

As R increases, the width of the G* versus reduced frequency curve increases. Since an increase in the breath of this curve should be a reflection of increased molecular weight, the proportional relationship between R and M_n makes sense. Also, an increase in the Gaestel index indicates an increased potential for agglomeration of the asphaltenes; this should also contribute to the increase in R. Because R is defined by the location of the crossover frequency, and a decrease in the frequency results in an increase in R, the reduction of ω_c with the increase of percent asphaltenes is also logical.

Since these models were based on the assumption of a uniform hyperbolic shape for the master curve, it is unclear if any of these parameters would also be applicable to polymer modified asphalt cements. The applicability of SHRP models to polymer modified asphalts will need to examined. If this model for asphalt cement has been incorporated into the final SUPERPAVE pavement design computer program, this SHRP product will also have to be evaluated.

Resilient Modulus (Mixture Testing)

This test is a standard research test that has been used extensively over the last three decades to define changes in mixture stiffness with temperature. Briefly, a repeated load is applied to a diametrically positioned compacted sample. The corresponding horizontal deformation is measured and the resilient modulus is defined as the ratio of the applied peak stress to the recoverable strain. The American Society for Testing and Materials (ASTM) D4123 describes this test method and the subsequent calculations in detail (36). Typically, the applied load duration is 0.1 seconds followed by a rest period of either 0.9, 1.9, or 2.9 seconds. Test temperatures usually range from -18 to 40°C (about 0 to 104°F).

PERMANENT DEFORMATION

Viscosity (Binder Testing)

Since one of the approaches to reducing thermal cracking is to use a soft grade of asphalt, the potential creation of a rutting problem at warm temperatures needs to be addressed. Viscosity measurements have historically been the most common binder property measured at warm temperatures. However, standard methods of measuring viscosity need to be altered when polymer modified asphalts are evaluated.

In 1992, Swager indicated that conventional vacuum viscosity measurements for modified asphalt cements should use the straight-sided Asphalt Institute (AI) tubes in order to obtain accurate results (37). This is due to the shear rate dependency (i.e, non-Newtonian behavior) of most modified binders, a material property that is not accounted for with the standard Cannon Manning (CM) tubes. Collins et al. compared both the vacuum viscosities determined with AI tubes and those obtained from dynamic shear testing (9). They found that these results confirmed the Cox-Merz rule which states:

$$\eta\ (\dot{\gamma}) = \eta^*\ (\omega) \qquad \textit{with}\ \dot{\gamma} = \omega$$

That is, a steady state viscosity (vacuum viscosity) is equal to the frequency dependence of the linear viscoelastic viscosity, η^* (dynamic shear viscosity) (5).

SHRP researchers also recognized the importance of viscosity and incorporated a variation of this measurement in the final SHRP binder specification. For test temperatures 42°C and above, the properties of both the original and RTFO aged asphalts are defined in terms of $G^*/\sin\delta$. Figure 4.4 shows the relationship between this parameter and rutting for a laboratory study reported by SHRP researchers (21).

Since most unmodified asphalt cements at these temperatures can be considered both Newtonian and fluid, $\sin\delta$ can be estimated at 1. This implies that the minimum limits of 1 kPa and 2.2 kPa set by SHRP for unmodified original and aged asphalts, respectively, are simply minimum limits for G^*.

The relationship between G^* and the complex viscosity, η^* is:

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

When viscosity is expressed in terms of Poise and the modulus is in terms of Pa, $\eta^* = G^*$ when ω is 10 rad/sec. Using this concept, the trends in Figure 4.4 follow the expected pattern: increasing rut resistance with increasing viscosity. Using the assumption that $\sin\delta$ is approximately 1, the warm temperature portion of the SHRP binder specification becomes essentially a minimum in-service viscosity graded specification.

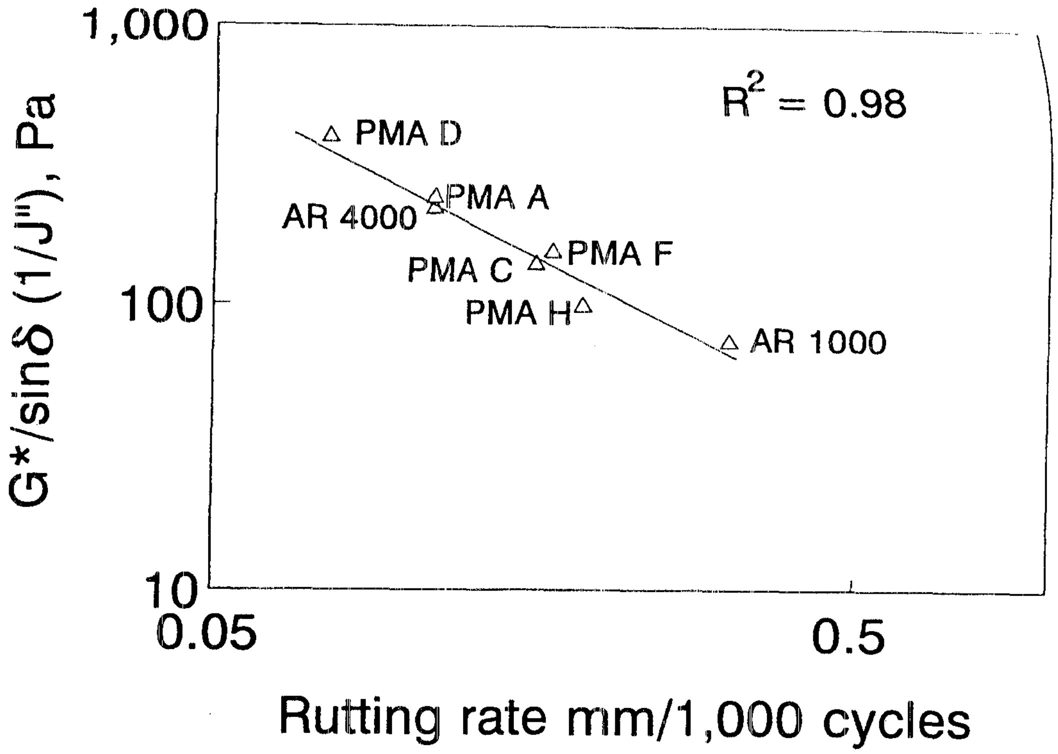


Figure 4.4. Relationship Between G*/sinδ versus Rutting Used by SHRP Researchers to Validate the Selection of Specification Parameter (21, pg 55).

The relationship between the complex viscosity and complex modulus would also be true for modified asphalts. However, conversions from steady state vacuum viscosities would not be as accurate as with unmodified asphalt cements as modified asphalts are typically non-Newtonian in behavior. This would lead to an overestimation of viscosity since the highest shear rate that is typically developed with the AI tubes is less than 5 sec^{-1}.

Yield Stress from Dynamic Shear Rheometry (Binder Testing)

One of the more common methods of identifying a plateau in the polymer industry is to measure a yield stress at a critical temperature, or in the case of a master curve, at a critical reduced frequency. Figure 4.5 shows typical data for an unmodified and modified asphalt cement. Typical results for an unmodified asphalt cement show that the shear stress should approach zero within a certain range of reduced frequencies while modified asphalt cement can show a constant shear stress which can also be expressed as a yield stress, τ_y.

The durability of the yield stress should be dependent upon whether the plateau region is primarily due to the flocculation of the asphaltenes or the development of a polymer network. A plateau due to flocculation should be less durable and be able to be disturbed at some critical temperature or strain level. A network formation, which is a more durable structure, should be more difficult to disrupt.

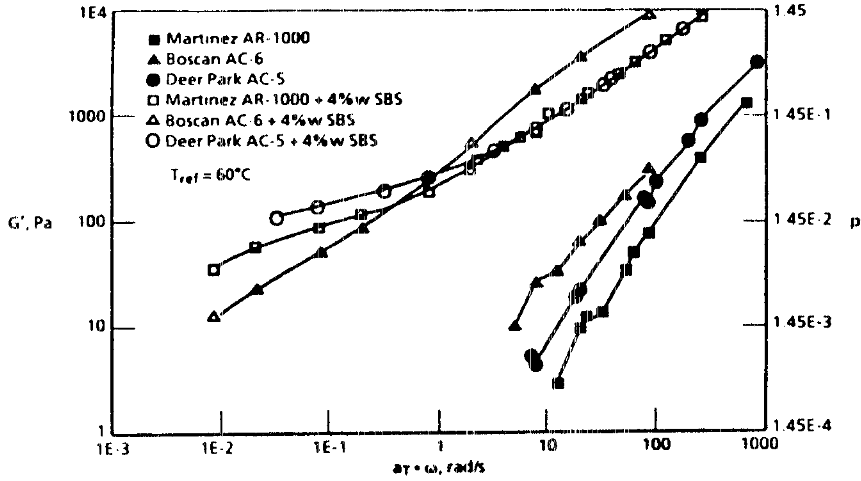


Figure 4.5. Typical Shear Stress - Frequency Relationships for Unmodified and Modified Asphalt Cements (9).

Creep Testing (Mixture Testing)

The most common method found in the literature for evaluating the permanent deformation characteristics of mixtures was the standard triaxial compression creep test. This test applies either a static or repeated load to a 100 mm (4 in) diameter by 200 mm (8 in) tall cylindrical sample. The corresponding axial strain is measured over the center 1/3 of the sample by placing retaining collars holding three linear variable differential transducers (LVDT) space at 120°. Testing parameters have differed according to researchers, with the axial load being more commonly around 103 kPa (15 psi); confining pressure (air only) varied between 0 and 200 kPa (about 30 psi). Test temperatures were typically between 25 and 40°C (77 and 104°F). A full description of the test method can be found in other references (38).

LOW TEMPERATURE BEHAVIOR

Glass Transition Temperature, T_g

Dynamic Mechanical Testing

The glass transition temperature can be determined in two ways from dynamic mechanical testing. The first method makes use of the shift factor equations for master curves. The second method estimates T_g from the peak of the loss modulus, G", curve seen at cold temperatures.

T_g from Shift Factors: The development of master curves for dynamic mechanical testing requires shift factors to move the curves to the right and left toward the selected reference temperature. There are two methods of calculating shift factors, both based on a reference temperature which is usually the glass transition temperature: 1) the William-Landel-Ferry (WLF) equation, and 2) the Arrhenius function. The WLF equation has been most commonly used for shifting data from test temperatures above the glass transition temperature. When test temperatures are below the glass transition temperature, an Arhennius function is used.

$$\textit{WLF:}\quad \log A_T = \log\frac{\eta}{\eta_o} = \frac{-C_1\,(T - T_o)}{C_2 + T - T_o}$$

$$\textit{Arhennius:}\quad \log A_T = \log\frac{\eta}{\eta_o} = \frac{2.303\,E_a}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

where

T = a selected temperature of interest, °C or °K

T_o = a reference temperature, typically the glass transition temperature, T_g, °C or °K

A_T = calculated shift factor

η = viscosity at selected temperature

η_o = viscosity at reference temperature

The universal constants, C_1 and C_2, in the WLF equation are commonly assumed to be 17.44 and 51.6, respectively, for polymers when T_o is taken to be the glass transition temperature, T_g. When T_o is assumed to be approximately 50°C above the glass transition temperature, the universal constants are 8.86 and 101.6, respectively (3, pg. 341). The constants for the Arrhenius function are R, the universal gas constant 8.34 J/mole-°K, and E_a in kJ/mole which varies with the material being tested.

Since T_o in either equation can be the glass transition temperature, both equations have been used to estimate T_g. Additionally, the WLF equation has been used to estimate binder viscosity at selected temperatures above the glass transition temperature. However, in order to use this equation in this manner, specific testing conditions must be defined.

WLF Equation Applied to Binders: In 1966, Heukelom indicated that the WLF equation was applicable for materials above the softening point or for viscosities less than 1,000 Poise

(39). For asphalts with low wax contents or penetration indices less than +1, the WLF equation was applicable to viscosities up to 1,000,000 Poise. He hypothesized that departures from the WLF equation were due to deformations occurring in viscous flow and a higher amount of crystallized waxes. He assumed that C_1 represented the internal friction mechanisms within the asphalt cement and that C_2 represented the temperature susceptibility. Both C_1 and C_2 should be dependent upon the selection of the reference temperature.

A range of constants can be found in the literature. Sisko and Brunstrum found that C_1 and C_2 were 28.9 and 292 (for temperature in °F) for a reference temperature of 20°F (-6.7°C) (40). They showed that aging the binder changed the constants by reducing the slope of the log a_T versus log (T - T_g) plot. The hypothesis was that changes were due to the development of a gel structure with the asphaltenes acting as the nucleating agents.

In 1966, Schmidt and Santucci used values of 17.44 and 92.88 for C_1 and C_2, respectively (41). They used these constants, steady state viscosities determined at 140°F (60°C), and a shear rate of 0.1 sec^{-1} for estimating steady state viscosities at other temperatures. They found better agreement between estimated and measured steady state viscosities when the constants were changed based on shear rate. Table 4.2 shows their calculated values for several viscosity shear rates. These researchers restricted the use of these constants from T_g to T_g + 180°F.

Table 4.2. WLF Constants from Steady State Viscosity Testing (41).

Viscosity Shear Rates, sec^{-1}	C_1	C_2
0.001	24.80	188.3
0.05	34.94	461.0
0.1	38.42	555.7

In 1992, Anderson et al. reported the values of C_1 and C_2 to be 17.5 and 80 (for temperature in °C), respectively, (42). They also indicated that above some critical temperature a vertical shift factor was needed. Figure 4.6 shows how the vertical shift factors change for a range of binders. The authors considered the need for vertical shift factors a reflection of the change in solubility of the structured phase of the asphalt and/or modifier. A lower temperature should be equivalent to a lower solubility with agglomeration of discrete particles within the dispersed phase. An increase in temperature should result in an increase in solubility which would lead to an expansion of the structured phases, which would in turn result in changes in density. This change in density would then result in the need for a vertical shift factor.

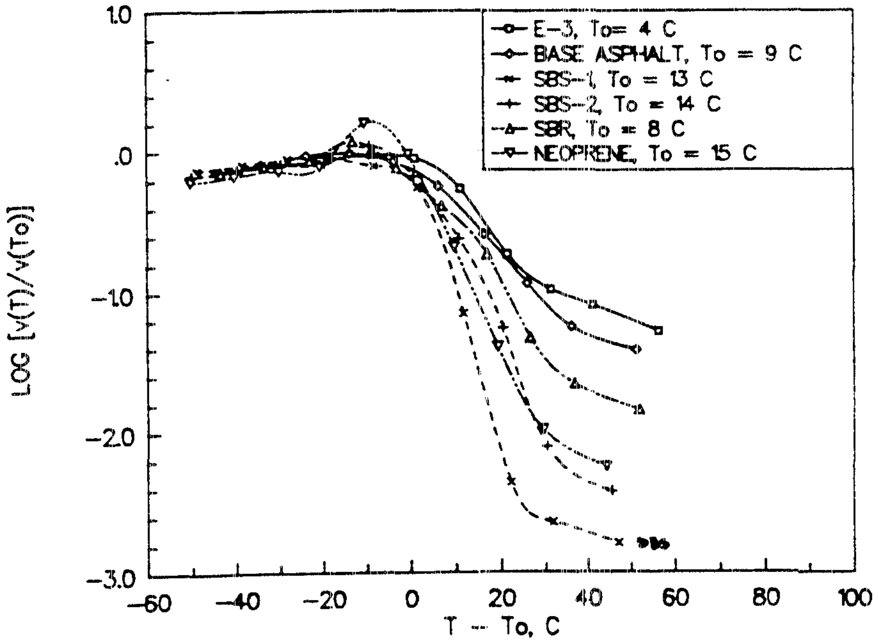


Figure 4.6. Vertical Shift Factors versus Temperature (42).

In 1994, Anderson et al. adjusted recommendations for C_1 and C_2 slightly to 19 and 92 (for temperature in °C), respectively, for a reference temperature of 25°C (77°F). They also indicated that these constants for the WLF equation should only be applied above a defining temperature, T_d (approximately T_g) and below the development of Newtonian flow behavior (21, pg. 74).

Arrhenius Function Shift Factor: Anderson et al. used an activation energy value, E_a, of 261 kJ/mole to calculate a defining temperature, T_d (33). This temperature was calculated using an nonlinear least squares analysis for the master curve developed for a full temperature range dynamic characterization of the binder. The precision of determining the defining temperature was reported to be ±3°C (±5.4°F).

The authors also related the defining temperature to molecular weight, M_n, and the percent of asphaltenes, A:

$$T_d = 18 - \frac{22{,}000}{M_n} \; ; \; r^2 = 0.27$$

$$T_d = 16 - 0.57A - \frac{12{,}400}{M_n} \; ; \; r^2 = 0.53$$

The relationship between an increase in the defining temperature and a corresponding increase in molecular weight is reasonable, although not strongly correlated. Adding the percent asphaltenes as an independent variable improves the correlation. However, a decrease in the defining temperature with an increase in the asphaltene content is not logical as the asphaltenes have been identified as the major high viscosity contributor in asphalt which would increase the defining temperature. The authors attempted to provide an explanation for this departure from logic by assuming that it was an artifact of the asphalt cement grading process. Briefly, for a refinery to produce a product within a given viscosity range, only certain combinations of molecular weights and overall polarity would produce and acceptable product. Therefore refineries might be juggling the percentage of these components to meet certain viscosity requirements which would result in these unusual correlations.

T_g from the Maximum Loss Modulus: This method of determining T_g has been used extensively in polymer science where the peak of the G" curve is taken as the glass transition temperature and the area under the curve is related to the chemical structure of the polymer. The area under the curve is related to the chemical structure of the material and the width of the peak is sensitive to the state of molecular mixing (3, pg. 317).

In 1980, Pinke et al. reported using dynamic torsion bar testing to determine T_g (Figure 4.7) (43). The breadth of the curve indicates that there is no sharp delineation of a specific glass transition temperature although there appears to be a narrower peak for the slower frequencies. The authors noted that faster frequencies resulted in a shift of the peak towards a higher transition temperature. The large area under all of the curve indicates the diverse molecular nature of asphalt cements.

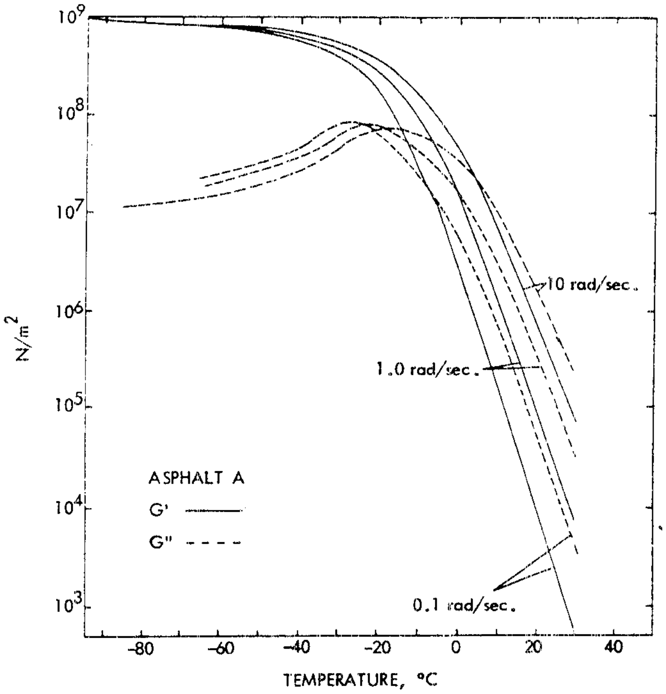


Figure 4.7. Determining the Glass Transition Temperature from the Peak Loss Modulus (43)

Test Methods

Dilatometry

Dilatometry measurements are one of the classical methods for determining the glass transition temperature. This method identifies the T_g by the presence of a discontinuity in the volume contraction with decreasing temperature relationship. The concept is that the coefficient of thermal expansion, α, is constant on either side of the transition temperature, but greater above this point than below. This difference has been attributed to the ability of molecules to move above the transition temperature while motion is limited to molecular vibrations below T_g.

Above T_g the material's ability to contract is dependent upon the free volume within the material and the ability of the molecules to move into the free volume. Larger molecules reflect materials with less free volumes; higher viscosities also make it difficult for molecules to utilize free volume. Both an increase in molecular size and/or viscosity will increase the T_g. Below T_g it is assumed that there will be very little change in the free volume with a subsequent decrease in temperature (21). At the glass transition temperature, the free fractional volume is commonly assumed to be 0.02 to 0.03 regardless of the material tested (3).

Schmidt and Santucci used this method in 1966 to show that the coefficient of thermal expansion (above T_g) was approximately 3.93×10^{-4} per °F (Figure 4.8) (41). Below T_g, the value decreased substantially to 1.93×10^{-4} per °F. This would indicate that there should still be a slow but steady volume decrease for asphalt cement at approximately one third of the rate as that above the T_g.

In 1994, Anderson et al. showed that the coefficient of thermal expansion of 6.4×10^{-4} per °C above T_g and 3.5×10^{-4} per °C below T_g for a wide range of asphalt cements. Using this value, a fractional free volume at the glass transition temperature was determined to be 0.028, which was within the expected range of 0.02 and 0.03 for polymers.

This research indicated that the rate of volume decrease below T_g was half of that above this point; this finding showed a greater tendency for volume decrease than indicated by Schmidt and Santucci. Anderson et al. also indicated that this continual decrease in volume was responsible for a gradual but continual increase in binder stiffness. He has referred to this time and temperature dependency as a physical hardening of the asphalt cement (33).

Bending Beam Rheometry

SHRP researchers developed the bending beam, or flexural beam, rheometer to measure the viscous behavior of asphalt cements at cold temperatures. It can be used as a cold temperature constant stress creep test and the results used to develop a master curve for the creep modulus. The test consists of applying a 100 g load to the center of a simply supported rectangular beam of asphalt cement. Deflections are measured between 4 and 240 seconds of loading at four temperatures [-35, -25, -15, -5°C (-31 -13, 5, and 23°F)]. These results are used to develop a master curve as defined in the previous sections.

Figure 4.8 shows rheological model parameters similar to those defined for the dynamic mechanical shear rheometry testing can be determined from the master curve. Differences in the key parameters determined from this figure is that the glassy creep stiffness, S_g, is determined instead of the glassy modulus, G_g, and the time to the crossover frequency, t_c, in place of the crossover frequency, ω_c. The values of stiffness in general are defined by the working equations:

$$\mathit{Stiffness} = S(t) = \frac{\sigma}{\epsilon\ (t)} = \frac{\dfrac{3\ PL}{2\ bh^3}}{\dfrac{6\ \delta(t)\ h}{L^2}} = \frac{PL^3}{4\ bh^4\ \delta(t)}$$

where

σ = stress, kPa

$\epsilon(t)$ = strain at time, t, mm/mm

P = applied load, N

L = span length, mm

b = width of beam, mm

h = depth of beam, mm

$\delta(t)$ = time-dependent deflection of beam

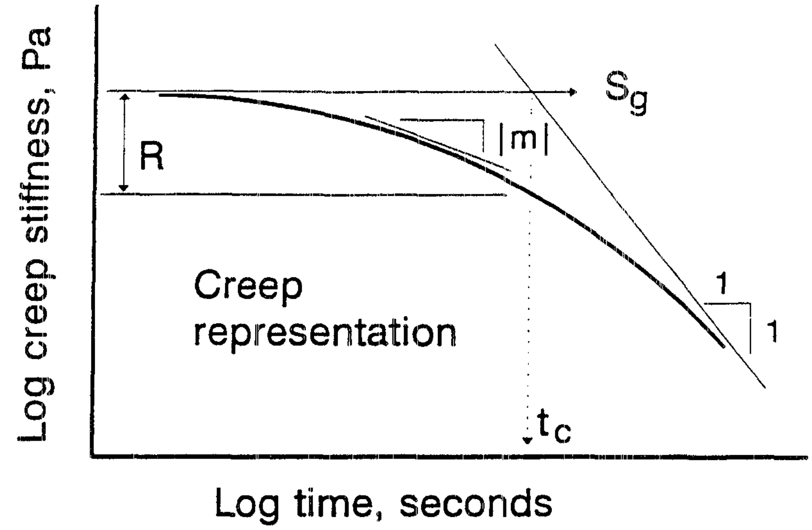


Figure 4.8. Rheological Model Parameters Defined by SHRP Researchers for Bending Beam Rheometer Results (21).

One major problem with using the bending beam rheometer is that SHRP researchers reported that it was not sensitive to changes in binder properties due to the addition of polymers. They reported that modified binders could have similar creep stiffness, but show distinct differences in their ability to deform at cold temperatures. This lack of sensitivity resulted in the development of the direct tension.

Direct Tension (Binder Only)

The original SHRP research on the direct tension test subjected dog-bone style binder specimens to various constant rates of elongation: 2.54, 7.62, 15.24, 25.4 and 50.8 mm/min (0.1, 0.3, 0.6, 1.0 and 2.0 in/min). Five different test temperatures were used: -30, -20, -10, -5, and 0°C (-22,

-4, 14, 23, and 32°F) (33). Typical strains are between 0.1 and 10 percent for the slowest rate of elongations.

A final limited round of testing with a slower 1.0 mm/min (0.0394 in/min) was used to set the final SHRP specification test parameters. When this test is conducted over a range of temperatures and the log of the percent strain at failure is plotted against temperature, a failure temperature at which the strain is equal to 1 percent can be determined (Figure 4.9) (44).

The need for determining the direct tensile properties of modified asphalts instead of just the bending beam results was confirmed by research conducted at the Shell laboratory (44,45). Figure 4.10 shows the results from the bending beam rheometer indicate no differences between the modified binders. However, the direct tension test results show a distinct improvement in the ability of the modified binders to deform before failure. This figure also shows that the relationship between the direct tension binder test results and increasing polymer concentration are similar, although higher, to those for the constrained beam test for mixtures.

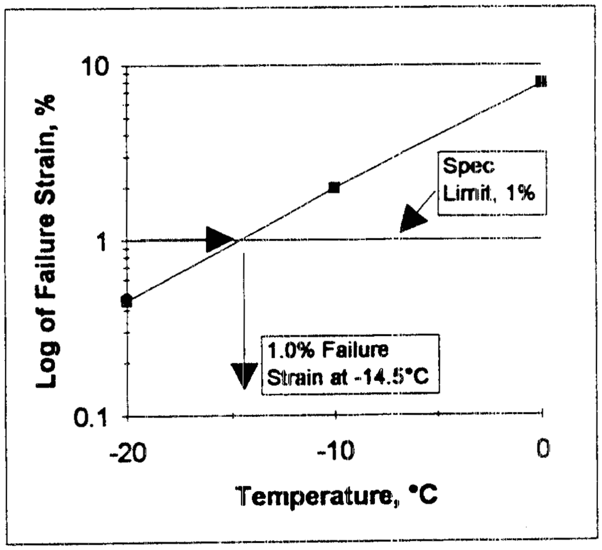


Figure 4.9. Determination of a Critical Low Temperature from Direct Tension Test Results (44).

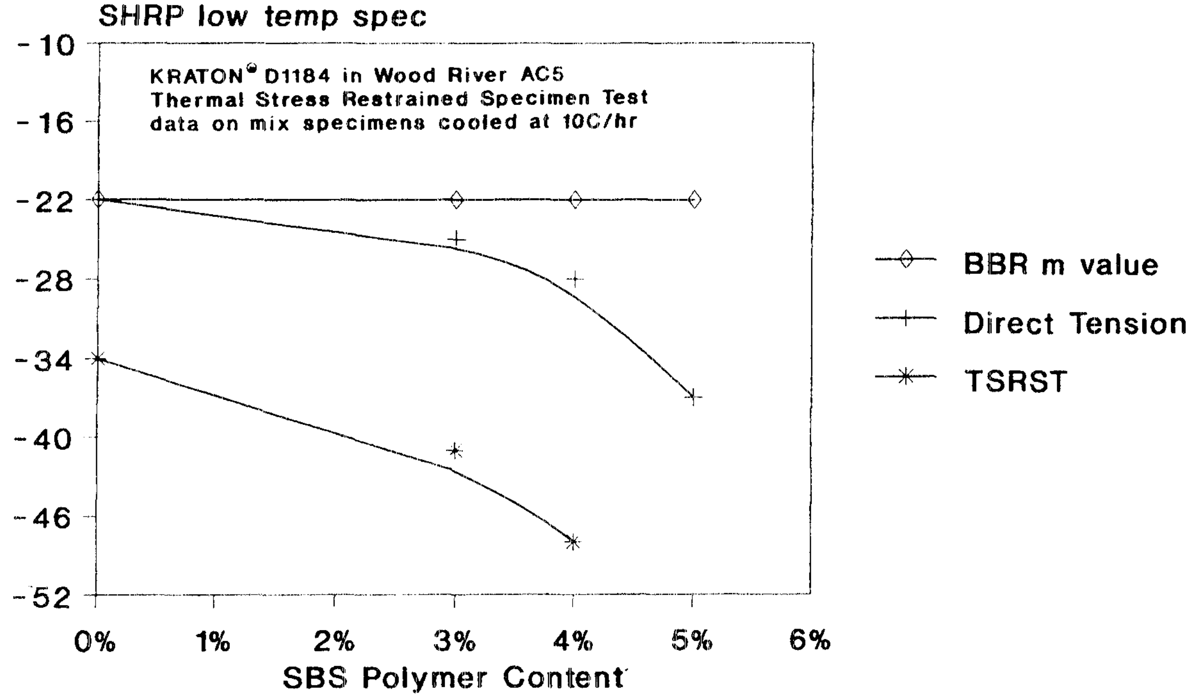


Figure 4.10. Comparison of Critical Low Temperatures for Various Binder and Mixture Tests (45)

Fraas Brittle Point (Binder Only)

Cracking of all binders is assumed to occur at an equiviscous (approximately 4 x 10^9 Poise) temperature (46). Research has shown that this is also an equistiffness temperature of approximately 0.94 x 10^8 N/m^2 as determined from the equation (46):

$$S = \frac{3\eta}{t}$$

where

S = stiffness of bitumen, N/m^2

η = viscosity of bitumen, N-s/m^2

t = loading time, seconds (approximately 11 seconds for Fraas test)

The Fraas test determines the temperature at which a thin film of binder first becomes brittle. The test is conducted by placing a thin spring steel plate coated with a film of binder in a small, dual-walled chamber. Dry ice is used in the outer portion of the chamber to produce a given constant drop in temperature. A hand crank system is used to repeatedly flex the coated plate. The brittle point is determined as the temperature at which cracking of the film is initiated.

CHAPTER FIVE

Since polymers are not always inert additives but can interact with specific portions of the asphalt cement, they can alter the chemistry and hence the structure of the asphalt cement. This chapter will present an evaluation of previous research which has documented the importance of polymer-asphalt interactions as well as their influence on binder and mixture properties.

COMPATIBILITY

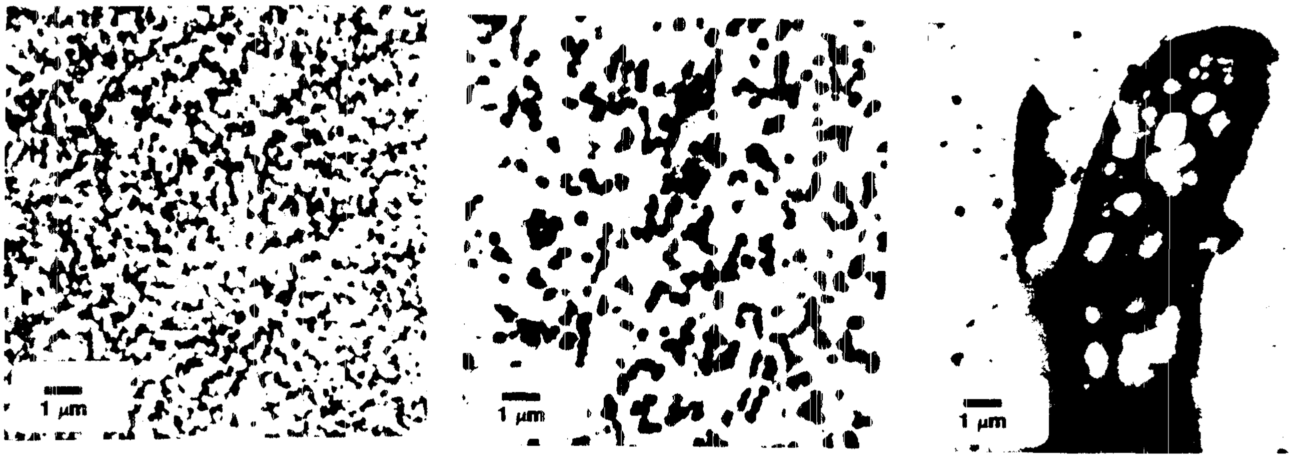
The literature review revealed that there are two common interpretations for the term "compatability". The first interpretation simply defines compatibility as the ability of the polymer to remain distributed in the asphalt cement without significant evidence of phase separation. Evidence of phase separation has been defined by a substantial change in penetration values between the top, middle, and bottom portions of a tube of aged binder (47). Based on this definition, the compatibility of a polymer with an asphalt can be altered by simply changing the specific gravity of the polymer to more closely match that of the asphalt (48). These asphalts and polymers can be relatively compatible by this definition but show a wide range of polymer-asphalt interactions.

The second interpretation defines compatibility based on the level of interaction between the polymer and the asphalt with more compatible combinations showing greater the volume increases (i.e., swelling) of the polymer within the asphalt matrix. Brule' found that when a polymer was compatible with an asphalt cement, the polymer could swell from 400 to 550 percent (27). The percent of swell decreased with increasing polymer concentration. This would indicate that there was only a limited portion of the asphalt's maltene fraction available for interaction with the polymer. Based on an understanding of asphalt chemistry, the hypothesis can be made that the removal of a substantial portion of the maltene fraction could lead to substantial structuring of the asphalt due to asphaltene agglomeration.

One of the results of excessive structuring of the asphaltenes would be to change a sol-type to a gel-type asphalt cement. Since a gel-type asphalt would exhibit property changes such as lower ductility and higher viscosities the reduced ductility of the base asphalt cement could result in a decreased resistance to thermal cracking for binders that are dependent upon the properties of the base binder for low temperature ductility. This structuring would also make it difficult to determine if rheological changes in binder properties are due to the addition of a polymeric structure or to the structuring of the asphalt cement.

When the polymer shows a substantial increase in volume, less polymer by weight is needed to achieve a specific volume concentration. This variability in polymer swell is the factor that controls the critical concentration, c*, of a given polymer when blended with various asphalt cement sources. Brule' (1988) and Linde (1992) indicated that compatibility was not only a function of the asphalt chemistry but the grade of asphalt cement for any given source (27, 13). Both researchers showed that compatibility decreased with increasing asphalt cement viscosity.

The size of the polymer particles distributed within asphalt matrix has also been used to identify compatible polymer-asphalt blends. Lenoble proposed that SBS particle sizes of around should 10 μm indicate a compatible polymer-asphalt blend (5% SBS polymer by weight). Particle sizes of around 20 and 100 μm for SBS polymer concentrations of 3 and 5 percent, respectively, should indicate poor compatibility (49). Collins, et al. used high level magnification photographs from scanning transmission electron microscopy (STEM) to show a wide range of polymer particle sizes for a given polymer and concentration with different asphalt cement sources (Figure 5.1) (9). Figure 5.1a. shows a fine dispersion of a 4 percent by weight concentration of an SBS modifier in the Martinez AR 1000 asphalt cement with some evidence of a polymer network formation. Figure 5.1b shows that the particle size for the same polymer was greater with the Deer Park AC-5 and showed only limited network formation. Figure 5.1c shows that the same polymer did not disperse in the Boscan AC-6.



Martinez AR-1000

Deer Park AC-5

Boscan AC-6

Figure 5.1.a

Figure 5.1.b

Figure 5.1.c

Figure 5.1. STEM Photographs of 4 Percent (by Weight) of an SBS in Different Asphalt Cements (9).

The impact of these different morphologies can be seen in the storage modulus, G', determined from dynamic shear testing (Figure 5.2) (9). The authors stated that the result of the finer dispersion (Figure 5.1.a) can be seen as a plateau region. While the authors' did not discuss the results further, Figure 5.2 shows the slightly coarser dispersion also results in an apparent G' plateau. These results would tend to reduce the desirable maximum polymer particle size suggested by Lenoble from 10 μm for a compatible blend to less than 1 μm. In all cases, the inclusion of the polymer substantially increased the storage modulus, whether the polymer was well dispersed or not.

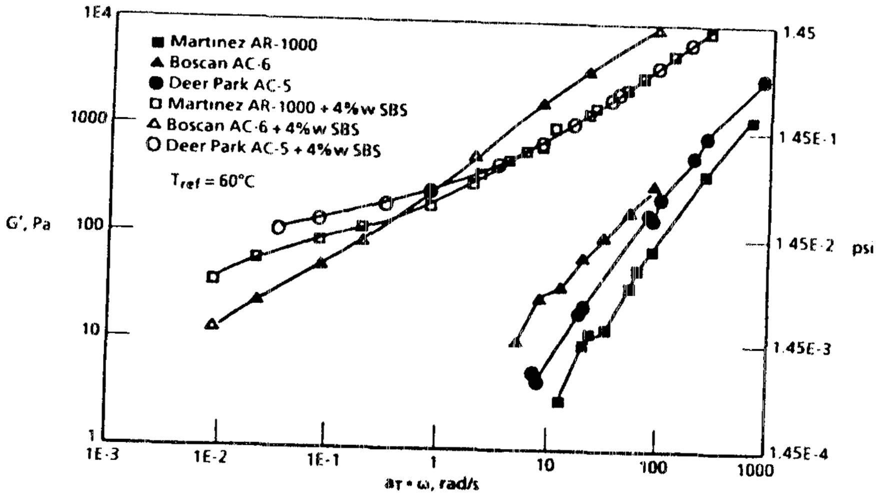


Figure 5.2. Storage Modulus Master Curves for Modified and Unmodified Asphalt Cements (9).

LABORATORY TEST RESULTS

Historically, the optimum polymer concentration for a given combination of polymer and asphalt has been determined by trial and error. The optimum percentage has usually been defined as the percentage of polymer that results in a substantial change in binder properties, with the definition of "substantial" based on the subjective evaluation of individual researchers. In some cases, mixture properties were also assessed for substantial changes in properties. The following sections will discuss general comparisons of unmodified and modified binders and mixtures found in the literature.

Binder Only

Unmodified and modified binders have been compared in a number of ways: 1) evaluation of conventional binder properties such as penetration, ring and ball (R & B) softening point, and viscosity measurements, 2) dynamic rheology to define binder properties over a range of temperatures and/or frequencies, and 3) low temperature properties such as the assessment of the glass transition temperature, direct tension, and bending beam rheology. Very little information was found in the literature regarding what magnitudes of binder properties improvement were necessary to benefit performance.

Conventional Binder Properties

The bulk of information comparing unmodified and modified binder properties deal with results from conventional tests. Penetration values at 4°C were found to increase with increasing polymer concentration indicating a softening due to the polymer (50). For example, the penetration values for an unmodified asphalt cement of 1 dmm increased to 6 and 8 dmm for 4 and 8 percent by weight of an Enichem SBS modifier, respectively.

The ring and ball (R&B) softening point temperature was shown to be dependent upon asphalt cement source as well as polymer structure. Collins et al. determined that the softening point increased about 75 percent for 3 percent Kraton D1101 in one source of AC-5 while there was little change for the same percentage in a second source of AC-5 (51). When a 3 percent concentration of different polymers from the same source were blended with the more reactive AC-5 source, both the Kraton D1101 (linear structure) and the Kraton D1184 (radial structure) increased the softening point of the binder about 75 percent. The saturated SBS Kraton G1652 (linear structure) only increased the softening point by about 60 percent. Results reported for the Enichem products indicated that the linear 6302 polymer structure resulted in the least increase while the radial T-161C structure had the greatest increase in softening point temperature; any increases were enhanced with increasing percentages of polymers. For the linear 6302 SBS, the softening point increased 67, 89, and 100 percent for 4, 6, and 8 percent polymer, respectively. For the radial T-161C SBS, it increased from 89, 110, and 140 percent, respectively.

King also attempted to relate the softening point to the loss modulus, G", for modified binders (52). Figure 5.3 shows the relationship he developed for three grades of asphalt cement and three levels of polymer concentration. This figure shows a general relationship between an increase in the softening point with an increase in the loss modulus. It also shows that as the percentage of polymer increased, the influence of the polymer concentration on the softening point decreased. This can be seen from the lines added to the original figure presented by the authors.

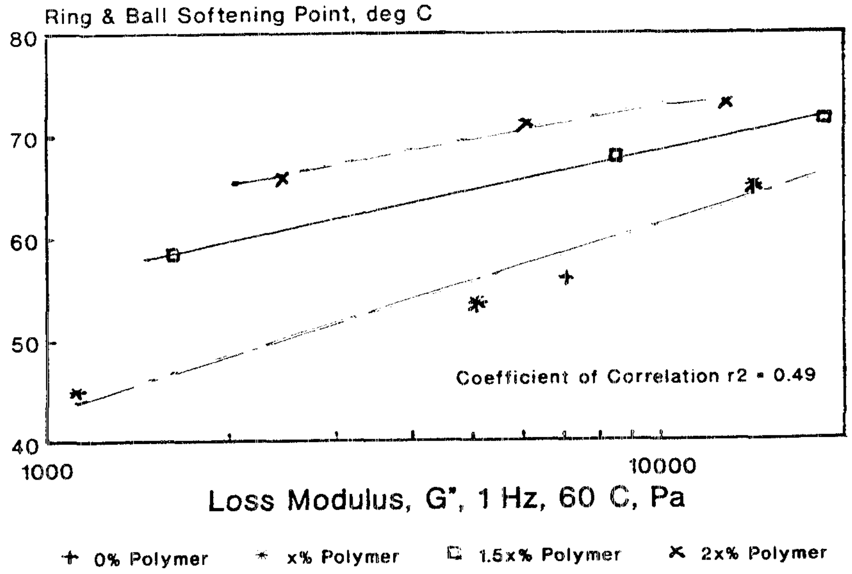


Figure 5.3. Relationship Between Softening Point and Loss Modulus (After Ref. 52).

Collins et al.'s research showed increased viscosities at 60°C (140°F) with the addition of polymers, with the magnitude of the increase depending on the polymer structure (12). The addition of 3 percent of the linear Kraton D1101 SBS resulted in a 650 percent viscosity increase over the base asphalt viscosity. The same percentage of radial Kraton D1184 SBS resulted in a viscosity increase of more than 2,000 percent. The saturated SBS (Kraton G1652, linear structure) showed the least increase in viscosity with an increase over the base asphalt cement of only 270 percent. These trends in structural dependency were similar to those seen for the softening point results.

When the test temperature was increased to 120°C (48.9°F), the influence of polymer structure on viscosity disappeared, although all polymer modified asphalts had viscosities about 300 percent higher than the base asphalt.

Collins et al. also showed the influence of polymer modification on the traditional Shell Bitumen Test Data Chart (BTDC) which combines penetration versus temperature and viscosity versus temperature relationships on one graph (51). Typically, paving grade asphalts can be represented as a straight line on this graph. However, when a modified binder was plotted on this graph, the straight line relationship disappeared (Figure 5.4) (51). This relationship indicates that a polymer modified asphalt cement should be expected to have more ductile behavior at cold temperatures with higher viscosities at higher temperatures. Based on the limited results presented, it appears that the properties of unmodified and modified binders should be similar around 25°C (77°F). Figure 5.4 also indicates that the traditional penetration index (PI), based on the slope of the line on this graph, would have no meaning for modified asphalt cements since the viscosity-temperature relationship is not linear.

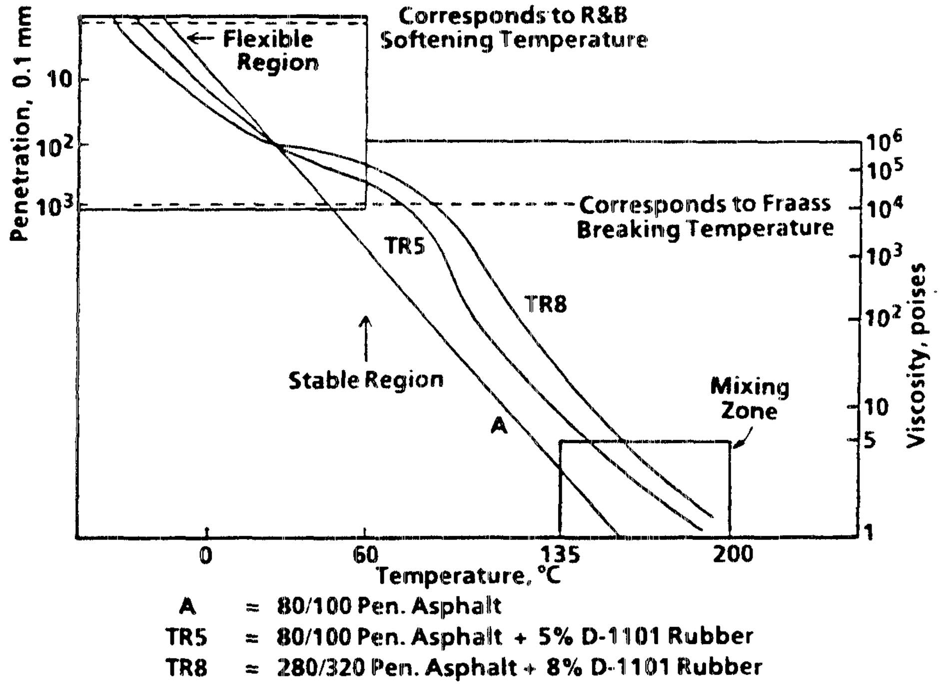


Figure 5.4. Penetration and Viscosity Data Presented on the Traditional Shell BTDC Graph (51).

Dynamic Shear Rheology

In 1993, Daly used dynamic shear rheology to indicate whether a polymer modifier was acting as a separate inclusion within the asphalt cement or was interacting with the asphalt cement (33). He interpreted a similar slope for the relationship between the log of storage modulus, G', and frequency for both the modified binder and the base asphalt as a sign of discrete, separated polymer particles within the asphalt matrix even though there was a substantial increase in the overall viscosity. It was assumed this was due to the rigidity of the polymer with the softer asphalt matrix; that is, the polymer was acting like an inert particle inclusion. When both the magnitude and the slope of the G' curve changed, this was interpreted as an indication that the polymer was selectively absorbing portions of the asphalt resulting in an increase in viscosity due to both the polymer addition and a structuring of the asphaltene phase.

Daly used this concept to indicate that polyethylene modifiers were not interactive with asphalt cements: the G' curves for both unmodified and polyethylene modified asphalts were similar (48). This was as expected since polyethylenes were considered paraffins, not readily compatible with any of the asphalt cement fractions.

Lenoble used the Black diagram as another method of representing data from dynamic shear testing. This approach graphs the complex modulus, G*, versus the phase angle (Figure 5.5) (49). A rapid decrease in the phase angle for a given level of G* was interpreted as an indication of asphaltene micelle interactions. Polymers blended with a compatible asphalt cement showed this type of trend.

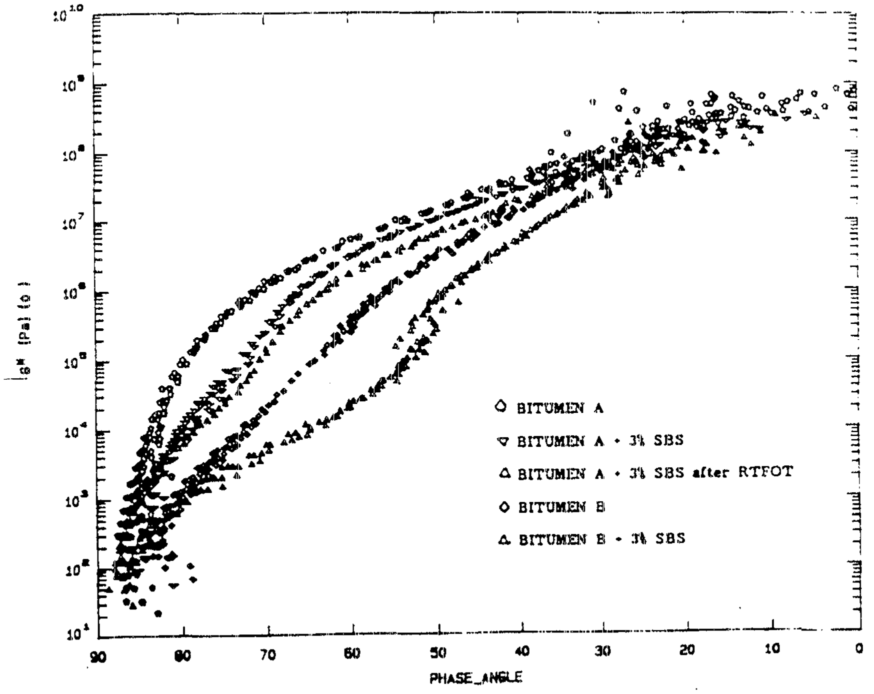


Figure 5.5. Black Diagram for Typical Dynamic Shear Rheometry Data.

Low Temperature Behavior

Various methods have been used to determine changes in low temperature properties due to polymer modification. One of the more common binder tests for determining low temperature cracking behavior is the Fraas brittle point test. Jain et al showed that the inclusion of either an SBS, LDPE, or EVA polymer resulted in lowering the cracking temperature between about 2 to 4°C for about 2 percent of polymer and between about 5 to 7°C for 5 percent polymer concentrations (47). These trends were fairly uniform, regardless of the type of polymer. Serfaas, et al. agreed with these results (28). King showed similar results with SBR reacted in-situ within the asphalt cement (52). King also showed that these trends were consistent for a range of base asphalt cement grades ranging from 40/50 pen to 180/200 pen. In general, the use of polymer decreased the Fraas brittle point; the magnitude of the decrease increased with increasing polymer concentration.

King used cold ductility (4°C) test results to show that polymer modified asphalts were more ductile than the unmodified base asphalts (53). While the use of polymers uniformly decreased the Fraas Brittle Point, the same concentrations of modifiers with the same range of base asphalts indicated little influence on ductility results for various polymer concentrations with the 40/50 and 60/70 penetration graded asphalts. The modified 80/100 and 180/200 pen asphalts showed that optimum results were obtained at the lower polymer concentrations.

In 1966, Schmidt attempted to correlate both dilatometry measurements and standard viscosity measurements at 60°C with the number of thermal cracks per lane mile. The author found little correlation between the 60°C viscosity measurements and the number of thermal cracks. However, asphalts with a glass transition temperature of less than -23°C (-10°F) had no thermal cracks per mile while asphalts with a T_g of greater than -11°C (12°F) had about 348 cracks/mile (41).

In 1991, Collins et al. calculated a critical cracking temperature based on Hills method for relating cracking to the penetration index (PI) (9,54) . These calculated values were then compared to the temperature at which a thin film of asphalt was observed to crack. There was not a good agreement between the calculated and observed cracking temperature; the calculated method showed that there was little difference in results between either unmodified or modified asphalt cements. While not stated, this result was most likely a result of the non-linear relationship on the bitumen test data chart (BTDC) chart as discussed in the previous section. The observed critical cracking temperature decreased from -33°C for the unmodified asphalt to -35, -42, and -52°C for 2, 4 and 6 percent SBS, respectively.

Lenoble used direct tension to show that the percent elongation at a constant rate of 500 mm/min increased from 50 percent for the unmodified asphalt cement to about 1,400 percent for a rolling thin film oven aged SBS modified asphalt (49).

In 1992, Anderson, et al. described the use of the bending beam rheometer for conducting constant stress creep tests at -35, -25, -15, and -5°C. Master curves prepared from these results were used to compare both unmodified and polymer modified emulsion residues (42). The results in Figure 5.6 show that there was essentially no difference in the products used for this research project. The authors confirmed these results with the Fraas Brittle Point results of -18°C for the unmodified base asphalt and about -20°C for the Neoprene and various SBS and SBR modified asphalt products. The within-laboratory precision for this test was reported as ± 1 log unit.

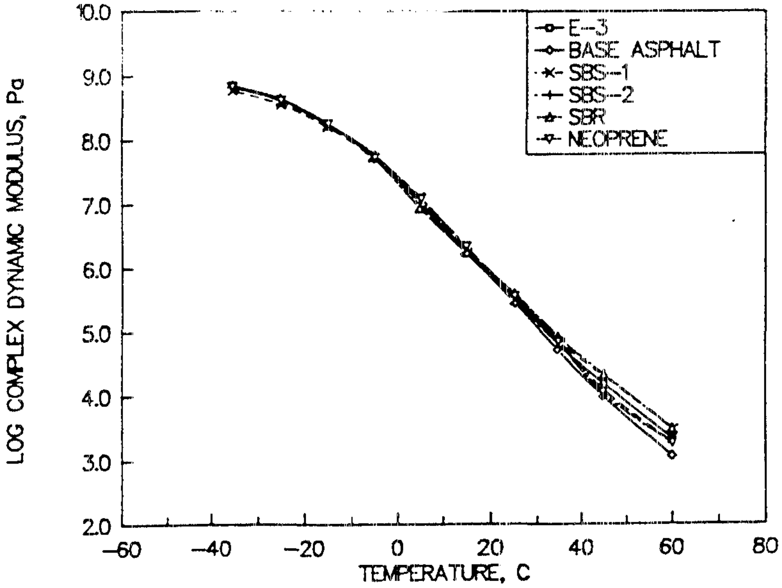


Figure 5.6. Typical Master Curves for Bending Beam Rheometer Data for Emulsion Residues (42).

In 1993, Daly used the bending beam rheometer in two ways to determine the properties of polymer modified asphalt cements (48). He used a constant 0.1 percent strain of the beam while decreasing the test temperature at a constant rate of 1°C/min to define T_g as the peak in the loss modulus (G") curve. The second method used a dynamic loading of 50 Hz and 1 percent strain while the temperature was decreased at the same 1°C/min. The temperature at which the sample failed was defined as the cracking temperature. Unmodified asphalts showed a cracking temperature higher than T_g while polymer modified asphalts showed cracking temperatures below T_g.

Comparison of Binder and Mixture Properties

Permanent Deformation

Collins et al. compared the complex modulus results from the dynamic shear rheometer at 1 rad/sec to the results of wheel tracking tests (9). They found that a G* at 60°C (140°F) of 0.08 kPa produced a mixture that had a rut depth of 10 mm at less than 5,000 cycles of the wheel tester (Figure 5.7). Mixtures with 2 and 7 percent SBS-modified binder, which had G* values of 0.250 and 1.0 kPa needed about 10,000 and 90,000 cycles, respectively, to achieve the same rut depth of 10 mm.

King et al. compared the loss modulus, G", from the dynamic shear rheometer [1 Hz (i.e., 1.67 rad/sec) and 60°C)] with results from the French rut tester which was also operated at 60°C and 1 cycle per second (52). They found that the regression equation (Figure 5.8) for predicting rut depth at 30,000 loading cycles was:

$$\textit{rut depth} = 113.25 - 27.36\,(\log G'')$$

This equation was valid for G" values up to 8.5 kPa at which point the rut depth of the mixtures leveled off at 5 mm after 30,000 cycles regardless of an increase in G".

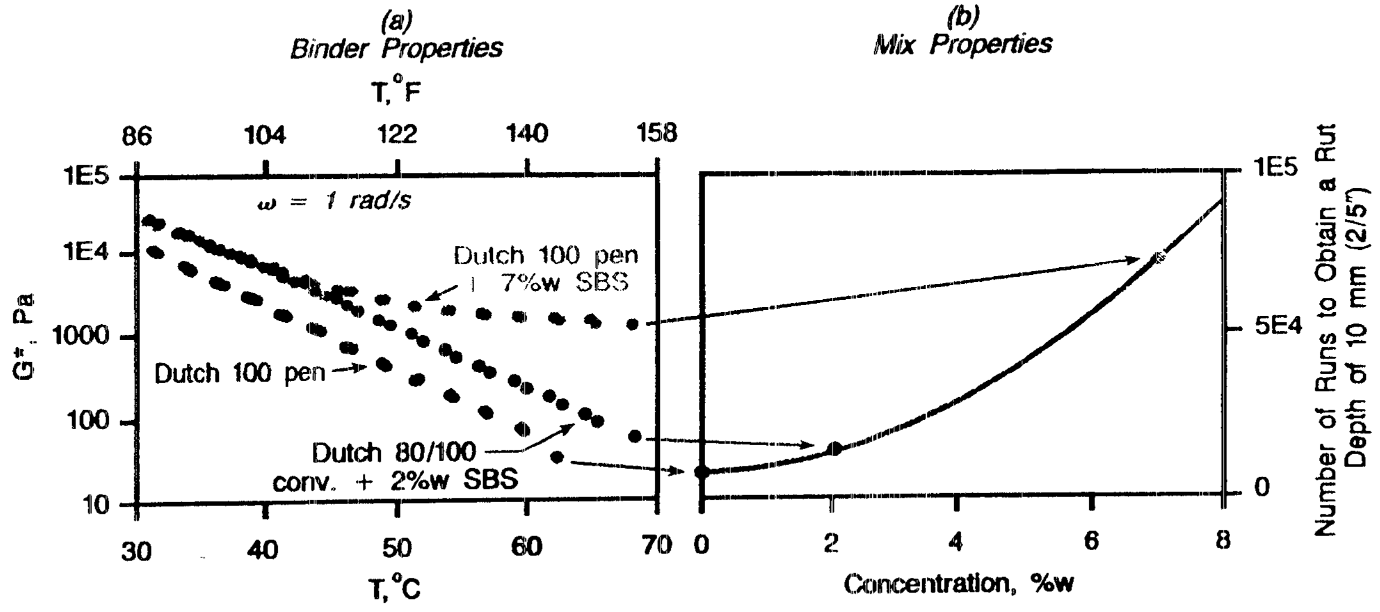


Figure 5.7. Relationship Between Polymer Concentration and Wheel Tracking Performance (9).

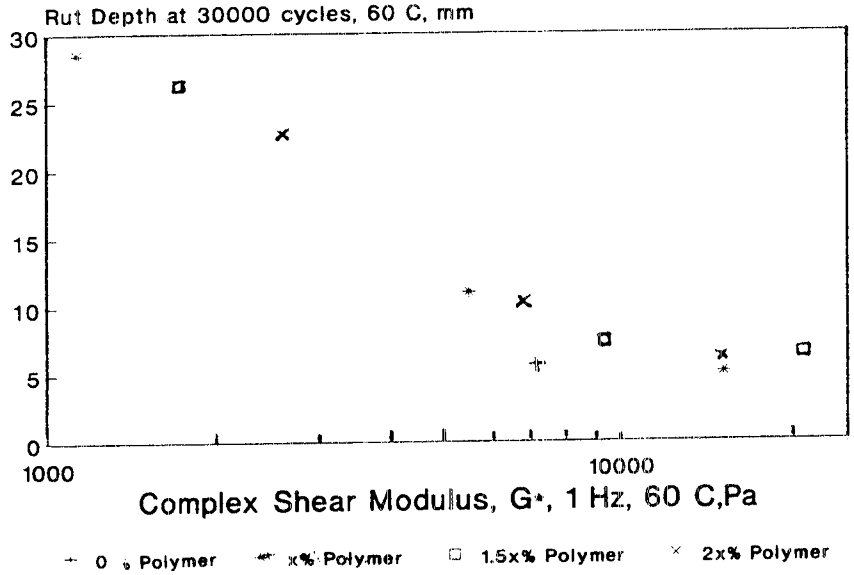


Figure 5.8. Relationship Between French Wheel Tracking Device and Dynamic Shear Binder Properties (52).

Low Temperature Behavior

Button et al. related force-ductility test results at 4°C to RTFO aged binder properties and the indirect tensile strength of mixtures at a constant loading rate of 50 mm/min at 0.6°C (55). These researchers reported a good correlation between the second peak seen in the modified asphalt forced ductility tests and the mixture tensile strengths: high force-ductility indicated high tensile strengths. This relationship was not altered even after the mixture samples were subjected to freeze/thaw conditioning.

In 1988, Goodrich found a good correlation between G" and the limiting stiffness temperature (LST) (56). The LST was defined as the temperature at which a stiffness of 10.3 GPa (1.5 x 10^6 psi) was obtained. An indirect tensile creep test [552 kPa (80 psi), 60 min load/ 30 min unload] was conducted at 4, -7, -17, and -29°C (38.2, 20, 0 and -20°F) and the results used to determine the limiting stiffness temperature (LST). Goodrich noted that all polymer modified asphalt mixtures had lower LST than the unmodified control mixtures. He indicated that a shift in the peak of the G" towards lower frequencies would relate to improved mixture properties, however no estimate of the magnitude of the shift required to see a difference in mixture properties was reported. Similar result were obtained when comparing a softer asphalt to a harder asphalt from the same source.

In 1993, King compared constrained beam test results with a wide range of binder tests (52). Correlations with cold penetrations had an r^2 of 0.69. The r^2 progressively increased from 0.73 for cold ductilities to 0.85 for Fraas Brittle Point and to 0.91 for stiffness determined from the bending beam rheometer at 15°C and a 60 second load. Direct tension binder tests conducted over a range of 20, 5, -10, and 025°C and a constant rate of deformation of 1 mm/min showed an r^2 of 0.83 with the constrained beam test (unmodified binders were the only binders used with this test).

The bending beam rheometer was also used to define a critical cracking temperature as previously defined. This value correlated with the constrained beam test with an r^2 of 0.96; the bending beam rheometer always predicted a higher temperature. This was attributed to the faster loading time used with the bending beam rheometer (60 seconds) than with the constrained beam test (typically 2 to 4 hours). The regression equation was reported as:

$$Temp_{Constrained\ Beam\ Temp} = -9.5 + 1.3\ Temp_{BBR}$$

Fatigue Testing

In 1966, Schmidt and Santucci showed that the shift factor developed for the dynamic shear rheology data was related to the number of cycles to failure of mixtures (unmodified binder only data reported). As the shift factor increased, the number of cycles to failure increased (constant strain) (41).

Goodrich indicated that the loss tangent values (G"/G') correlated well with bending beam fatigue tests (0.05 sec load/0.55 sec unload) although he did not report any magnitudes of test results (56).

Mixture Testing Only

Several research projects evaluated the influence of polymer modified binders based solely on the comparison of modified mixture properties.

Temperature Susceptibility

Temperature susceptibility for mixtures is commonly evaluated by developing relationships between resilient moduli and temperature. Test temperatures typically range from -18 to 40°C (0 to 104°F).

Khosla (1989) showed that the use of polymer modified binders reduced the slope of the resilient modulus versus temperature relationship (57). However, the polymers tended to increase the cold temperature modulus. Newcomb et al. showed that EAA modifiers increased the resilient modulus at warmer test temperatures while not significantly increasing the cold temperature stiffness (58). Shuler presented similar results for either SBS, EVA, and SBR polymer modified mixtures with polymer concentrations of between 2 and 3 percent by weight of asphalt cement (59). When the polymer concentrations increased (> 5 percent) for the same polymers, the extender oil modified SBS (Kraton K4463) had lower moduli at cold temperatures and similar moduli as the control mixtures at the warm test temperatures. The EVA (Elvax 150W) modified mixtures had higher moduli at colder temperatures and similar moduli at warmer temperatures. The SBR (Styrelf) had consistently lower moduli, regardless of test temperature.

Permanent Deformation

Khosla used incremental static creep testing as input into the VESYS performance prediction computer program to show that softer grade asphalt cements modified with polymers would be significantly more resistant to rutting than the unmodified control mixtures (57).

Goodrich indicated that the rutting potential of a poor performing aggregate such as a partially crushed river gravel could be improved with the use of polymer modified binder. However, in most cases, changes in mixture properties such as air voids, and binder content overshadowed any changes in mixture properties due solely to polymer modification (56).

Tayebali showed that the plastic strains measured with axial creep testing were significantly lower for Kraton K4460 modified binders than for conventional mixtures (47). When the same test was conducted with a 103 kPa (15 psi) confining pressure, the differences between the modified and unmodified mixtures disappeared.

Terrel demonstrated that the rut depth as measured with a loaded wheel tester was reduced by about 50 percent for any modified mixture in general (2).

Fatigue Testing

Khosla used diametrial fatigue testing to demonstrate that polymer modification of binders would increase the numbers of cycles to failure (57). This conclusion was based on using the test results as input into the VESYS pavement performance prediction computer program.

Tappeiner et al. presented general information based on beam fatigue testing at 25 and 275 kPa (40 psi) (61). Their results indicated the numbers of cycles to failure at the lower pressure were about 4,000 and 14,000 for unmodified AC 10 and AC 20, respectively. When an LDPE modifier was added, the numbers of cycles to failure increased to 27,000. When a higher pressure of 483 kPa (70 psi) was used, the differences between the unmodified and modified mixtures disappeared.

In 1966, Schmidt attempted to relate the shift factor for the construction of master curves to the numbers of cycles to failure in a constant strain bending beam test (41). In general, as the shift factor increased, the numbers of cycles to failure increased.

SUMMARY

The following is a summary of the literature review information presented in this chapter:

1. The term "compatibility" can refer to the suspension of a polymer within the asphalt cement matrix; this is primarily a function of matching specific gravities. It can also refer to thermodynamically "compatible" due to a matching of solubility parameters at given temperatures

2. The addition of a polymer will increase the viscosity of asphalt cement. This is true for polymer particle sizes in excess of 10 μm (longest dimension of coalesced particle).

3. Most modified binders have historically been evaluated with conventional test methods such as cold penetration (4°C) and softening point. Results from the penetration test are only slightly sensitive to the addition of polymer. Results from the softening point appear to differentiate between polymer type (i.e., SBS, SEBS), polymer concentration, and structure. The softening point has also been related to the loss modulus, G".

4. A change in the slope of the storage modulus versus frequency relationship for modified compared to unmodified binders could be an indication of polymer-asphalt interactions.

5. There appears to be a correlation between the glass transition temperature and the number of observed thermal cracks. Asphalts with a T_g below -23°C showed a good resistance to thermal cracking.

6. Rut depth of mixtures has been related to the loss modulus, G", of the binder. There is a linear decrease in the rut depth with a corresponding increase in G". However, after about 8,500 Pa at 60° C and 1 Hz, increased G" does not influence the resistance of the mixture to rutting.

7. Constrained beam test results for mixtures correlated well with the Fraas brittle point test results for binders. There was also a linear relationship between the mixture test results and the bending beam rheometer results at 15°C and a 60 second load duration.

8. There have been mixed results in evaluating the temperature susceptibility of modified mixtures. Modifiers can either increase the mixture stiffness (i.e., resilient modulus) at cold temperatures, not influence it, or soften it. These observations can hold true for a wide range of temperatures or be reversed between cold and warm test temperatures.

9. Axial creep testing of mixtures usually indicates that polymer modification of the binder

wide range of temperatures or be reversed between cold and warm test temperatures.

9. Axial creep testing of mixtures usually indicates that polymer modification of the binder increases the mixtures resistance to permanent deformation. The magnitude of improvement can be reduced by testing at either very high temperatures, high confining pressures, or fast loading frequencies.

10. There is some indication that an increase in the shift factor as measured for the binder should reflect an increase in the fatigue life of a mixture (based on constant strain mixture testing).

CHAPTER SIX

Actual field performance of any product is typically determined by placing and monitoring field test sections. Ideally, these test sections should include preconstruction, construction, and periodic post-construction testing and evaluation. Work prior to construction should include the selection of appropriate material variables such as the type and level of modifier(s), asphalt and aggregate properties, and aggregate gradation. Construction variables such as appropriate selection of construction project, and definitions of structural variables (e.g., lift thickness, location - wear course, surface course, etc.). Preconstruction testing should include the development of mix designs and possibly fundamental mixture properties. Construction testing ensures that what was produced was similar to what was intended by the original mix design. Laboratory testing and any specifications used to order atypical materials should then be evaluated and rated based on periodic pavement performance measures. While the above summary describes an ideal field evaluation, a review of the literature showed that very few modified test sections have been constructed in this manner.

Several projects included extensive laboratory testing followed by field performance lacked basic information about the type, supplier, or percentage of modifiers. Some projects classified modified binders by preliminary, non-standardized terms (e.g., PMA I, etc.). Others documented the construction and mix design but failed to include follow-up information regarding pavement performance.

Many test sections with various modifiers have been placed over the years, however these were usually limited joint efforts between a specific polymer supplier and a state, county, or city. Without an individual canvasing of each agency, this information was not accessible. The little information that was obtained in this manner indicates that there is usually not a complete set of information from preconstruction to post construction evaluation. Therefore, the information presented in this chapter will be primarily restricted to findings published in typical industry publications.

EXISTING FIELD TEST SECTIONS

In evaluating reported field results, care was taken to critically evaluate the information reported. For instance, one report compared longitudinal and transverse cracking but in this case the test sections were an overlay over a portland cement concrete pavement (61). While transverse cracking is a term commonly used to refer to thermal cracking, the cracking reported for these projects were probably more a measure of reflective cracking than either traffic or weather-induced distresses.

Table 6.1 provides a general summary of the type of information that was found in the literature. It can be seen from this table that only general information exists. This lack of specific information made it difficult to draw more than a couple of specific observations. First, it appears that mixtures with EVA has a tendency for brittle behavior as seen by the reports of premature cracking. Secondly, there was no consistent trends in resistance to rutting for any of the modifiers reported.

Table 6.1. Summary of Typical Test Section Information.

Location	Date Constructed	General Information	Polymer Information	Performance
Alabama US 231 Idaho, District Rd. Ada County Maine I-95 Michigan M-35 Texas US 83 (Ref.58)	1986 & 1987	AC-30, 68,000 ADT AC-10, 3,664 ADT AC-20, 13,390 ADT 120/150 Pen 2,900 ADT AC-20, 14,000 ADT	Each project had: Control Section 3% SBR latex 5% polyolefin No. 1 5% polyolefin No. 2 2% polyolefin No. 1 & 3% SBR latex 5% polyolefin No. 1 & 3% SBR latex 2% polyolefin No. 2 & 3% SBR latex	Air voids much higher in place than in lab compacted samples No performance information presented - too new for conclusions
Texas, District 15 near San Antonio, TX (Ref. 62)	1987	AC-20 for control 1.5" overlay over HMA AC-10 for modified	4.5% SBR Latex Emulsion 3% SBS 3% SBS (Styrelf) 3% EVA 5% SBR/Polyolefin combination	Both plastomers (i.e., EVA, SBS/polyolefin) showed more problems with both thermal and longitudinal cracking than either the control section or the SBS modified sections. Construction problems noted with the SBR included sticking to haul trucks, workability problems through the paver, and smoking.
Oregon: Lava Butte-Fremont Hwy. Junction	1989	AC-20, dense graded, 6,100 ADT	5% EVA, with and without lime	Not performing as well as control-more thermal and fatigue cracking. Attributed problems with high (170°C) binder temperature during mixing. In-place voids lower for modified sections.
Farewell Bend-N. Fork Jacobson Gulch	1988	AC-20, dense graded 5,500 ADT	5% (?) EVA	No difference between sections after 2 years.
Murphy Road-Lava Butte (Ref. 63)	1989	AC-20, open graded 8,100 ADT	EVA SB SBR	All modifiers improved pavement resistance to raveling, weathering, and abrasion. Same in other respects.

Table 6.1 (Continued). Summary of Typical Test Section Information.

Location	Date Constructed	General Information	Polymer Information	Performance
Barrie, Ontario Highway 400 (Ref. 64)	1988	36,000 ADT	Control LDPE (Novophalt) Vestoplast Neoprene (No info. on % polymer or AC)	Novophalt section showed 50% less rutting after 2 years than the control. Other modified asphalts were in between
Sherman, Texas Route 75 (Ref. 65)	1986	AC-20 for control section 3 & 4" overlay over PCC 17,000 to 28,000 ADT AC-10 for modified sections 3" overlay over PCC	Novophalt (LDPE) Kraton (SBS) SBR Latex EVA	No longitudinal or thermal cracking for first 4 years in any of the sections. Degree of transverse cracking ranked materials from most to least as: AC-20 3" > SBS > EVA > SBR > AC-20 4" = Novophalt Degree of longitudinal cracking ranked materials from most to least as: EVA > AC-20 4" > 3" > SBS > SBR > Novophalt
Alabama				
US 31 Limestone County	1988/1989	10,870 ADT	Control	40% less rutting, similar thermal cracking
US 231 Madison County	1988/1989	41,070 ADT	SBR Latex modified	200% more rutting, no thermal cracking
AL 69 Walker County	1985	3,980 ADT		70% less rutting, 80% less thermal cracking
US 82 Autauga County	1989	8,500 ADT		60% more rutting, no thermal cracking
267 Lee County	1987	5,112 ADT		Similar rutting, no thermal cracking
(Ref. 66)				

Table 6.1 (Continued). Summary of Typical Test Section Information.

Location	Date Constructed	General Information	Polymer Information	Performance
Ocotilla, California State Route (SR) 98 (Ref. 67)	1986	AR 4000 for control 0.13 ft. leveling course + 0.15 ft surface course	Kraton SBS SBR	Lab evaluation of extracted asphalt showed that the SBS modified binder had not aged while the control viscosity had increased 13 fold. Steel wheel rollers recommended to avoid pick up on rubber tired rollers.
Roseville, Minnesota Prior and Oakcrest Aves. (Ref. 68)	1987		200/300 pen + Polysar 125/160 pen + Polysar	Limited construction problems due to the screed dragging.
Swift, Minnesota Warroad and Williams (Ref. 68)	1989	AC-20 for control 2.75 " leveling course + 1.5" surface course over PCC Sections placed with and without RAP	3% Neoprene 3% Neoprene + RAP	Some pick up during rolling noted. A silicone additive was used to retard pulling behind the paver. Boxes were not greased on haul trucks to prevent contamination of the additives (manufacture recommendation). Belly dumps or end dumps would have worked better as the modified AC was difficult to get out of the flowboys. No performance information reported.
City of Lethbridges, Canada (Ref. 69)	1988	150/200 Pen for control Refinery modified asphalt Dense graded + 30% RAP	150/200 modified (not identified) PMA 2 (not identified) PMA 4 (not identified) + 30% RAP 200/300 modified (not identified) + 30% RAP 150/200 modified (not identified + 30% RAP	Minor construction problems with pick-up on cold rubber tired rollers. Generally reported reduced rutting potential, but basis of conclusions unclear.

NON-STANDARD SPECIFICATIONS

Attempts to standardize specifications for modified binders have been limited to selecting existing tests and establishing or redefining limits for the modified binders. No specifications have been developed for polymer modified mixtures.

Pacific Coast Conference on Asphalt Specifications

A report, first issued in May, 1990, defined a performance based asphalt binder grading system which includes the use of both unmodified and modified binders (71). Table 6.2 shows the proposed grading system. This table shows that while standard tests such as penetration, ductility, and kinematic and vacuum viscosities have been used in the development of this grading system, the non-Newtonian nature of polymer modified asphalts has been addressed to a limited extent by specifying the use of Asphalt Institute tubes for viscosity measurements.

Briefly, PBA-1, PBA-2, and PBA-4 designate desired properties for moderate, cold, and hot climates, respectively. These are the only three grades that could be met by unmodified asphalts typical of the conference states (i.e., Arizona, California, Nevada, Oregon, and Washington). The PBA-3, PBA-5 designate binders for very cold, and extremes in hot and cold temperatures, respectively, and would require polymer modification. Both PBA-6 and PBA-7 are also for extreme climate conditions (hot/very cold, and very hot, respectively) and would require polymer modification.

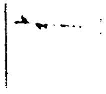
AASHTO-AGC-ARTBA Joint Committee Proposed Specifications

Tables 6.3 through 6.5 show the 1992 proposed specifications from this joint committee (72). PMA I was developed for asphalts modified with styrene block copolymers with either a diblock or triblock structure. PMA II and PMA III specifications were intended for either SBR or Neoprene latex modified binders, and EVA or PE polymers, respectively.

Table 6.2. AASHTO-AGC-ARTBA (71)

April 20, 1992

TENTATIVE PERFORMANCE BASED ASPHALT BINDER GRADES (Note 1)

			Moderate Climate		Cold Climate	Very Cold Climate	Hot Climate	Hot/Cold Climate	Hot/Very Cold Climate	Very Ho Climat
	Environmental Guidelines for Selecting the PBA Grade: Lowest recorded temperature		above 5F		above -20F	below -20F	above 5F	above -20F	below -20F	
	Highest mean monthly temperature		below 90F		below 90F	below 90F	above 90F	above 90F	above 90F	above 1
Asphalt Binder Performance Issue	Asphalt Binder Test Method Correlated with the Performance Issue	AASHTO Test Method	PBA-1 	PBA-1a	PBA-2 	PBA-3 	PBA-4 	PBA-5 	PBA-6 	PBA-7 
Low temperature thermal cracking.	Penetration (4C [39.2F], 200g, 60s), dmm RTFO Aged Residue (Note 2.)	T-49	Report (Note 3.)	Report	15+	30+	Report	15+	30+	Report
Low temperature thermal cracking.	Penetration (25C [77F], 100g, 5s), dmm RTFO Aged Residue	T-49	25+	25+	Report	---	20+	---	---	
Low temperature thermal cracking.	Ductility (7.2C [45F], 1 cm/min), cm RTFO Aged Residue (Note 4.)	T-51	---	---	10+	---	---	Report	---	
High ambient temperature mix stability (tenderness, rutting).	Absolute Viscosity (60C [140F]), P.(Note 5.) Original Binder RTFO Aged Residue	T-202 T-202	800+ 2500-5000	1600+ 8000-	1100+ 2500-6000	1100+ 3000+	2800+ 14000-	2000+ 4000+	2000+ 5000+	1100+ 3000+
Consistency during construction: - Pumpability, handling - Mix tenderness.	Kinematic Viscosity (135C [275F]), cSt Original Binder RTFO Aged Residue	T-201 T-201	--- 275+	--- 275+	--- 275+	2000- 275+	--- 350+	2000- 400+	2000- 275+	2000 275+
Hardening during the hot mix paving process.	Absolute Viscosity Ratio (60C [140F]) RTFO Viscosity/Original Viscosity		4.0-	4.0-	4.0-	4.0-	4.0-	4.0-	4.0-	4.0
Severe climate aging.	Penetration (25C [77F], 100g, 5s), dmm Tilt Oven Residue (Note 6.)	T-49	---	---	---	Report	---	---	Report	30+
Severe climate aging.	Ductility (25C [77F], 5 cm/min), cm Tilt Oven Residue	T-51	---	---	---	Report	---	---	Report	40+
Severe climate aging.	Absolute Viscosity (60C [140F]), Poise Tilt Oven Residue	T-202	---	---	---	Report	---	---	Report	50000
Safe Handling.	Flash Point, Cleveland Open Cup, C [F] Original Binder	T-48	232+ (450+)		232+ (450+)	232+ (450+)	232+ (450+)	232+ (450+)	232+ (450+)	232+ (4
Environmental Impact.	Mass Loss after RTFO Test, %	T-240	Report	Report	Report	Report	Report	Report	Report	Report
Asphalt Binder Purity.	Solubility in Trichloroethylene, % Original Binder	T-44	99.0+	99.0+	99.0+	Report	99.0+	Report	Report	Report
Asphalt Cement Internal Compatibility.	Ductility (25C [77F], 5 cm/min), cm RTFO Aged Residue	T-51	75+	75+	75+	75+	50+	50+	60+	75+

Note 1. This tentative grading system is intended for Conference evaluation only. The evaluation process may lead to changing the PBA Grades, the test methods, the test limits, and the environmental guideline

Note 2. "RTFO Aged Residue" means the asphaltic residue obtained using the Rolling Thin-Film Oven Test ("RTFO Test"), AASHTO T-240 or ASTM D 2872.

Note 3. Where "Report" or actual limits are indicated, the Committee will require actual test values (not, for example "75+"). This will permit the determination of appropriate specification limits.

Note 4. Use AASHTO T-51 as modified by Washington DOT (using a special mold release agent, and a special method of applying the release agent)

Note 5. The Absolute Viscosity (60C) of PBA-3, PBA-5, PBA-6 and PBA-7 will be determined at 1 sec-1 using ASTM D4957-89 (Vol. 4.03) with Asphalt Institute Vacuum Capillary Viscometers

[illegible]

Table 6.3. PMA I: Diblock (SB) or Triblock (SBS) Copolymer Modified Binder Specification (72).

		I-A	I-B	I-C	I-D
Penetration, 77F, 100g, 5sec	Min Max	100 150	75 100	50 75	40 75
Penetration, 39.2, 200g, 60sec	Min	40	30	25	25
Viscosity, 140F, P	Min	1000	2500	5000	5000
Viscosity, 275F, cSt	Max	2000	2000	2000	2000
Softening Point, R & B, F	Min	110	120	130	140
Flash Point, F	Min	425	425	450	450
Solubility in TCE, %*	Min	99.0	99.0	99.0	99.0
Separation**, R & B difference, F	Max	4	4	4	4
RTFOT Residue					
Elastic Recovery***, 77F, %	Min	45	45	45	50
Penetration, 39.2F, 200g, 60s	Min	20	15	13	13

* Solubility of original asphalt by ASTM D2042.
** Method described in Appendix A
*** Method described in Appendix B

Table 6.4. PMA II: SBR or Neoprene Latex Modified Binder Specifications(72).

		II-A	II-B	II-C
Penetration, 77F, 100g, 5sec	Min	100	70	80
Viscosity, 140F, P	Min	800	1600	1600
Viscosity, 275F, cSt	Max	2000	2000	2000
Ductility, 39.2, 5 cpm, cm	Min	50	50	25
Flash Point, F	Min	450	450	450
Solubility*, %	Min	99	99	99
Toughness, 77F, 20 ipm, in-lbs	Min	75	110	110
Tenacity, 77F, 20 ipm, in-lbs	Min	50	75	75
RTFOT or TFOT Residue				
Viscosity, 140F, P	Max	4000	8000	8000
Ductility, 39.2, 5 cpm, cm	Min	25	25	8
Toughness, 77F, 20 ipm, in-lbs	Min			110
Tenacity, 77F, 20 ipm, in-lbs	Min			75

* Solubility of original asphalt by ASTM D2042.

Table 6.5. PMA III: EVA or Similar Product Modified Binder Specifications (72).

		III-A	III-B	III-C	III-D	III-E
Penetration, 77F, 100g, 5sec	Min	30	30	30	30	30
	Max	130	130	130	130	130
Penetration, 39.2, 200g, 60sec	Min	48	35	26	18	12
Viscosity, 275F, cSt	Min	150	150	150	150	150
	Max	1500	1500	1500	1500	1500
Softening Point, R & B, F	Min	125	130	135	140	145
Flash Point, F	Min	425	425	425	425	425
Separation*		Homog	Homog	Homog	Homog	Homog
RTFOT Residue						
Loss, %	Max	1.0	1.0	1.0	1.0	1.0
Penetration, 39.2, 200g, 60sec	Min	24	18	13	9	6

* Method described in Appendix C

All three PMA types have subcategories to cover a range of polymer-asphalt interactions as well as a range of percentages of polymers. These tables show that the AASHTO-AGC-ARTBA specifications are based on a more limited range of tests than the Pacific Coast specifications. Also these specifications make no effort to address non-Newtonian behavior of polymer modified asphalts.

Proposed ASTM Designations for Polymer Modified Asphalt Cements

ASTM is currently working on adopting specifications similar to those developed by AASHTO-AGC-ARTBA. These specifications are not available for review at this time.

CHAPTER SEVEN

The information presented in the preceding chapters has been used to suggest several laboratory and field experimental designs. These are presented below.

LABORATORY EXPERIMENTAL DESIGNS

The literature review revealed key polymer properties that should be included in the laboratory experiments are polymer structure (linear, radial), molecular weights, types (i.e., SBR, SBS), and variations due to manufacturers' processes. The minimum asphalt cement properties that should be included are different grades of the same source, and various sources. It is assumed that a range of asphalt chemistry can be obtained by selectively identifying asphalt cement sources with differing chemistry.

Laboratory tests for modified binders should include dynamic mechanical rheology over a wide range of test temperatures, estimates of low temperature behavior, and a study of the morphological structure of the polymer within the asphalt cement. Laboratory tests for modified mixtures should also include measurements of rheological properties for a wide range of temperatures, and a specific characterization of low temperature properties. Several experimental designs are suggested below.

Polymer Structure/Source, and Asphalt Grade/Source

This experimental design was developed to investigate the interactions between elastomeric block copolymers (i.e., SBS) and asphalt cement. According to the literature, these interactions should theoretically be influenced by the polymer structure and possibly the source of polymer, and the asphalt source and grade. Radial polymers should provide a greater increase in viscosity than linear polymers at the same concentration level. With a thermodynamically compatible asphalt cement, a lower viscosity asphalt cement should show significant changes in viscosity for a given polymer and concentration.

While these changes have been documented in the literature, there is little information available as to how and why these changes in binder properties occur. This study will attempt to link fundamental properties for the binders to changes in the morphological structure of the polymer within the asphalt. If the supplier literature is correct and the polymer is forming a network within the asphalt cement, then various levels of network formation should be seen as changes in binder properties. In order to establish the durability of the initial polymer morphology, a limited aging study is also suggested.

Tests and key parameters selected for defining fundamental binder properties include:

1. Dynamic mechanical rheometry to measure changes in the viscosity, modulus, and phase shift over a range of temperatures.
2. Traditional binder properties such as penetration at 4 and 25°C (39.2 and 77°F), and absolute viscosity measurements (Asphalt Institute tubes).
3. Estimates of the glass transition temperature from the WLF and/or Arrhenius shift factors, and the peak loss modulus. Both values are obtained from the rheological testing.
4. Fraas brittle point.
5. Rolling thin film oven for aging binders.

Rheology testing was selected because it measures fundamental material properties and is compatible with the current SHRP/FHWA research efforts. Traditional binder tests have been included in order to confirm the findings reported in the literature. Estimates of the glass transition temperature have been suggested because of the difficulty in obtaining actual measurements; the literature showed that estimates from rheological data should be reasonable. The Fraas brittle point was included because it has been directly linked by several researchers to the cold temperature behavior of mixtures. The rolling thin film oven aging conforms with the new SHRP binder specifications. Table 7.1 shows the suggested experimental design based on the above discussion.

Table 7.1. Experimental Design for Investigating the Influence of Polymer Structure/Source, and Asphalt Grade/Source.

		Polymer Structure											
		Linear						Radial					
		Polymer Source											
		Shell Kraton D1101		Dexco Vector 2518		Enichem 6302		Shell Kraton D1184		Dexco Vector 2411		Enichem T 161C	
		Percentage of Polymer											
AC Source	AC Grade	2	4	2	4	2	4	2	4	2	4	2	4
AAF	AC 20	A	ABC	A	ABC	A	ABC	A	ABC	A	ABC	A	ABC
	AC 10	A	ABC	A	ABC	A	ABC	A	ABC	A	ABC	A	ABC
AAA	200/300	A	ABC	A	ABC	A	ABC	A	ABC	A	ABC	A	ABC
Koch	120/150		AB		AB		AB		AB		AB		AB
Koch	AC 20		ABC		ABC		ABC		ABC		ABC		ABC

A: Dynamic Mechanical Rheology (-30 to 64°C), estimated T_g, and Fraas brittle point.
B: Rolling thin film oven aged binders
C: Morphological study

Asphalt cements for this study have been selected from both the SHRP materials reference library and a local refinery. The SHRP asphalts were suggested because of the extensive amount of asphalt chemistry information that is available for these materials. One source of local asphalt cement was suggested so that the applicability of polymer modification of a typical Minnesota asphalt could be assessed.

Modification of Asphalts Generally Incompatible with SBS Products

While the main emphasis of this study is to investigate the use of elastomeric polymers as a means of improving cold temperature properties, some asphalts are thermodynamically incompatible with standard SBS polymers. However, with the new SHRP binder specification, some locations in the country will have to modify neat asphalt properties in order to meet all of the requirements. If the only local asphalt sources are incompatible with standard SBS products, then there will be a potential problem with the adoption of the specifications. Therefore, a limited study is proposed to investigate possible approaches for modifying an otherwise incompatible asphalt cement.

Potential approaches include using plastomers, low molecular weight SBS products, or SBS products designed to interact with asphalt components. Low molecular weight SBS products should make it easier for the polymer to disperse within the asphalt. Product suppliers have also indicated there are several proprietary products that will "react" with asphalt components so that the polymer remains dispersed within the asphalt matrix.

Preliminary laboratory results have shown that the SHRP MRL asphalt AAM-1 is generally incompatible with standard SBS polymers. Blending with 4 percent of a radial SBS product resulted in almost immediate phase separation of the asphalt and polymer upon cessation of blending. However, plastomer modifiers appear to stay well dispersed for the same asphalt. The small laboratory study shown in Table 7.2 is suggested.

Because of the reported problems with premature cracking in field sections with these products, a special emphasis will be placed on evaluating cold temperature properties. Additional testing for this program should include an evaluation of bending beam rheometry and direct tension results, if possible. It is likely that this testing will need to be conducted by other laboratories as the University does not currently have the capability for this testing.

Table 7.2. Experimental Design for Investigating Plastomers and Non-Standard SBS Products.

	Plastomers			Elastomers			
Asphalt Cement	EVA 150W	Elvaloy AM	Polybuilt 503	Reactive SBS (Proprietary)	Low MW Radial SBS	High MW Linear SBS	Low MW Linear SBS
AAM	ABCD	ABCD	ABCD	ABCD	ABCD	ABCD	ABCD

A: Dynamic Mechanical Rheology (-30 to 64°C), estimated T_g, and Fraas brittle point.
B: Rolling thin film oven aged binders
C: Morphological study
D: Bending beam, direct tension

Comparison of Binder and Mixture Properties

The literature indicated that large changes in binder properties did not necessarily relate to significant changes in mixture properties. No information was found which directly related the contribution of binder rheology to mixture rheology. Therefore, the suggested mixture analysis experiment was designed to address these concerns. The minimum mixture variables that were considered essential in this design were:

1. Air voids.
2. Voids in mineral aggregate (VMA).
3. Binder film thickness.
4. Percent crushed coarse aggregate.

Both air voids and VMA can be varied by changing the aggregate gradation, and/or the asphalt cement content. Binder film thickness will be a covariable with both the air voids and VMA. The percent crushed material can be incorporated by selecting an aggregate source that produces materials for both portland cement and asphalt concrete. The source of aggregates should be held constant if at all possible in order to prevent the introduction of the aggregate chemistry as an uncontrolled variable.

Mixture testing should include:

1. Dynamic and resilient modulus over a range of temperatures.
2. Creep testing.
3. Indirect tensile creep testing.

Measurements of resilient modulus over temperature are commonly used to assess the temperature susceptibility of mixtures. The dynamic modulus was added so that rheological properties such as the phase shift, storage modulus, and loss modulus of the mixture could be assessed. Static creep testing was selected because it has been used historically to evaluate the permanent deformation characteristics. The indirect tensile creep test is a proposed SHRP mixture test which provides fundamental rheological measurements for the stress relaxation behavior of mixtures at cold temperatures.

In order to attempt a direct comparison of mixture and binder properties, two binder tests should be added for this study. They are a constant stress creep test at the same test temperature as the static creep test, and a constant strain test over the range of temperatures used for the indirect tensile creep test. The phase shift, storage modulus, and loss modulus from the dynamic mechanical rheometer testing of the binder in the first experiemental design can be compared to the similar fundamental properties of the mixtures. Table 7.3 shows a suggested experimental design.

Anticipated results from these comparisons include an estimate of the contribution of:

1. Binder properties to the total mixture rheological properties.
2. Volumetrics to the rheological properties of the mixtures.

This experimental design should be limited to one source of local asphalt cement; SHRP asphalt can not be used due to the limited supply of this material. This experimental design should serve as an initial study; further laboratory evaluations or additional tests may be needed after these results are evaluated.

Table 7.3. Experimental Design for Relating Binder and Mixture Rheological Properties.

	Percent Crushed Coarse Aggregate											
	100%						50%					
	Gradations											
	A		B		C		A		B		C	
	Asphalt Cement Content											
Polymer	Opt.	+0.5 Opt.	Opt.	+0.5 Opt.	Opt.	+0.5 Opt.	Opt.	+0.5 Opt.	Opt.	+0.5 Opt.	Opt.	+0.5 Opt.
None	C	C	C	C	C	C	C	C	C	C	C	C
Radial	AB	A	AB	A	AB	A	AB	A	AB	A	AB	A
Linear	AB	A	AB	A	AB	A	AB	A	AB	A	AB	A
SEBS	A		A		A		A		A		A	
EVA	A		A		A		A		A		A	

A: 4 percent polymer
B: 2 percent polymer
C: None - Control Sections

FIELD EXPERIMENTS

The significant lack of performance evaluations over several years was evident in the majority of the field sections reported in the literature. In order to establish as long an evaluation period as possible for any test sections constructed for this project, it is suggested that test sections be placed as soon as possible. Both the literature review and the preliminary binder evaluation experiments should provide a sufficient amount of information to design the field experiment.

Important variables for binders will be type and percentage of polymer. Key mixture properties will include film thickness, air voids, and aggregate gradation. A suggested procedure for the design of field test sections is as described below.

Select at least two types of polymers. Define the polymer concentration of each polymer on an equiviscous basis. That is, use the SHRP concept and set a maximum viscosity limit at the cold temperature, and a minimum viscosity at the warm temperature. The concentration of any polymer should be chosen so that these values are met.

Select one aggregate gradation. Preferably a coarse gradation so that the anticipated increase in film thickness of the modified binders do not have an adverse effect on the mixture properties. Use both traditional mix design methods and results from the testing described in the previous experiment to select optimum binder contents. Since the properties of the modified binders will be defined on an equiviscous basis, theoretically the optimum binder contents should be equal for both modified mixtures.

Select an appropriate construction project. New construction would be preferred, but it is doubtful if this is practical. Therefore, an overlay construction project would be the next best selection as long as the lift thickness is sufficiently thick to allow for coring and testing of the in-place material. Preconstruction field work should include a pavement condition survey and crack mapping, if appropriate. Traffic information such as the average daily traffic (ADT), percent trucks, and equivalent single loads (ESALs) should be collected.

Sampling during construction should include obtaining both behind the paver samples and corresponding samples of the modified binder. Both sets of materials should be evaluated with to the original testing program.

In-place materials should be obtained immediately after construction in order to determine the properties at the outset of the performance evaluation program. Pavement performance should be evaluated at least four times a year and subsequent cores taken as these evaluations indicate substantial changes in performance. These aged samples should be evaluated for both mixture properties and any changes in the binder itself such as polymer degradation or coalescence.

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Appendix A - Glossary of Polymer and Chemistry Terms

Acidifins Two of the five fractions obtained during Rostler-Sternberg fraction. The first acidifin is an unsaturated resinous hydrocarbons; the second acidifins are only slightly unsaturated. Believed to help peptize the asphaltenes.

Amorphous Polymer Polymer with a low crystallinity; will exhibit a tendency to flow (e.g., glass, water).

Aliphatic Saturated straight or branched chain molecules.

Arrhenius Function A relationship between temperature, activation energy, and viscosity used to develop shift factors for constructing master curves.

Aromaticity Indicates the presence of cyclic compounds with some number of conjugated double bonds. The overall negative electrical charge of the compound is dissipated by the delocalization of the pi bonds.

Asphaltenes Non-volatile, highly polar, friable particles precipitated from crude oils in the presence of added *n*-alkanes. They contribute significantly to changes in viscosity.

Block Copolymer A polymer made from two or more homopolymer groups.

Cis A term describing the configuration of a molecule. Indicates that the two non-hydrogen components are on the same side of a carbon-carbon bond.

Chromophores Groups of molecules typically held together due to attractive forces.

Colloid A dispersion of discrete particles ranging in size from 1 to 1,000 nm in a continuous phase.

Complex Modulus The total elastic and time dependent response of a material subjected to either an applied stress or strain.

Copolymer A polymer made from two or more different monomers.

Corbett An adsorption-desorption method of separating asphalt cement into two major fractions: asphaltenes and maltenes. The maltenes are then separated into saturates, naphthene aromatics, and polar aromatics.

Crack Pinning The impediment of crack propagation due to the obstruction of a crack by an inclusion. More energy is required to progress around an obstruction hence the crack formation is slowed.

Critical Concentration The concentration of polymer molecules that allows the molecules to just touch each other without overlapping.

Crosslinked The bonding of polymer chains to form a network. This is called vulcanization when rubber is crosslinked (3, pg. 16). Crosslinks can be either physical (e.g., thermodynamically-induced) or chemical (e.g., the addition of sulfur to rubber).

Diblock A polymer with only two groups of homopolymers.

Dipole Interactions Attractive forces between polar molecules due to their positive-negative charge characteristics.

Elastomers A crosslinked amorphous polymer above its glass transition temperature (T_g).

Glass Transition Temperature (T_g) Indicates the temperature at which the material properties change from glassy to rubbery. This is due to the increased molecular motion in the polymer chain. In the glassy region, only vibrational motions of the molecules are possible. As the material gets warmer, the amorphous portions of the material also gets softer and the chains can begin to move.

Homopolymer A group of the same monomer units.

Hydrogen Bonding A strong intermolecular bond between a nonbonding pair of electrons and an electrophilic O-H or N-H hydrogen.

IEC Ion exchange chromatography. A method of separating asphalt cement into fractions: strong acids and bases, weak acids and based, and neutral.

Loss Modulus G": The time dependent material response to either an applied stress or strain.

London Dispersion Forces Bonds developed between nonpolar molecules due to temporary dipole characteristics induced by adjacent molecules.

Maltenes Also called petrolenes, defined as the low viscosity components remaining after the asphaltenes have been removed.

Master Curve A method of combining test results from various loading frequencies and test temperatures into one curve for a selected reference temperature.

Melt Flow Index (MFI) An indication of molecular weight. Measures how long it takes to extrude a polymer sample under a given load. Higher molecular weight materials take longer to extrude so the MFI is low.

Molecular Weight Can be expressed as either an average molecular weight, M_n or a molecular weight distribution, M_w. Units are g/mole. (See polydispersity).

Monomers One unit of molecules. These are the building blocks of polymers, meaning many monomers.

Napthene Aromatics One of the three components of the maltene phase as determined by Corbett fractionation; considered to be the softening agent in the asphalt cement and a contributor to the change in binder properties during aging.

Natural Rubber A naturally occurring cis-polyisoprene.

Newtonian A material whose viscosity is independent of shear rate.

Nitrogen Base Resins One of the five fractions obtained by Rostler-Sternberg fractionation; considered the most reactive and contains essentially all of the nitrogen-containing compounds.

Non-Newtonian A material whose viscosity will change depending on the shear rate used to determine the viscosity.

Oxidative Scission A free radical chain reaction which can be accelerated upon irradiation by UV rays. Results in the shortening of the polymer chains.

Paraffins The least reactive class of organic compounds (also called alkanes). Also one of the fractions obtained during either Rostler-Sternberg or Corbett fractionation.

Peptizers Agents that help in dispersion.

Pi Bonds One of two bonds between double-bonded molecules and is responsible for the negative charge characteristics at the double bond. This bond is also one of the reasons double bonds sources of reactions.

Phase Angle The lag between the application of either a stress or strain and the material's response.

Plastics Amorphous materials below their glass transition temperature or crystalline polymers either above or below their glass transition temperature.

Triblock A polymer made up of three groups of homopolymers.

Unsaturated No double bonds present. Increases potential of degradation of polymer due to aging.

van der Waal's Forces Attractive forces between molecules; includes both dipole-dipole and London forces.

Vulcanization Crosslinking of rubber polymers.

Vulcansate The product of vulcanization.

William-Landel-Ferry (WLF) A relationship between viscosity and temperature that is used to develop shift factors needed to construct master curves. This relationship is typically applied to materials above the glass transition temperature.

component.

SEBS (Styrene ethylene-butadiene styrene) A synthetic rubber triblock copolymer. This polymer is considered saturated because the double bond in the butadiene component has been reduced to a single bond with the addition of the ethylene.

SEC Size exclusion chromatography. This is a sieve analysis for determining the molecular size "gradation". The molecular size determined is a function of the size of the agglomerated molecules so the test results are dependent upon the polarity of the solvent used to dissolve the asphalt cement.

Solubility The ability of one material to dissolve another.

Solubility Parameter The simplest concept in chemistry is that "like dissolves like". The solubility parameter is used to define "like" and was developed from an expression for the heat of mixing (i.e., enthalpy). When the solubility parameters of components are equal, no heat is required for mixing.

Stability In colloidal systems, stability refers to the balance of attractive and repulsive forces between the suspended particles. For combinations of polymers or polymers and solvents (e.g., asphalt cement), it refers to the thermodynamic compatibility between the components; this compatibility is a function of both temperature and the solubility parameters of the components.

Storage Modulus G': The elastic portion of a material's response to either an applied stress or strain.

Synthetic Rubber Styrene-butadiene rubber (SBR) which can be either a random or block copolymer.

Thermoset A crosslinked polymer (3, pg. 16).

Thermoplastic A material that flow above either its glass or melt transition temperature(T_g or T_m, respectively) but recovers its elastic behavior upon cooling below these temperatures **(70, pg. 218)**

Trans A term describing the configuration of a molecule. Indicates that the two non-hydrogen components are on opposite sides of a carbon-carbon bond.

Appendix B - Glossary of Highway Research and Construction Terms

Plasticizer A nonvolatile liquid added to increase flexibility and reduce brittle behavior below a materials glass transition temperature. Has the effect of reducing crystallinity and lowering the glass transition temperature.

Polar Aromatic One of the three components of the maltene phase as determined from Corbett fractionation; it is considered to be related to both ductility and changes due to aging.

Polychloroprene Chemical name for Neoprene.

Polydispersity An indication of the variation of lengths of polymer chains in a given polymer sample. It is expressed as a ratio of molecular weight measurements, M_w/M_n. When all polymer chains are the same length, the ratio is 1. More variability results in numbers greater than 1.

Polymer Chains of monomer units. While continually debated, can generally be assumed to have a molecular weight of greater than 25,000 g/mole (3, pg. 6)

Radial A star shaped configuration of the polymer.

Reptation Refers to theories used to describe the snake-like motion of polymer chains through entanglements created by surrounding chains.

Resins Are the portion of the asphalt cement believed to help disperse the asphaltenes.

Rheometer A piece of equipment capable of measuring the flow characteristics of a material. Traditional vacuum and kinematic viscosity equipment are rheometers for Newtonian materials (i.e., unmodified asphalts). A dynamic shear rheometer can measure properties for either Newtonian or non-Newtonian materials.

Rostler A chemical precipitation method of separating asphalt cement into components: first and second acidifins, nitrogen based resins, asphaltenes, and paraffins.

Saturates One of the maltene fractions obtained during Corbett fractionation

Saturated No double bonds present for hydrogenation. Reduces degradation of the polymer due to aging.

SBR (Styrene butadiene rubber) A synthetic rubber diblock copolymer.

SBS (Styrene butadiene styrene) A synthetic rubber triblock copolymer. This polymer is considered unsaturated because there is a double bond present in the butadiene

Air Voids The space between the binder-coated particles of aggregate.

Asphalt Cement Paving product from the bottom of a barrel of crude. Provides the "glue" to hold aggregates in place and enhances aggregate durability by providing protection to the aggregate from environmental factors (e.g., water).

Asphalt Concrete A combination of asphalt cement and aggregate used to construct pavements.

Binder The "glue" that holds the aggregate together in an asphalt concrete pavement. It can be either unmodified or modified asphalt cement.

Compacted Sample Asphalt concrete mixture that has been formed into a sample in such a way as to represent the compaction that takes place during highway construction. A typical size sample would have a cylindrical shape approximately 100 mm (4 in) in diameter by about 60 to 70 mm high (about 2.5 in). Beam samples can also be prepared; the typical sizes are either 37.5 x 37.5 x 325 mm (1.5 x 1.5 x 15 in) or 75 x 75 x 325 mm (3 x 3 x 325 mm).

Direct Tension For asphalt cement, a dog bone-shaped sample is subjected to a constant rate of deformation. For asphalt concrete, a compacted beam sample is subjected to the same loading procedure.

Ductility Measures how far a dog bone-shaped (hour glass shape center section) sample of asphalt cement can be stretched, usually at 5 cm/min without breaking.

Effective Binder Film Thickness The thickness of the binder that is not absorbed into the surface of the aggregate.

Force Ductility Measures the force it takes to stretch a dog bone-shaped (rectangular center section) asphalt cement sample. This test has been shown to be sensitive to the presence of additives when run at 1 cm/min and at 4°C (39.2°F).

Fraas Brittle Point The temperature at which the film of asphalt on a thin steel plate will crack after repeated flexing.

Hot Mix Asphalt (HMA) Asphalt concrete produced in a hot mix plant. This does not include cold mixed products such as emulsion mixtures or cold recycling.

Indirect Tensile Measurements Uses compression to produce a tensile response by applying a strip load along the circumference (i.e., diametral orientation) of a compacted asphalt concrete sample. This loading configuration is used to determine resilient modulus and the tensile strength of asphalt concrete mixtures.

LST Limiting Stiffness Temperature. The temperature at which a stiffness of 10.3 GPa (1.5 x 10^6 psi) for a constrained beam was obtained.

Optimum Binder Content The amount of binder needed to achieve a maximum load carrying capability with a limited amount of deformation, a maximum density, and air voids between 3 and 5 percent. The optimum binder content is strongly dependent upon aggregate characteristics such as gradation, aggregate shape, and absorption capacity.

Penetration An old but still used method for grading asphalt cement. It is the distance a needle with a 100 gram load will sink into a container of asphalt cement at 25°C after 5 seconds in units of 0.1 mm.

Resilient Modulus An estimate of Young's modulus for viscoelastic-plastic materials. A repeated load is applied briefly (typically 0.1 or 0.05 seconds) at various frequencies (typically 0.33, 0.5, and 1.0 Hz). The modulus is a function of the sample thickness, Poisson's ratio, applied vertical stress, and recoverable horizontal strain measured between loads.

Ring and Ball Softening Point Used as a measurement of the phase change of an asphalt cement. It is the temperature at which a small disk of asphalt can no longer support he weight of a steel ball.

RTFO Rolling Thin Film Oven Test. This is a procedure for simulating the aging of the asphalt cement that takes place during mixing operations. 35 grams of asphalt cement are placed in jars which are placed in a rotating carriage fitted; air is blown across the surface of the asphalt as the carriage rotates. The oven is held at 163°C (325°F) for 85 minutes.

Rutting Longitudinal depressions in the wheel paths due to traffic loads on soft paving materials.

Stability A measure of the ability of a compacted asphalt concrete sample to withstand a load. Marshall stability measures the maximum quasi-indirect load while Hveem stability measures a maximum axially applied load.

SUPERPAVE The Strategic Highway Research Program name for the entire process of designing an asphalt concrete mixture for highway construction. This includes not only the selection of the binder but an evaluation of the aggregate gradation as well as measurements of mixture strength and volumetric considerations.

Tensile Strength The stress required to fail the sample by indirect tension at a constant rate of deformation [typically about 50 mm/min (2 in/min)].

Thermal Cracking Fairly uniformly spaced transverse cracks due to the contraction of the paving material at cold temperatures.

Triaxial Testing The application of an axial load to a tall, cylindrical sample of compacted asphalt concrete. This test can be conducted with or without a confining pressure and is typically used for determining creep and dynamic modulus characteristics.

TSRST Thermal stress restrained sample test and determines a cold temperature cracking temperature for compacted beam samples of asphalt concrete. Once fabricated, the beams are placed in an environmental chamber and then subjected to a constant rate of cooling; the initial length of the beam is held constant and the resulting increase in stress necessary to maintain this length is measured. The fracture temperature is the temperature at which a peak stress occurs.

Voids in Mineral Aggregate The room left between aggregate particles; includes both air voids and the effective binder film thickness.

Appendix C - Key Word List and Annotated Bibliography

This appendix contains annotated bibliographies for all of the papers reviewed for this project. The majority of these papers were used as references for the body of the literature review. This section is intended to provide the reader with a well documented source of reference information on a wide range of topics related to polymer modifiers, modified binders, modified mixtures, and field performance. Therefore, a key work list has been prepared which lists common topics in alphabetical order followed by relevant references. The annotated bibliographies are organized in alphabetical order (by primary author) at the end of the key work list.

Key Words

APP

Enichem Supplier Information

Binder Tests - Basics

Armijo, Montana State University, March 1989
Bouldin, Rubber Chem. and Tech., 1991
Bouldin, ASTM STP 1108
Button, AAPT Vol. 56, 1987
Collins, ACS, 1991
Collins, AAPT Vol. 61, 1991
Collins, Rubber World, 1992
Enichem Technical Report No. 4 (no date)
Jain, ASTM STP 1108, 1992
Little, ASTM STP 1108, 1992
King, AAPT Vol. 62, 1992
King, AAPT Vol. 61, 1991
Mayam ASTM STP 1108, 1992
Shuler, ASTM STP 1108, 1992
Swager, ASTM STP 1108, 1992
Tappeiner, Novophalt America Literature
Zanzotto, CTAA Vol. 34, 1989
Zanzotto, CTAA Vol. 32, 1987

Colloidal Instability Index

Brule', AAPT Vol. 57, 1988

Compatibility

Brule', AAPT Vol. 57, 1988
Serfass, ASTM STP 1108, 1992

Constrained Beam (TSRST)

King, AAPT Vol. 62, 1992

Critical Concentration of Polymer

Bouldin, Rubber Chem and Tech., 1991
Collins, AAPT Vol. 61, 1991

Cox-Merz Rule

Bouldin, Rubber Chem. and Tech., 1991

IEC

Youcheff, Center for Applied Energy Research, University of Kentucky, 1991
Youcheff, unpublished, 1994

Infrared Spectroscopy

Choquet, ASTM STP 1108

Indirect Tensile Constant Strain

Buttlar, TRB preprint 940773, 1994
Button, AAPT Vol. 56, 987

HDPE

Daly, TRB preprint 930642, 1993
Hesp, ASTM STP 1108
Shida, Poly. Eng. and Sci., 1971

LDPE

Button, AAPT Vol. 56, 1987
Jain, ASTM STP 1108, 1992
Park, Appl. Poly. Sci Vol. 47, 1993

Limiting Stiffeness Temperature

Goodrich, AAPT Vol. 57, 1988

Low Temperature Mixture Testing

Goodrich, AAPT Vol. 57, 1988

Moisture Sensitivity

Button, AAPT Vol. 56, 1987
Shell Supplier Information

Molecular Weights

Bueche, J. Poly. Sci., 1960
Youcheff, unpublished, 1994

Neoprene - Binder Only

Anderson, ASTM STP 1108
Park, Appl. Poly. Sci Vol. 47, 1993
Swager, ASTM STP 1108, 1992

EVA - Polybilt
Armijo, Montana State Unversity, March 1989
Exxon Supplier Information

Fatigue Testing
Button, AAPT Vol. 56, 1987
Goodrich, AAPT Vol. 57, 1988
Khosla, AAPT Vol. 58, 1989

Flow Index
Sabia, J. Applied Poly. Sci., 1963

Flourescence Microscopy
Bouldin, Rubber Chem. and Tech., 1991
Collins, AAPT Vol. 61, 1991
Daly, TRR 1391, 1993
Daly, TRB preprint 930642, 1993

Fraas Brittle Point
Anderson, ASTM STP 1108
Jain, ASTM STP 1108, 1992
King, AAPT Vol. 62, 1992
Serfass, ASTM STP 1108, 1992

Fractionation
Youcheff, unpublished, 1994

Fracture Toughness
Lee, TRB preprint 940185

FTIR
Daly, TRB preprint 930642, 1993

GPC
Brule', AAPT Vol. 57, 1988
Collins, ACS, 1991
Collins, Rubber World, 1992
Zanzotto, CTAA Vol. 34, 1989

Direct Tension - Binder Only
- Brule', AAPT Vol. 57, 1988
- Linde, ASTM STP 1108, 1992
- King, AAPT Vol. 62, 1992

Direct Tension - Mixture Only
- King, AAPT Vol. 62, 1992
- Mayama, ASTM STP 1108, 1992 (constant strain)

DSC (Differential Scanning Calorimetry)
- Daly, TRR 1391, 1993
- Daly, TRB preprint 930642, 1993
- Jain, ASTM STP 1108, 1992

EAA (ethylene acrylic acid)
- Newcomb, ASTM STP 1108, 1992

EEA - SBR
- Mayama ASTM STP 1108, 1992

EMA - Polybilt
- Exxon Supplier Information

EVA - Binder Only
- Hesp, ASTM STP 1108
- Jain, ASTM STP 1108, 1992
- Swager, ASTM STP 1108, 1992

EVA - Elvax 150
- Bouldin, ASTM STP 1108
- Collins, AAPT Vol. 61, 1991
- Shuler, ASTM STP 1108

EVA - Lab/Field
- Bouldin, ASTM STP 1108
- Button, AAPT Vol. 56, 1987
- Jones, TRB 1993 preprint
- Rogge, ASTM STP 1108, 1992
- Tappeiner, Novophalt America Literature

NMR
Daly, TRB preprint 930642, 1993
Youcheff, unpublished, 1994

PB
Jain, ASTM STP 1108, 1992

PE
Collins, ACS, 1991
Collins, Rubber World, 1992
Daly, TRR 1391, 1993
Hesp, ASTM STP 1108
Lee, TRB preprint 9940185, 1994
Park, Appl. Poly. Sci Vol. 47, 1993

PE - Novophalt
Button, AAPT Vol. 56, 1987

PE - Maleated or Chlorinated
Daly, TRB preprint 930642, 1993

Permanent Deformation - Creep Testing
Collins, ACS, 1991
Collins, AAPT Vol. 61, 1991
Khosla, AAPT Vol. 58, 1989
Goodrich, AAPT Vol. 57, 1988
Little, ASTM STP 1108, 1992
Tayebali, AAPT Vol. 61, 1991
Tappeiner, Novophalt America Literature

Permanent Deformation
Button, AAPT Vol. 56, 987
Bouldin, ASTM STP 1108
Collins, AAPT Vol. 60, 1991
King, AAPT Vol. 60, 1991
Tappeiner, Novophalt America Literature

PMA Grading System
Zanzotto, CTAA Vol. 32, 1987

Polymers - General
Zanzotto, CTAA Vol. 32, 1987

Polyolefins

Hesp, ASTM STP 1108
Jones, TRB 1993 preprint
Newcomb, ASTM STP 1108, 1992

PP

Jain, ASTM STP 1108, 1992

Relaxation Times

Bouldin, Rubber Chem and Tech., 1991
Sabia, J. Applied Poly. Sci., 1963

Resilient Modulus

Khosla, AAPT Vol. 58, 1989
Newcomb, ASTM STP 1108, 1992
Shuler, ASTM STP 1108, 1992

Rheology - Bending Beam

Daly, TRR 1391, 1993
Daly, TRB preprint 930642, 1993
King, AAPT Vol. 62, 1992

Rheology - Parallel Plate

Anderson, ASTM STP 1108
Bouldin, Rubber Chem. and Tech., 1991
Bouldin, ASTM STP 1108
Collins, ACS, 1991
Collins, AAPT Vol. 61, 1991
Daly, TRB preprint 930642, 1993
Goodrich, AAPT Vol. 57, 1988
King, AAPT Vol. 61, 1991
King, AAPT Vol. 62, 1992
Tayebali, AAPT Vol. 60, 1991
Youcheff, unpublished, 1994
Zanzotto, CTAA Vol. 32, 1987

Rheology - Torsion Bar

Anderson, ASTM STP 1108
Bouldin, Rubber Chem. and Tech., 1991
Daly, TRR 1391, 1993

Rolling Thin Film Oven Test

Collins, ACS, 1991
Goodrich, AAPT Vol. 57, 1988

SB - Binder Only

King, AAPT Vol. 61, 1991
King, AAPT Vol. 62, 1992
BASF Corp. Literature
Swager, ASTM STP 1108, 1992

SBR - Binder Only

Anderson, ASTM STP 1108
Jebro Supplier Information
Park, Appl. Poly. Sci Vol. 47, 1993
Swager, ASTM STP 1108, 1992
Zanzotto, CTAA Vol. 34, 1989

SBR - Lab/Field

Button, AAPT Vol. 56, 1987
Collins, ACS, 1991
Tappeiner, Novophalt America Literature
Rogge, ASTM STP 1108, 1992

SBR - Ultrapave

Armijo, Montana State Unversity, March 1989
Bouldin, Rubber Chem. and Tech., 1991
Button, AAPT Vol. 56, 1987
Collins, ACS, 1991
Collins, AAPT Vol. 61, 1991

SBS - Binder Only

Anderson, ASTM STP 1108
Brule', AAPT Vol. 57, 1988
Serfass, ASTM STP 1108, 1992
Swager, ASTM STP 1108, 1992

SBS - E Sol T

Enichem Technical Paper No. 1 (no date)
Enichem Supplier Information

SBS - Kraton D1101 or D1184
Bouldin, Rubber Chem. and Tech., 1991
Bouldin, ASTM STP 1108
Button, AAPT Vol. 56, 1987
Collins, ACS, 1991
Collins, AAPT Vol. 61, 1991
Collins, Rubber World, 1992
Linde, ASTM STP 1108, 1992
Shell Supplier Information

SBS - Kraton D4141, D4460, or D4463X
Armijo, Montana State Unversity, March 1989

Bouldin, Rubber Chem. and Tech., 1991
Collins, ACS, 1991
Collins, Rubber World, 1992
Shuler, ASTM STP 1108, 1992

SBS -Lab/Field
Bouldin, ASTM STP 1108
Collins, ACS, 1991
Jones, TRB 1993 preprint
Rogge, ASTM STP 1108, 1992
Tayebali, AAPT Vol. 60, 1991
Tappeiner, Novophalt America Literature

SBS - Maleated
Shell Supplier Information

SBS - Vector (Either 2518 or 2411)
Dexco Supplier Information

SEBS - Kraton RP6904, G1657, or G1652
Bouldin, ASTM STP 1108
Collins, Rubber World, 1992
Linde, ASTM STP 1108, 1992
Shell Supplier Information

SEC

Linde, ASTM STP 1108, 1992
Youtcheff, Center for Applied Energy Research, University of Kentucky, 1991
Youcheff, unpublished, 1994

Solubility Parameter

Painter, SHRP Report, 1993
Youcheff, unpublished, 1994

Storage

Zanzotto, CTAA Vol. 34, 1989

Styrelf

Khosla, AAPT Vol. 58, 1989
Jones, TRB 1993 preprint
Shuler, ASTM STP 1108, 1992

Swelling

Park, Appl. Poly. Sci Vol. 47, 1993

TEM and STEM

Bouldin, Rubber Chem. and Tech., 1991
Collins, ACS, 1991
Collins, AAPT Vol. 61, 1991
Collins, Rubber World, 1992
Lee, TRB preprint 940185, 1994
Zanzotto, CTAA Vol. 34, 1989

T_g

Daly, TRR 1391, 1993

Vapor Pressure Osmometry

Youcheff, unpublished, 1994

Zero Shear Viscosity

Bueche, J. Poly. Sci., 1960
Sabia, J. Applied Poly. Sci., 1963
Shida, Poly. Eng. and Sci., 1971

Armijo, J.D., Pradha, M.N., Franchi, M.A.

"Effects of Commercial Modifiers on the Physical Properties of Montana Asphalts," Report by Montana State University, March, 1989

Materials:

Various refinery sources (Cenex, Conoco, Exxon, Montana) of 85/100, 120/150
SBR latex (Ultrapave)
SBS (Kraton D4141 (29% oil), D4463X (50% oil))
EVA (Polybilt - Exxon)

Binder Tests:

Basics: Viscosities, penetrations, R&B, ductility, TFOT

Results:

An evaluation of the results from the basic binder tests were used to establish a weighting system to compare one modified binder to another. Desirable binder properties were based on common sense and traditional concepts of "good" and "bad" test results (e.g., low penetrations = resistance to rutting but increased tendency for thermal cracking).

Anderson, D.A., Christensen, D.W., Roque, R., Robyak, R.A.

"Rheological Properties of Polymer-Modified Emulsion Residue," ASTM STP 1108, 1992, pg. 20

Materials:

2 sources of AC-10 base asphalt cement; a second one was used because one of the SBS polymers was not compatible with the original.

2.8% SBR, 2.8% SBS, 2.3% SBS, 2.8% Neoprene - no specific information included on polymers

Binder Tests:

Rheology:	Parallel plate (15, 25, 35, 45, 60°C) = 25 mm
	Torsion bar (-35, -25, -15, -5, 5°C)
	Bending beam
Fraas brittle point	

Results:

Development of master curves for emulsion residue indicated the need for both vertical and horizontal shift factors. The need for the vertical shift was hypothesized as a reflection of the change in solubility of the structured phase of the asphalt and/or modifier. A lower temperature is equivalent to lower solubility with agglomeration into discrete lumps within the dispersed phase. An increase in temperature results in an increase in solubility which leads to an expansion of the structured phase. This should indicate an increased association within the structured phase with a corresponding increase in density of the associated network; this should hypothetically result in the vertical shift.

The vertical shift factor was noted to increase beyond some critical temperature, designated T_o, with increasing temperature. T_o was increased with the use of the SBS and Neoprene modifiers; no change was noted for the SBR modifier. The horizontal shift factor varied between systems; authors suggested that this shift factor be adjusted with 2 (log (v_T) in the anomalous region.

Authors used WLF equation when $T > T_g$ and the Arhennius function when $T < T_g$.

$$\log \frac{a_T}{a_{T_g}} = \frac{-C_1(T-T_g)}{C_2+T-T_g}$$

$$Log \frac{a_T}{a_{T_g}} = \frac{2.30E_a}{R} [\frac{1}{T} - \frac{1}{T_g}]$$

C_1 assumed to be 17.5; C_2 calculated as 80; E_a = 251 kJ/mole.

Polymers extended the relaxation process to longer times on the master curves.

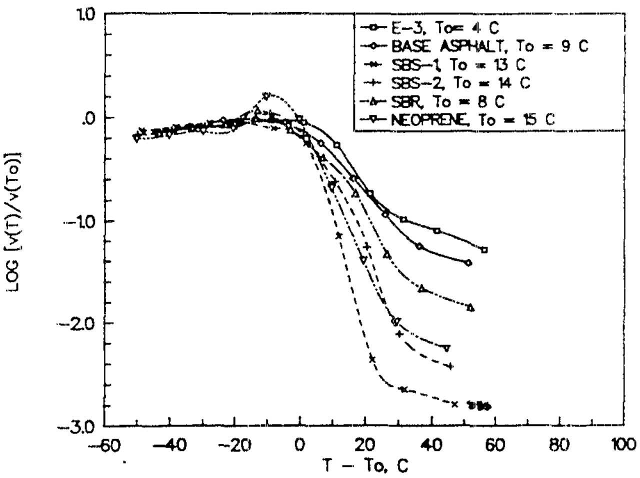


FIG. 7 -- Log of vertical shift factors, v(T), versus temperature, normalized to temperature T_o.

Anderson, D.A., Dukatz, E.L.

"Asphalt Properties and Composition 1950 - 1980," AAPT Vol. 49, 1980, pg. 1

Materials:

Wide range of unmodified asphalt cements (FHWA asphalt cement finger print file)

Binder Tests:

Basic Asphalt Cement Testing
Rostler Fractionation

Results:

A range of basic asphalt cement testing as well as the Rostler-Steinberg results were evaluated for over 400 asphalt cements obtained from 1950 through 1980. The Rostler parameter a ratio of more reactive fractions to the less reactive fractions:

$$\frac{A_1 + N}{A_2 + P}$$

Asphaltenes (A) increase as the asphalt cement ages. The nitrogen base resins (N) components act as peptizers for the asphaltenes. The acidifins (A_1 and A_2) are unsaturated hydrocarbons and act as solvents for peptized asphaltenes. The paraffins (P) are saturated hydrocar bonds and as gelling agents.

A variation of the Rostler parameter is the Gotolski parameter:

$$\frac{A_1 + A_2 + N}{A + P}$$

Either high or low Rostler parameters and high Gotolski parameters appeared to indicate asphalt cements with potentially poor pavement performance. The Rostler parameter was more closely related to temperature susceptibility while the Gotolski parameter was more closely correlated with the change in binder properties due to aging.

Anderson, D.A., Goetz, W.H.

"Mechanical Behavior and Reinforcement of Mineral Filler-Asphalt Mixtures," AAPT Vol. 42, 1973, pg. 37

Materials:

Not noted
Additives - Mineral filler, Silica (SiO_2), calcium carbonate ($CaCO_3$)

Binder Tests:

Rheology - sliding plate
Direct Tension

Results:

The relative viscosity, η_r, for mineral fillers were independent of the original viscosity of the suspending fluid. A greater reinforcement was obtained for smaller sized particles. Calcium carbonate was thought to strongly absorb the asphaltene portion of the asphalt cement. This resulted in an increase in the filler volume concentration.

BASF Corp. Supplier Information

Polymer:

SB latex, used in doses of 3 to 5 percent SB solids by wt. of asphalt cement

Trade Names:

Butonal NS 117 - for cationic asphalt cement emulsions
Butonal NS 120 - for anionic asphalt cement emulsions
Butonal NS 134
Butonal NS 175 - for anionic asphalt cement emulsions
Butonal NS 198 - for cationic asphalt cement emulsions

Properties:

Butonal NS 175 - a high solids, cold polymerized anionic SB dispersion

Property	Typical Value
Total Solids, % wt.	69
Bound Styrene, %	24
Residual Monomer, %	0.08 max
Brookfield viscosity, RVT, #2, 20 RPM, MPa	0.93

Bitumar, Inc. Supplier Information

"Paving the Way to a Better World"

Polymer:
Crumb rubber - wet process

Trade Names:
Ecoflex

Properties:
A patented process for "complete dissolution of the crumb rubber" in the asphalt cement.

Boduszynski, M.M., McKay, J.F., Latham, D.R.

"Asphaltenes Where Are You?," AAPT Vol. 49, 1980, pg. 123

Materials:

Not specified

Binder Tests:

- Molecular Weight determined by:
  - VPO
  - Field Ionization mass specoscropy (FIMS)
- Separation
  - Based on reactivity (See below)
  - Corbett

Results:

Separation procedures used chromatography on anion/cation resins to separate asphalt cement components capable of hydrogen bonding. This was followed by an additional chromatography process to separate out the Lewis bases and hydrocarbon fractions which was followed by an absorption chromatography on silica gel to obtain the saturates and aromatic hydrocarbons. The Corbett analysis was used to separate the asphalt cement into 5 fractions: asphaltenes, saturates, napthene-aromatics, and polar aromatics-1 and -2.

Results indicated that the asphaltenes are agglomerates of polar and polarizable compounds and are present in both the acid and base fractions.

Bouldin, M.G., Collins, J.H.

"Influence of Binder Rheology on Rut Resistance of Polymer Modified and Unmodified Hot Mix Asphalt," ASTM STP 1108, 1992

Materials:

Asphalt cement - AR 1000 (source not noted)
3% SBS Kraton D1101 (Shell)
3% EVA Elvax 150 (Dupont)
3% SEBS Kraton RP6904 (Shell)

Binder Tests:

Basics: R&B, Visc., Pen (4, 25°C), elastic recovery, ductility (4°C)
Rheology: RMS 800

Mixture Test:

TRRL wheel tracking apparatus; 535 kPa (77.6 psi), 60°C, 42 passes/minute; dry specimens
Unusual compaction procedure, mix temp. 170°C

Field Test Sections:

Mesquite, Nevada May 1989

Results:

Rheology indicated that the straight asphalt cement showed little elasticity. This resulted in difficulties in measuring tan delta because of the small G'. Authors suggested that an increase in G* with a correspondingly high G' should indicate a binder that will be resistant to rutting. Results indicated that the G* was greatest for the SEBS > SBS > EVA > Unmodified. G' was greatest for the SEBS = SBS > > EVA > Unmodified. These results correlated well with the occurrence of mm of rut per 1000 cycles. No information/correlation to field sections presented (too early in project life??).

Difficult to follow authors conclusions due to lack of information on air voids and asphalt cement content. Conclusions appeared to be overly generalized and not sufficiently supported by data presented.

Bouldin, M.G., Collins, J.H., Berker, A.

"Rheological and Microstructure of Polymer - Asphalt Blends," Rubber Chemistry and Technology, Vol. 64, 1991., pg. 43

Materials: Wide range of asphalt cements
SBS Kraton D4460X, D1101
SBR Ultrapave 70

Binder Testing: Vacuum viscosities - AI tubes
Basics: R&B, ductility, penetrations, elastic recovery
RMS 800 with parallel plates (25 mm for $T > 60°C$, 12.5 mm for $25 < T < 60°C$, 6.5 mm for $5 < T < 25°C$)
An RSA was used with rect. bars for low temperature testing (good up to 10GPA; 0.05 percent strain)
Fluorescence microscope
STEM

Results:

Rheology results indicated that smaller plates gave smaller values of storage modulus, G'; this appeared to be due to wall slip. When the values of G' developed for two tests with varying plate size agreed, slip was not considered to be a problem. Authors suggested grooving the plates with: $H_{gap}/h_{groove} > 100$ to prevent significant influence of groove depth on test results.

Authors stressed the importance of specific sample preparation procedures for polymer modified asphalt cements so that phase separation is not a problem. Guidelines for sample preparation, handling, and storage were presented; preparation and handling procedures agreed with the general guidelines used by the polymer suppliers. No change in the properties of the modified asphalts were seen using a storage temperature of 25°C for 5 to 7 days.

Rheological results were calculated using an Arrehnius function to shift the data for all temperatures. Results from the parallel plate rheometer and the AI tubes were used to confirm the Cox-Merz rule applied to the dynamic data. The authors reported that the tan δ measurements were very erratic for the neat asphalts; a better fit was obtained with either the addition of polymer or the increase in polymer concentration. A plateau G' modulus was seen for blends with a network formation.

The STEM showed that the configuration of the SBS domains were dependent upon the properties (undefined) of the neat asphalt cement (Figure 1).

The need for a critical concentration, c^* of polymer was discussed. The critical concentration is the minimum volume of polymer that is needed so that there will be some level of polymer entanglement between the dispersed polymer regions. The authors indicated that the level of c^* is dependent upon the asphalt cement used; this value varied from 2 to greater than 4 percent for three of the asphalts used in this study.

Bouldin, M.G., Collins, J.H., Berker, A. - Continued

"Rheological and Microstructure of Polymer - Asphalt Blends," Rubber Chemistry and Technology, Vol. 64, 1991.

Results (Continued):

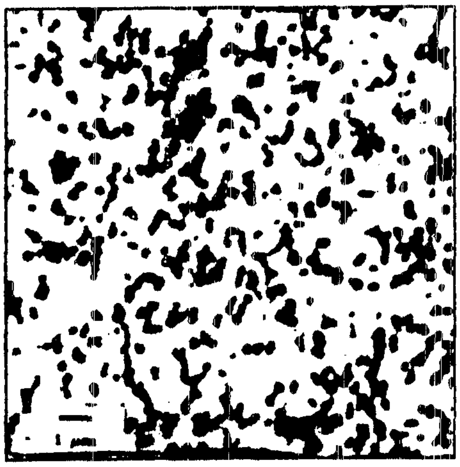
Changes in the relaxation times, λ, of polymer modified mixtures were discussed on a limited basis. An increase in the relaxation time was used as an indication of the formation of the polymer network. The authors suggested that this follows the $\lambda_{network} = h\ \lambda_{Rouse}$ relationship.

More network formation was observed with the softer grade of the same source of asphalt cement. Mixing temperatures were decreased and a lower percentage of polymer was needed to obtain c^*. Temperature susceptibility increased with increasing viscosity. A much greater increase in G' was seen when the viscosity of the neat asphalt was decreased.

Asphalt A

Asphalt B

FIG. 15.—4%w of Polymer B (SBS) in different asphalts.



Asphalt C

Brule', B., Brion, Y., Tanguy, A.

"Paving Asphalt Polymer Blends: Relation Between Composition, Structure, and Properties," AAPT, Vol. 57, 1988, pg. 41

Materials: SBS (MW = 120,000, linear, rang of percentages)

Binder Testing: GPC
Direct tension 10 and 20°C (50 and 68°F), 500 mm/min
Compatibility measured by evaluating centrifuged polymer modified asphalt cement at various times during curing

Results:

The authors suggest that the general use of the term "compatability" implies that the polymer modified asphalt cement is homogenous, with good ductility, cohesion, and adhesion; this is not the definition of chemical compatibility.

The colloidal instability index [(asphaltenes + saturated oils)/(resins + aromatic oils)] suggests that when the polymer is added to the asphalt cement at high temperatures, the asphaltenes flocculate which causes oil bleeding. The colloidal instability was used to estimate a threshold value of approximately 0.10, below which SBS polymer becomes soluble in asphalt. The authors suggest this would lead to loss of adhesion. Asphalt cements with a high level of aromaticity should solubilize the polymer; as the macromolecular structure increases, the viscosity should increase along with the binder's resistance to flow.

If the polymer-polymer interaction is 0, then the polymer-solvent interactions can swell the polymer with the oily fractions of the asphalt cement at low polymer concentrations. This increases the concentration of resins and asphaltenes in the continuous phase could lead to an increase in the elastic properties at some given percent of polymer. If and when phase inversion (i.e., asphalt cement dispersed in discrete particles within the polymer phase) occurs, the properties of the polymer should control the system properties.

A series of GPC analyses over time showed that there was only a minor change in the molecular weight of the polymer with time. The physical properties of the binders however, changed substantially with time. When stored at 200°C and tested at 20°C, the percent elongation to yield increased about 40 percent, the yield stress increased about 0.06 MPa, elongation at break increased 1,000 percent, and the stress at fracture increased 0.3 MPa from 1 to 7 hours of storage. Similar results were obtained for a test temperature of -0°C. When the storage temperature was increased from 200 to 220°C, a peak in the maximum improvement in binder properties occurred; the longer storage time began to produce increasing less improvement.

The extent of polymer swelling was calculated by determining the chemistry of the asphalt cement portion of the binder after 2 hours of centrifuging at 140 to 160°C at 12,000 g. These results showed about a 4.5 to 5.5 times increase in the polymer size; the percentage of asphaltenes increased in the asphalt phase. The percent of swelling was slightly reduced by an increase in the percent of polymer used.

A finer dispersion of the polymer within the asphalt cement led to better cold temperature properties while a coarser dispersion made the cold temperature properties worse.

Bueche, F.

"Melt Viscosities of Polymers: Effect of Polydispersity," Journal of Polymer Science, Vol. XLIII, 1960, pg. 527-530.

Results:

Showed that for polymers with low polydispersity values, the general equation for relating the zero shear viscosity and the molecular weight was:

$$\eta_o = K M_t^{3.5}$$

where $M_t = M_w$. However, when there was a broad distribution of molecular weight components in a polymer, the second moment molecular weight (i.e., M_w) needed to be increased to at least the third order molecular weight (i.e., M_z) or higher. If the moment of the molecular weight was not increased, then the exponent, 3.5, should be increased to compensate.

Button, J.W., Little, D.N., Kim, Y., Ahmed, J.

"Mechanistic Evaluation of Selected Asphalt Additives," AAPT, Vol. 56, 1987, pg. 62-90

Materials: Asphalts: AC 5, AC 10, AC 20 (Texas Coastal)
AR 1000, 2000, 4000 (San Joaquin Valley, Calif.
Polymers: SBR (Ultrapave 70, Latex XUS 4005.2 (DOW))
SBS (Kraton TR G6-8774, D1101, DX1118)
EVA (EX042, Exxon, EVA 150 Dupont)
PE (Novophalt)
Carbon Black (Microfil 8)

Binder Testing: Forced ductility

Mixture Testing: Lottman
Creep (VESYS)
Overlay tester (simulates opening and closing of crack)
Low temperature cracking - indirect tensile 50mm/min, 0.6°C (33°F)

Results:

Authors used the second peak seen in the forced ductility test, which is an indication of the polymer properties, as a comparison for the mixture test results. A good correlation was achieved between the forced ductility results (4°C, after rolling thin film oven conditioning) and the tensile strength of the mixtures. High forced ductility results correlated with high tensile strengths. Results indicated that moisture conditioning had little influence on the test results.

The results from the overlay tester indicated that the SBR, SBS, and EVA additives increased the number of cycles to failure. At 20°C ((68°F), the Novophalt results were similar to the AC 5 and AC 20. At 0°C (34°F) the AC 5 asphalt cement with any of the additives performed similarly; all additives increased the number of cycles to failure when compared to the AC 20.

Permanent deformation testing indicated that at 4.4°C (40°F), the AC 5 the SBR additives showed the greatest deformation with all other modifiers performing similarly. At 37.8°C (100°F), the AC 5 + SBR additives still had the greatest deformation with the other AC 5 + modifier mixtures producing lower deformations than the unmodified AC 20. The Microfill additive showed significantly less deformation than any of the other mixtures.

Buttlar, W., Roque, R.

"Development and Evaluation of the SHRP Measurement and Analysis for Indirect Tensile Testing at Low Temperatures," TRB preprint 940773, 1994

Materials:

AAG-1
AAK-2

Binder Tests:

None

Mixture Tests:

Indirect tensile constant strain test at low temperatures.

Results:

The linear elastic range approach was assumed to be valid below $300\mu\epsilon$ after 1,000 seconds of loading; a minimum strain of 50 $\mu\epsilon$ was considered necessary to get repeatable results. The authors suggested an initial load to achieve between 40 and 120 $\mu\epsilon$ at about 30 seconds should be sufficient to meet all of the test requirements. LVDT noise requirements reported as needing to be less than 125 x 10^{-6} mm. Data was sampled at a rate of 10 Hz in the first 10 second and at 1 Hz thereafter. Typical test results are shown below.

Asphalt Cement	Temperature, °C	Poisson's Ratio		Compliance, 1000 sec.			
				Measured Poisson's Ratio		Poisson's Ratio Assumed 0.35	
		Low Voids[1]	High Voids[1]	Low Voids[1]	High Voids[1]	Low Voids[1]	High Voids[1]
AAG-1	-5	0.46	0.20	149	251	231	190
	-15	0.50	0.30	41	60	55	55
AAK-2	-5	0.49	0.18	1,260	3,220	1,600	2,350
	-15	0.50	0.33	297	432	353	425

Choquet, F.S., Ista, E.J.

"The Determination of SBS, EVA, and APP Polymers in Modified Bitumen," ASTM STP 1108, 1992

Materials:

SBS
EVA
Atactic Polypropylene

Polymer Tests:

Infrared spectroscopy

Results:

Discusses the specific development of using IR for characterizing typical polymers used in modifying asphalt cement. No specific information about modified asphalt cements provided.

Collins, J.H., Bouldin, M.G.

"Long and Short Term Aging Stability of Straight and Polymer Modified Asphalts," paper presented at a meeting of the American Chemical Society - Rubber Division, Detroit, MI, Oct. 8 - 11, 1991.

Materials: Wide range of both AC's
SBS - Kraton D1101, D4141, D4460, D1184
SEBS - Kraton G1657, RP1687
SBR - Goodyear Ultrapave 70
PE - Dow PE 2045

Binder Testing: GPC
Rolling thin film oven aging of modified binders
STEM

Mixture Testing: Texas gyratory used for compaction
Creep - repeated load (5,000 cycles or 6% strain), haversine wave, 78 psi axial load, 40°C (104°F)

Results:

Test results indicated that the rolling thin film oven aging of the polymer modified binders over estimated the severity of actual plant manufacturing conditions (laboratory modified and aged versus recovered binder properties). A finer dispersion of the polymer in the asphalt cement matrix was noticed after RTFOT testing; hypothesis was that the RTFOT testing was providing further mixing.

Long term aging was evaluated by extracting the modified binder from cores taken from pavements between 3 and 4 years old. These results indicated that there was no significant polymer degradation for the SEBS modifiers while there was about 80 to 85 percent of effective polymer for the SBS materials.

Article included a summary of several field projects.

Collins, J.H., Bouldin, M.G.

"Long and Short Term Stability of Straight and Polymer Modified Asphalts," Rubber World, 1992 (no other information on copy of paper).

Materials:

Range of asphalt cements: AC 5, 7, 10, 20, AR 1000, 2000, 4000, 8000 (includes range of refineries and crude sources)
SBS (Kraton D1101, D4141 (29% oil), D4460 (50% oil)
PE (Dow PE2045)
SEBS (RP6904, G1657)

Binder Tests:

Basics: Penetration 4, 25°C, RTFOT aging
GPC
STEM
Low temperature cracking (visual)

Mixture Tests:

Repeated load creep testing, haversine load for 0.1 seconds, 1 second rest, 5,000 cycles or 6% strain (failure criteria)

Results:

Oxidation of the neat asphalt cement appears to lead to more molecular structuring and a higher average molecular weight. Oxidation of polymer modified asphalts showed a decrease in the high polymer molecular weight with aging time. This indicated that the oxidation of the double bonds in the polymer were resulting in a decrease in the length of the polymer chain (i.e., decrease in molecular weight), primarily by chain scission. No problems with gelation (i.e., crosslinking) was noted, most likely due to concentrations of polymer below the critical level.

An investigation of penetration (25°C) over a range of RTFOT aging times showed that long term storage at 180°C results in a significant loss of penetration when compared to storage at 120°C; the authors interpreted this as evidence of the degradation of the polymer. Based on this, they recommended that if polymer modified asphalt cements are to be stored for any length of time, the temperatures be kept to a maximum of 135°C to prevent damage to the polymer.

A comparison of penetration values for SBS modified binder from both RTFOT and recovered binders (authors refer to loose mix without specifically stating recovered binders) showed that laboratory aging almost always over estimated the aging seen in the loose mixtures. (If the binders were recovered, this could be due to polymer degradation/softening during extraction). The saturated SEBS polymers showed no change in properties between RTFOT and loose mix.

An STEM (scanning transmission electron microscope) was used to examine the morphology of various mixtures. Results showed that an SBS mixed with a compatible asphalt cement showed no difference in morphology before and after RTFOT aging. The SEBS mixtures showed a finer dispersion after RTFOT; authors hypothesized that this was due to additional mixing during testing. The STEM was not appropriate for evaluating PE modified asphalts due the gross phase separation of the materials. A significant loss in both G* and G' after RTFOT was attributed to the phase separation and not the degradation of the polymer.

Collins, J.H., Bouldin, M.G., Gelles, R., Berker, A.

"Improved Performance of Paving Asphalts by Polymer Modifications," AAPT Vol . 61, 1991, pg. 43

Materials:

AC - 5, 10, 20, 30, 40 (Dear Park), AR 1000 (Martinez), AC-6 (Boscan)
4% SBS - Kraton D1101 (Shell)
6% SBR - Latex Ultrapave 70 (Goodyear)
4% (?) EVA - Elvax 150 (Dupont)

Binder Tests:

TEM
Fluorescence microscopy
Rheology: Temp. >60°C = 25 mm plate; 25 < Temp. < 60°C, 12.5 mm plate; 5 < Temp < 25°C, 6.25 mm plate
Basics: Visc., Brookfield, R&B, Ductility, elastic recovery

Mixture Tests:

Dynamic and static creep testing
Wheel track

Results:

Authors indicated that the use of larger platens led to smaller measured values of G' than when smaller platens were used; they suggested this was due to slip. Results at cold temperatures test results confirmed with one measurement with each size; results were considered reliable when both results were in good agreement (not defined). A good relationship between the capillary, Brookfield, and DMA viscosity measurements was reported. They reported that measurements of tan delta were unreliable at low polymer concentrations and/or high temperatures (tan delta poor for neat AC's, OK for 2% poly, good for 6% poly).

Authors address need for the polymer concentration to be above c* (i.e., critical concentration) but do not explain concept to the reader. Reports c* of about 2 percent for Martinez, greater than 4 for Boscan, and between 3 and 4 for Deer Park crudes.

General findings indicate that as the asphalt cement grade increased (for same crude source), its compatibility with the polymer decreased. This decrease in compatibility was seen as an increase in mixing time and an increase in c*. The temperature susceptibility of the modified binders increased with increasing AC grade. The most significant increase in G' was seen in the lower grades of asphalts modified with polymers. As the percent of polymer increased, the G* increased and tan delta decreased. The critical cracking temperature at cold temperatures decreased with increasing polymer concentrations and/or a corresponding decrease in the asphalt cement grade. Results include a good series of TEM photos and analysis.

Mixture testing indicated that the dynamic creep testing results were similar to the wheel tracking results; static creep testing however, was not similar. When rheology measurements were compared to mixture testing, the unmodified binder had a G* of about 80 Pa (60°C, 1 rad/sec) and 10,000 cycles with the wheel tester were needed to achieve a rut depth of 10 mm. At 2 and 7 percent SBS, the G* and number of cycles were 250 and 1,000 Pa, and 20,000 and 90,000 cycles, respectively.

Collins, J.H., Mikols, W.J.

"Block Co-Polymer Modification of Asphalts Intended for Surface Dressing Applications," AAPT Vol. 54, 1985, pg. 1

Materials:

Asphalt cements - 85/100, 280/320 penetration, AC 5
SBS - Kraton D1101 (5 and 8%), D1184 (3%)
SEBS Kraton G1652 (3%)

Binder Tests:

Basics - viscosities, R&B
Brookfield viscosities (concentric cylinders)

Results:

The authors report that the typical Shell Bitumen Test Data Chart (BTDC) becomes a curve rather than a straight line relationship (Figure 1). They also reported binder viscosities were dependent upon the asphalt source as well as the type and percent of polymer (Table 1). The radial SBS D1184 polymer produced a significantly higher viscosity than either linear (D1101) or the SEBS (G1652) polymers (Table 2).

Table 1. Influence of Asphalt Cement Source on Properties.

Properties	Shellwood River AC-5		Exxon Baytown AC-5	
	Percent D1101			
	0%	3%	0%	3%
Penetration, 25°C	164	115	128	100
Ring and Ball, °C	41	72	44	49
Viscosity, cP				
60°C	61,500	----	75,800	---
80	6,800	46,000	7,800	56,000
100	1,400	4,000	1,600	3,500
120	480	1,200	---	----
150	120	340	140	300

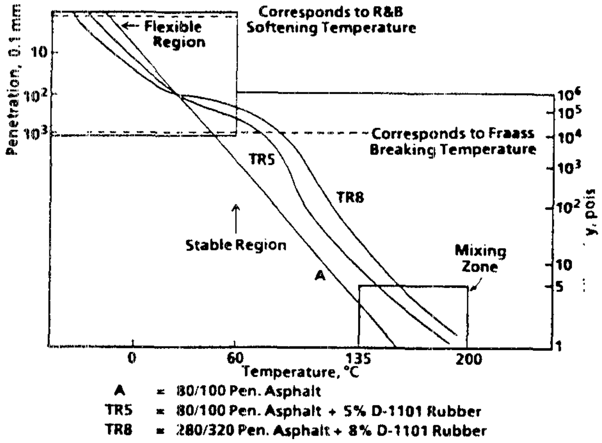


Table 2. Influence of Various SBS Products on Properties.

Properties	Unmodified AC-5	3% D1101	3% D1184	3% G1652
Penetration, 25°C	164	115	85	117
Ring and Ball, °C	41	72	70	65
Viscosity, cP				
60°C	61,500	---	----	---
80	6,800	46,000	112,000	18,500
100	1,400	4,000	5,250	4,100
120	480	1,200	1,200	1,200

Daly, W.H., Qui (Chiu), Z., Negulescu, I.

"Preparation and Characterization of Asphalt-Modified Polyethylene Blends," Transportation Research Record 1391, 1993

Materials: Polyethylene: chlorinated PE (CPE), HDPE, maleated PE (MGPE)

Binder Testing:
NMR
Bending beam 1°C/min, 0.1 percent strain; 50 Hz and 1 percent strain for failure
Differential Scanning Calorimetry (DSC)
Fluorescence Microscopy
Creep with constant stress rheometer

Results:

General information included a description of the maleating process for PE. The molecular weight of the HDPE was listed as 1.9 to 8.5 x 10^4.

The bending beam results were used to define the T_g as the maximum loss modulus, G", at a given frequency. These results indicated a wide peak for most of the materials tested. The bending beam was also used to develop a cracking temperature, T_{crack} which was equal to the temperature at which the sample failed (50 Hz, 1 percent strain). This value was used to estimate the influence of polymer addition on low temperature crack resistance.

The DSC results indicated that saturates and aromatics make the main contribution to properties; no crystallization was seen when the maltenes were removed. No asphalt cement melt point was observed; the melt point of the modified binder decreased with an increase in polymer concentration (compared to pure polymer). The magnitude of the shift appeared to be an indication of the polymer-asphalt interactions.

Low temperature cracking was very sensitive to the polymer concentration. T_{crack} was greater than T_g for pure asphalt cement. This relationship was reversed with the addition of the polymer.

The authors indicated that there was a development of partially separated regions of polymer within the asphalt matrix when the polymer modified asphalt cement produced a storage modulus curve with a slope equal to the unmodified asphalt cement but higher in magnitude. The authors suggested that this was due to the higher rigidity of the polymer than the asphalt cement., A difference in the slopes between the modified and unmodified G' values was suggested as an indication of the selective absorption of asphalt cement components by the polymer. This would leave the asphalt cement phase rich in aromatic resins and asphaltenes which are both high viscosity components.

Creep tests with the Bohlin Constant Stress rheometer indicated that the decrease in compliance was a function of both the asphalt cement and the polymer.

Dexco, a Dow/Exxon partnership, Supplier Information

"Vector - The New Direction in Styrenic Block Copolymers", no date

Polymer:
SBS

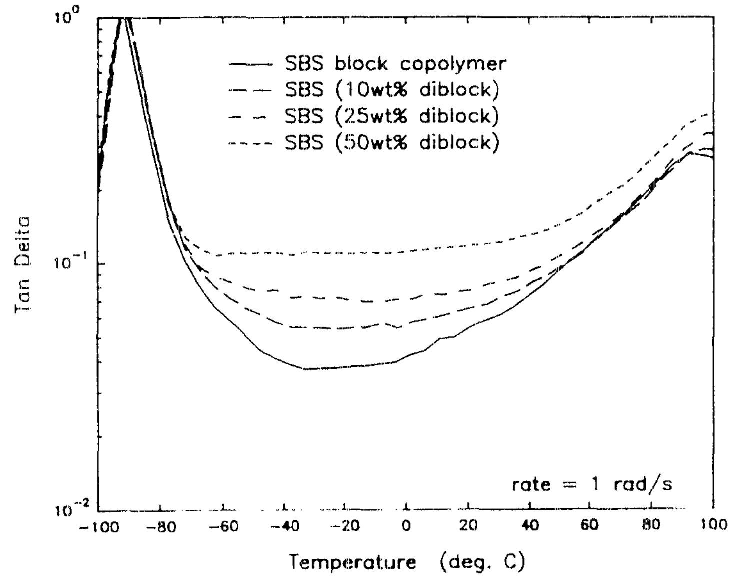
Trade Names:
Vector 2518
Vector 2411
Either product is available in the expanded crumb or powdered form.

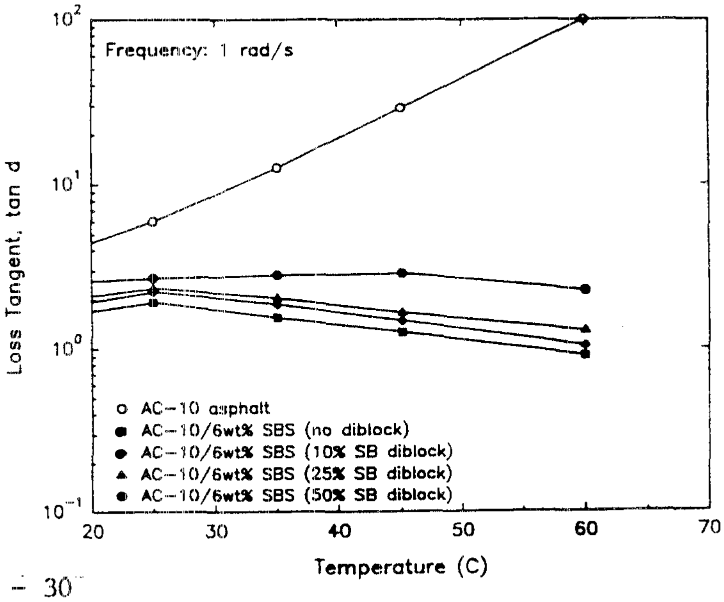
Properties:

Property	Vector 2518	Vector 2411
Conformation	Linear	Radial
Density	0.94	0.94
Hardness, Shore A (ASTM D2240)	NA	71
Tensile Strength, psi (ASTM D638)	NA	4,000
Modulus at 300%, psi (ASTM D638)	NA	650
Elongation at Break, % (ASTM D638)	NA	725
% Diblock	NA	<1%
Oil Content	NA	0
Melt Flow Rate, dm/min (ASTM D1228)	2.5 - 8.5	NA

NA: Information either not reported or not applicable

Diblock copolymers only have one stryrenic "anchor" rather than the triblock's two "anchors". Since a large number of diblock copolymers will significantly effect the modulus and tensile strength of the polymer, the percentage of diblocks are limited.





Dukatz, E., Anderson, D.A.,Rosenberg, J.L.

"Relationship Between Asphalt Flow Properties and Asphalt Composition," AAPT Vol. 53, 1984, pg. 160

Materials:

Asphalt cement - 12 different sources/grades; selected for a range of asphaltene contents

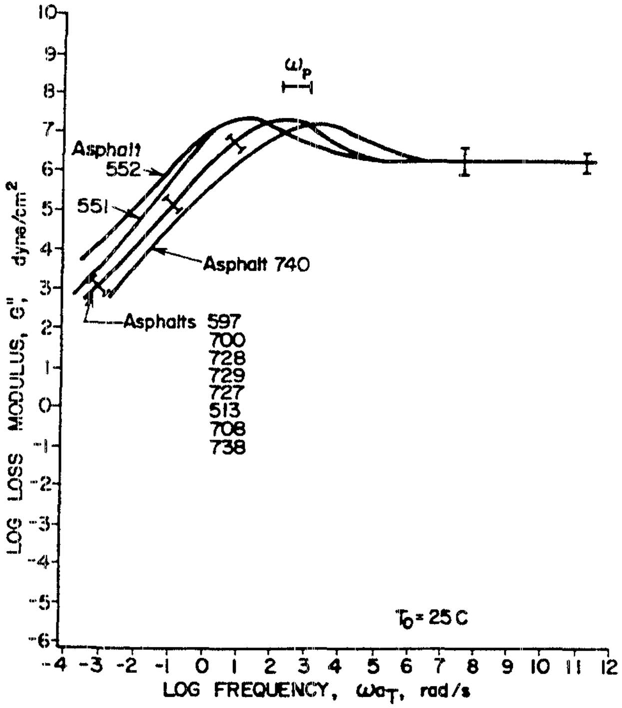
Binder Tests:

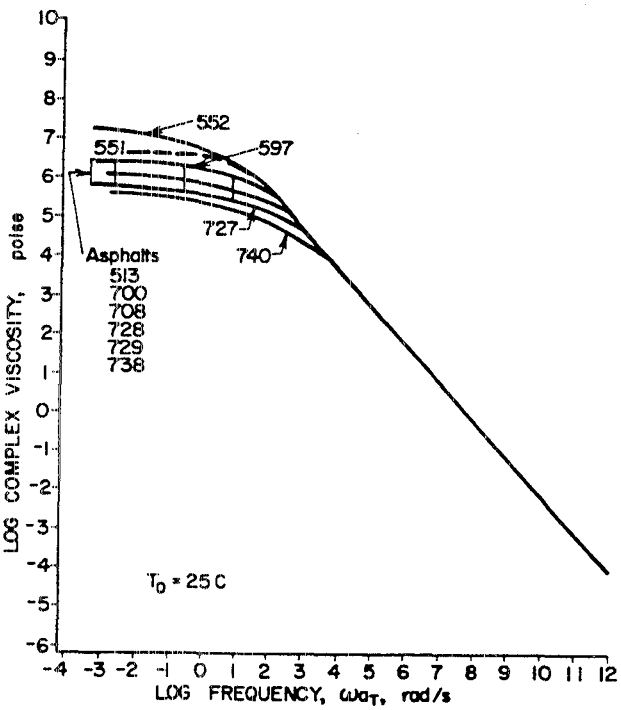
Rostler separation
Basics - Viscosities, penetration
Asphaltene settling test (Heitaus procedure)
HPLC

Results:

Asphaltenes have been thought to have a disk-like structure (about 10 to 15Å thick with a diameter of about 50 to 100Å) because the viscosity of the asphalt cement at high temperatures is greater than predicted by the inclusion of dilute spheres. Asphaltene content was found to be related to the percent of large molecule size as measured by high pressure liquid chromatography (HPLC). The authors suggest that this should be interpreted as highly polar assemblages of macromolecules rather than a measurement of discrete particle sizes.

The authors determined that the traditional colloidal model for asphalt cement was not adequate for explaining the flow behavior. Figures 1 through 3 show typical rheological results for a range of asphalt cements.





Enichem Supplier Information

"Enichem Technical Paper No. 1, Europrene Sol T"

Polymers:

SBS
SIS

Trade Names:

E Sol T : Series 160 to 169 are SBS
Series 170 to 179 are oil extended SBS
Series 190 to 199 are SIS

Properties:

Properties	E Sol 6302	E Sol T 161/C	E Sol T 161/B
Conformation	Linear	Radial	Radial
S/B Ratio, %	30/70	30/70	30.70
Molecular Weight	100,000	200,000	250,000
M_w/M_n	1.1	1.1	1.1

The oil extender is described as a "paraffinic oil containing a well defined quantity of naphthenics and aromatic fractions.

Enichem Supplier Information

"SBS Thermoplastic Rubber for Bitumen Modification," no date

Materials:

SBS (E Sol T 161 - Enichem)
APP

Results:

The atactic polypropylene was a saturated polymer 20 - 30 pph. This polymer did not significantly increase the asphalt cement viscosity, and was easily phase separated.

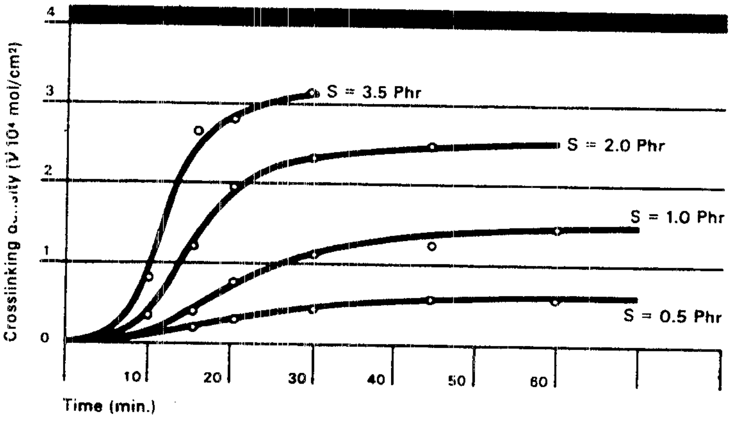
The E Sol T 161 product was a radial SBS. This polymer has a structure that it temporarily destroyed by dissolving the polymer in solvent and/or heating it above the glass transition temperature (T_g) of the styrene. A network structure is formed when the polymer reassociates as the temperature is reduced. The ability of the polymer to disperse in the asphalt cement is a function of the mixing temperature. The temperature needs to be above 180° C for the styrenic blocks to decompose and below about 200°C to prevent excessive aging of both the asphalt and polymer. The SBS is unsaturated, therefore an antioxidant was recommended to prevent aging of the polymer. When optimum conditions are present, the crosslinking of the polymer will be approximately equal to that of vulcanized SBS.

General properties for this product are shown in Table 1 (these are somewhat different than those reported for specific T 161 products in other supplier literature).

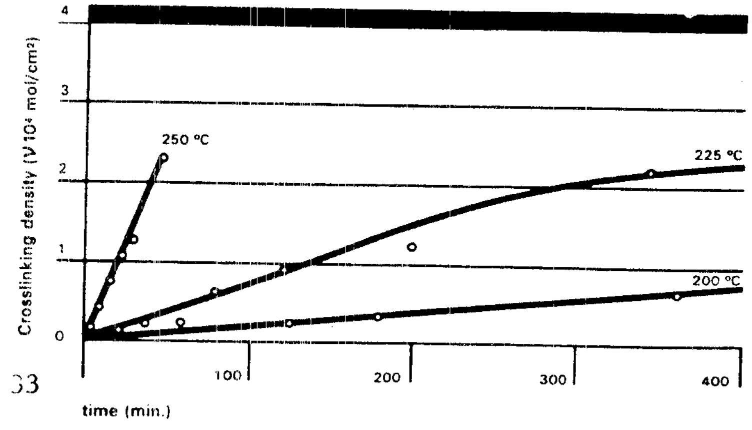
Table 1. General E Sol T 161 Product Properties.

Property	E Sol T 161
S/B %	30/70
Density	0.94
M_n	140,000
M_w	350,000
M_w/M_n	2.5
300% Modulus , Mpa	3
Tensile Strength, Mpa	15
Elongation at Break, %	700
Hardness, RDH	90

Crosslinking density variation of polybutadiene during a cure with sulphur



Crosslinking density variation of polybutadiene versus time at different temperatures



Enichem Supplier Information

"Enichem Technical Paper No. 4, Europrene Sol T SBS Block Copolymer in HMA Cement"

Materials:

SB (E Sol T 6302, T161/C, T161/B- Enichem)

Binder Tests:

Basics: Ductility, Pen
Fraas Brittle Point

Results:

Both the penetration index and the softening point increased with increasing percentage of polymer, regardless of type of SBS. Table 1 shows typical values obtained. The low values for each range represent asphalt cement modified with the E Sol T 6302 and the highest value the E Sol T161/B. The E Sol T161/C was consistently in the middle of the range.

Property	Percent of Polymer			
	0	4	6	8
Penetration Index	-1	5.5 - 6.1	6 -7	7 - 8
Fraas Brittle Point, °C	-15	-21 to -23	-30	-33 to -35
Softening Point, °C	45	75 to 85	85 to 95	90 to 110

Enichem Supplier Information, received June, 1994

Results:

Properties	161B	161C	6302	6205
Volatile Material, wt. %	0.29	0.01	0.94	---
Ash Content, wt %	0.18	0.07	0.91	1.12
Bound Styrene, wt. %	32.0	31.5	---	---
Inherent Viscosity, ml/g	1.29	1.08	0.91	1.12
Coupling Efficiency, %	87.4	96.1	---	---
MW	241800	192800	---	---
Tensile strength, psi	---	---	2870	---
300% Modulus	---	---	360	---
% Elongation	---	---	750	---
Brookfield Viscosity (toluene, 25°C, cps	---	---	4,150	8,000
Melt Flow Index g/dmin	---	---	NA	NA
Architecture	Radial	Radial	Linear	Radial

Exxon Supplier Information

"Polybilt for Asphalt Cement Modification"

Polymers:
EMA (500 Series)
EVA (100 Series)

Trade Names:
Polybilt

Properties:

Property	Polybilt 101	Polybilt 103S	Polybilt 104	Polybilt 152	Polybilt 502	Polybilt 503
Conformation	NA	NA	NA	NA	NA	NA
Density	0.94	0.957	0.941	0.942		
Hardness, Shore A (ASTM D2240)	86	67	85	90		
Tensile Strength, psi (ASTM D638)	NA	NA	NA	NA		
1 % Secant Modulus, psi (ASTM D638)	18,000	830	7,100	650		
Elongation at Break, % (ASTM D638)	75	900	675	650		
% Diblock	NA	NA	NA	NA		
Oil Content	NA	NA	NA	NA		
Melt Flow Rate, dm/min (ASTM D12238)	2,500	50	20	2.5	3.0	1.0

A high melt flow rate indicates a low molecular weight material.

Goodrich, J.

"Asphalt and Polymer Modified Asphalt Properties Related to the Performance of Asphalt Concrete Mixtures," AAPT, Vol. 57, 1988, pg. 116

Materials: Not specified (just referred to as polymer A and B)

Binder Testing: Parallel plate rheometer (40, 25, and 8 mm), strain limited to less than 0.5 percent at cooler temperatures, 0.1 to 10 rad/sec.
Rolling thin film oven aging
Long term durability testing (LTD) - California tilt oven variation of RTFOT (7 days at 111°C (231.8°F)

Mixture Testing: Axial creep, 25 psi load (60 min. load - 30 min. unload), 15 psi confining, deformation over the center 1/3 of the sample.
Low temperature testing - diametral creep (80 psi, 60 min. load - 30 min. unload), 4, -7, 17, and -29°C (38.2, 20, 0, -20°F)
Beam fatigue testing, 0.05 sec load with 0.55 sec unload (3.8 x 3.8 x 38.1 cm (1.5 x 1.5 x 15 in))

Results:

The limiting stiffness temperature (LST), which is the temperature at which 10.3 GPa (1.5 x 10^6 psi) stiffness is obtained, was used to compare the effects of polymer modification. All polymer modified mixtures had a lower LST, however the results were dependent upon the asphalt cement used (grades not specified). A good correlation was obtained for the peak loss modulus (G") and the LST. This indicated that the peak in the G" needs to be shifted to a colder temperature in order to see an improvement in the LST values.

Other results indicated a good correlation between the loss tangent and the number of cycles to fatigue failure. The loss tangent also correlated well with permanent deformation results. An investigation into the binder effect when mixture variables are included showed that changes in both the air voids and/or the asphalt cement content had more of an influence on mixture properties than when changes in the polymer additive alone were used. The author noted that a polymer additive could help the permanent deformation characteristics of a mixture with rounded aggregates.

Hagen, A.P., Jones, R., Hofener, R.M., Randolf, B.B., Johnson, M.P.

"Characteristics of Asphalt by Solubility Profiles," AAPT Vol. 53, 1984, pg. 119

Materials:

Not noted

Binder Tests:

Solubility

Results:

The authors noted that typical fractionation did not provide a good representation of the asphalt cement properties because of the overlapping chemistry of the asphaltenes and maltenes. Previous work with asphaltenes to maltene ratios have failed to correlate with asphalt performance.

The authors suggested the use of solubility profiles because typical precipitation tests on asphalt cement are based on solvent phobia while solubility profile testing is based on an affinity for solvents. The solubility parameters of the individual components are not necessarily compatible but because of the wide range of parameters within the whole asphalt cement, the whole asphalt appears soluble (Figure 1).

The solubility of the whole asphalt cement was determined in a wide range of solvents (Figure 2) and conical-based contour maps of the solubility parameters were prepared using the equation:

$$[(\delta_r - \delta_{rc})^2 + (\delta_v - \delta_{v_c})^2]\ [\phi^2 \cos^2 \psi\phi) + \sin^2 (\psi - \phi)] - |\frac{\ln sol - I}{m}|^2 = 0$$

Where:

sol = % sol of sample in given solvent

δ_r and δ_v are solubility properties of the solvent

δ_{rc} and δ_{vc} are the center of the ellipse (used to develop the contour map_

I = function of the solubility axis and the vertex of the cone

m = slope of the sides of the cone

ϕ = eccentricity of cone

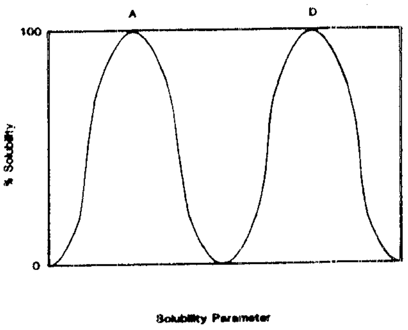
θ = angle between δ_r axis and the ellipse axis

χ = angle such that $\tan \theta = (\delta_v - \delta_{vc})/(r - r_c)$

This equation was re-formed into:

$$\ln sol = m([(\delta_r - \delta_{vc})^2 + (\delta_v - \delta_{vc})^2]\ [\phi^2\cos^2(\psi - \theta) + \sin^2 (\psi - \theta)])^{1/2} + I$$

which gives the general form of y = a + bx. An iterative process was used to determine δ_{rc}, δ_{vc}, θ, and ϕ; a linear regression was then used to determine m and I. A typical resulting contour is shown in Figure 3.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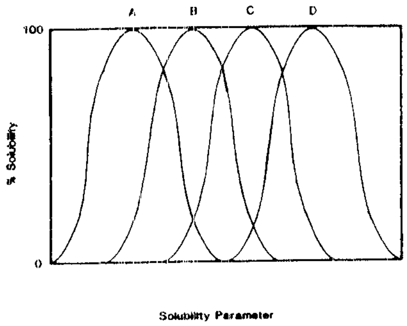
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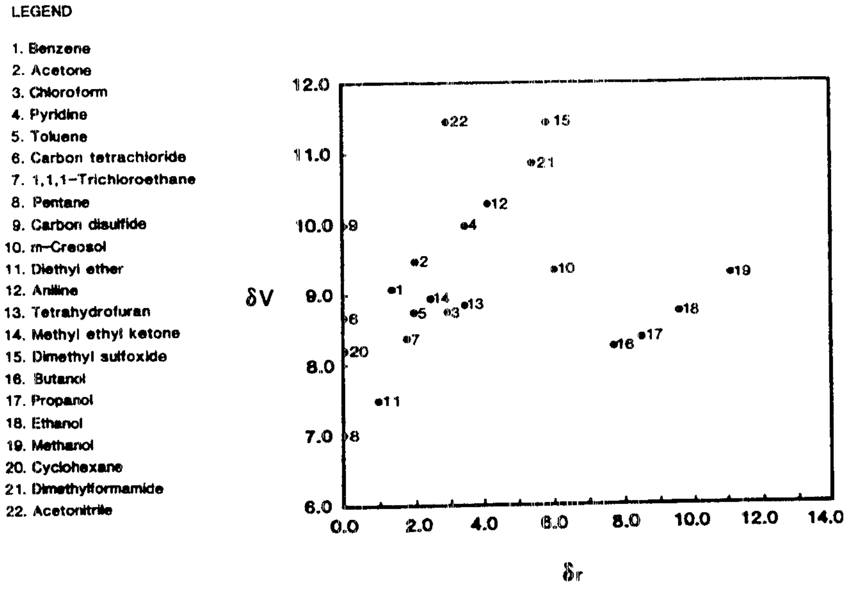
LEGEND
1. Benzene
2. Acetone
3. Chloroform
4. Pyridine
5. Toluene
6. Carbon tetrachloride
7. 1,1,1-Trichloroethane
8. Pentane
9. Carbon disulfide
10. m-Creosol
11. Diethyl ether
12. Aniline
13. Tetrahydrofuran
14. Methyl ethyl ketone
15. Dimethyl sulfoxide
16. Butanol
17. Propanol
18. Ethanol
19. Methanol
20. Cyclohexane
21. Dimethylformamide
22. Acetonitrile
12.0
11.0
10.0
9.0
8.0
7.0
6.0
δV
0.0
2.0
4.0
6.0
8.0
10.0
12.0
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δr
22
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21
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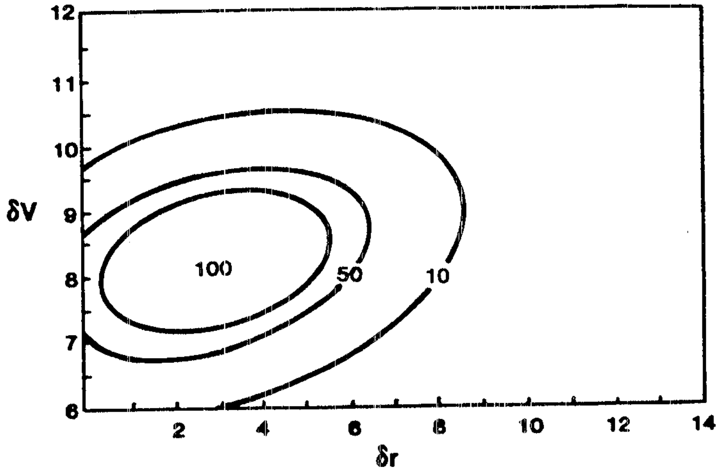
ASPHALT - AC-3


12
11
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9
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7
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δV
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8
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δr
100
50
10

Halstead, W.J., Rostler, F.S., White, R.M.

"Properties of Highway Asphalts - Part III, Influence of Chemical Composition", AAPT Vol. 35, 1966, pg. 91

Materials:

Bureau of Public Roads library of asphalt cements (1954-1955)

Binder Tests:

Rostler separation

Results:

The authors defined the Rostler parameters as:

Asphaltenes (A):	Constituents that are insoluble in n-pentane.
Nitrogen Bases (N):	Constituents that are soluble in 85% sulfuric acid. These are the most reactive of the asphalt cement components and contain essentially all of the nitrogen-containing compounds.
First Acidifins (A_1):	Constituents that are soluble in 98% sulfuric acid (after the removal of N). These components are unsaturated resinous hydrocarbons.
Second Acidifins (A_2):	Constituent that are obtained by fuming sulfuric acid. These components are only slightly unsaturated.
Paraffins (P):	Constituents that are non-reactive; they represent the saturated hydrocarbons.

The Rostler parameter, as defined by the equation below, was used to separate the asphalt cements into one of five groups.

Group	Rostler Parameter Range
I	min (0.54) to 1.0
II	1.01 to 1.20
III	1.21 to 1.50
IV	1.51 to 1.70
V	1.71 to max (2.24)

$$\textit{Rostler Parameter} = \frac{N + A_1}{A_2 + P}$$

Herrin, M., Marek, C., Strauss, R.

"The Appicability of the Absolute Rate Theory in Explaining the Behavior of Bituminous Mixtures," AAPT Vol. 35, 1966, pg. 1

Materials:

Asphalt cements: 2 sources; various grades

Binder Tests:

Sliding plate viscometer

Results:

The absolute rate theory equation was given as:

$$\dot{\gamma} = \frac{kT}{h} e^{-\Delta H/RT} e^{\Delta S/R} \sinh \frac{\tau q \delta l}{2kT}$$

Where:

k = Botzmann's constant (1.3805 x 10^{-16} ergs/°C)
h = Planck's constant (6.62 x 10^{-27} ergs sec)
q = stress concentration factor
A = projected area of the flow units on the shear plane
qAl = effective volume of the flow unit

Research showed that the change in entropy (ΔS) ranged from 95 to 120 cal/°K-mole, and the change in enthalpy (ΔH) was between 45,400 and 52,800 cal/mole. The authors considered that the high enthalpy explained why there was little or no flow at colder temperatures; the free energy of activation dropped sharply as the temperature increased. The large entropies were considered "as expected" because weakly bonded disordered structures typical of materials with large hydrogen contents should have a large degree of randomness. Also as expected, the ΔS decreased with decreasing temperature.

Other findings indicated that the size of the flow unit increased with decreasing temperature.

Hesp, S.A., Woodhams, R.T.

"Stabilizing Mechanisms in Polyolefin-Asphalt Emulsions", ASTM STP 1108, 1992

Materials:

HDPE, EVA, PE, Polyolefins (general)

Binder Test:

None

Mixture Test:

None

Results:

Paper provides general information on the mixing, stabilization, and polymer-asphalt interactions. General information is summarized below.

Polyolefins have a non-polar, non-aromatic nature with a solubility parameter of between 15.6 and 17.4 $MPa^{1/2}$. Polyethylene (PE) is a highly saturated aliphatic nature which is very insoluble in asphalt and is only compatible with paraffin-based asphalt cements (i.e., less than 5 percent of polar aromatic and asphaltene compounds). PE has the lowest solubility parameter of the polyolefin family. High molecular weight PE particles are stabilized by adding low molecular weight waxes to form stable outer particle layer. Vinyl acetate (VA) is added to ethylene (E) to increase the polarity of the polymer, however the VA also makes the polymer more brittle. EVA has also been used to stabilize PE but did not show very good results. SBR has been combined with PE for a stabilizing effect but results were unclear if it would work with more than a few select asphalt cements.

To improve low temperature properties, the polymer needs to be dispersed in a micron or sub-micron size; fewer, larger particles will have an adverse effect on the high temperature creep properties.

Heukelom, W.

"An Improved Method of Characterizing Asphaltic Bitumens with the Aid of Their Mechanical Properties," AAPT Vol. 35, 1966

Materials:

Not noted

Binder Tests:

Rheology

Results:

The author used the WLF equation for developing master curves. The author felt that this equation was applicable for temperatures above the softening point or for asphalts with viscosities less than 1,000 Poise. It was also assumed applicable to asphalt cements with a penetration index below +1 and a low wax content; this would increase the applicable viscosity range to a maximum of 1,000,000 Poise. Departures from the WLF equation were attributed to delayed elastic deformation occurring in viscous flow and the amount of crystallized waxes. The equation used was:

$$\log\frac{\eta}{\eta_{ref}} = \frac{-X\,(T - T_{ref})}{Y + T - T_{ref}}$$

Where X was considered characteristic of the internal friction mechanisms and 1/Y was considered an indication of the temperature susceptibility. Both X and Y are functions of the choice of the reference temperature.

Heukelom, W. Wijga, P.W.O.

"Viscosity of Dispersions as governed by Concentrations and Rate of Shear," AAPT Vol. 40, 1971, pg. 419

Results:

In general, as the volume concentration (V_c) of an additive increases, the concentration of the suspending fluid decreases; this results in an increase in viscosity. The maximum volume concentration can be approximated by the reciprocal of the packing volume (V_p).

Flocculation of particles occurs when peptization is incomplete and the influence of the shear rate on a yield stress due to flocculation is a function of the particle concentration. Three equations relating viscosity to particle concentration were used in the analysis:

$$\eta_r = \frac{\sqrt{1 + 0.5\,C_v}}{1 - C_v}\, e^{\frac{1.25C_v}{1 - C_v}} \quad (Mooney) \qquad \frac{1}{\eta_r} = 1 - 2.5C_v + 1.55C_v^2 \quad (DeBrijn)$$

$$\eta_r = \left(1 + \frac{1.25C_v}{1 - 1.35C_v}\right)^2 \quad (Euler)$$

All three equations give similar results for values of η_r up to about 100. That is, there is a linear relationship between $1/\sqrt{\eta_r}$ and C_v. A simplification of the Mooney and DeBrijn equations gives:

$$\frac{1}{\sqrt{\eta_r}} = 1 - (1 + k)\,(1 + m)\,C_v = 1 - \frac{C_v}{C_{max}}$$

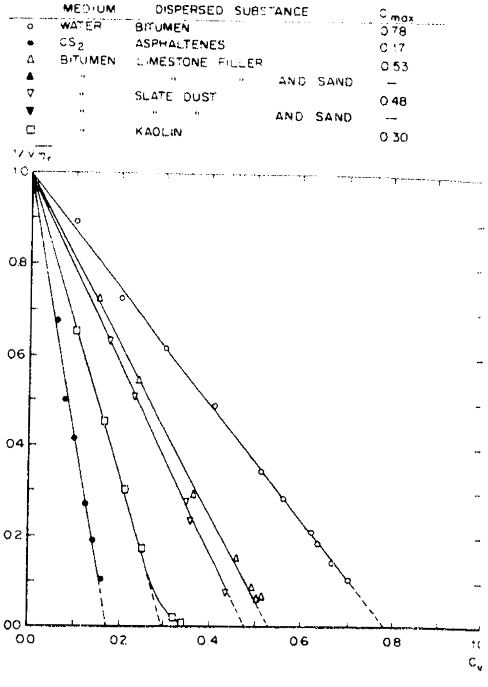
Where k allows for the introduction of the material shear dependence of dispersion of spheres. If peptization is poor and/or the particles are not spherical in shape, then an additional parameter, m, needs to be added. This parameter, m, also allows for the correction of particle swell in the fluid. For a given shear rate and additive, k and m are constants. The value of k is approximately 0.28 at low shear rates ($< 10^{-1}$)and low to moderate concentrations. The values of m depend upon the additive and decreases with increasing peptization (m equals zero if the particles are fully peptized). The parameter m is related to the maximum concentration of actual particles by:

$$(1 + m) = \frac{C_{max,\ spheres}}{C_{max,\ act.\ particles}}$$

Typical values of C_{max} and 1+m are shown in Table 1.

Table 1. Typical Values of Maximum Actual Particle Concentration

C_{max}	Asphalt + Additive	1 + m
0.53	Limestone Filler	1.47
0.48	Slate Dust	1.63
0.30	Kaolin (flaky shape)	2.64



Jain, P.K., Sangira, Bose, S., Arya, I.R.

"Characterization of Polymer Modified Asphalt Binders for Roads and Airfields," ASTM STP 1108, 1992.

Materials:

80/100 and 60/70 asphalts from various Indian crude sources (Bharat, Digboid (waxy crude), Haldis, Madras)
SBS
LDPE
EVA
PP wax
Hydroxyl-terminated PB

Binder Tests:

Basics: Ductility, Penetration, R&B, Viscosity (60°C)
DSC (Thermal Analyzer)
Fraas Brittle Point
Elastic Recovery

Results:

Compatibility was defined by the storage stability test. Briefly, a tube of modified binder (2.5 cm in diameter by 30 cm tall) is filled with binder and stored at 163°C for 6 hours. At the end of this time, the binder is cooled and the tube is separated into top, middle, and bottom lifts. The penetration of each lift is determined and the results compared to determine if any of the polymer has settled out.

DSC (differential scanning calorimetry) was used to find the melting temperature of the polymers used in this study. Results showed that the melting temperatures were 114.7, 90.3, and 121.6°C for the LDPE, PPW, and EVA, respectively. The SBS had no distinct endothermic transition.

Jebro, Inc. Supplier Information

Polymers:

Unvulcanized SBR

Trade names:

Flexform

Properties:

Information on pure polymer not included. Only information available covers several demonstration projects using AC 20R. A suggested AC 20R specification is included.

Jones, D.R., IV, Torshizi, H.F., Kennedy, T.W., Hazlett, D.G.

"Field Performance of Polymer Modified Asphalts," TRB Preprint No. 93099, 1993

Materials:

Asphalts varied by project; generally AC 10 or 20
3 or 6% SBS (not specified)
3% SBS process (assumed referred to Styrelf)
3% EVA
5% SBS/Polyolefin combination

Binder Tests:

Forced ductility (limited info)
Aging index of binder (not specified whether lab or recovered binder properties)

Field Test Sections:

District 15, Texas

Results:

A general summary of field performance indicated that plastomers (i.e., EVA, SBS/polyolefin) had more problems with thermal cracking than the control sections. All sections had longitudinal cracks with the elastomers have the worse cracking.

Khosla, N.P., Zahran, S.Z.

"A Mechanistic Evaluation of Mixes Containing Conventional and Polymer Modified (Styrelf) Asphalt," AAPT Vol. 58 1989, pg. 274.

Materials: Asphalt: AC 5, AC 10, AC 20
SBR (Styrelf)

Mixture Testing: Marshall mix design
Resilient modulus at -18, 4, 21, 38, and 60°C (0, 40, 70, 100, 140°F)
Creep (VESYS) 20 psi, -29, -18, -7, 4, 21, 32, and 40°C (-20, 0, 20, 40, 70, 90, 120, and 140°F)
Diamtral fatigue, 15 to 50 psi at 21°C (70°F), 0.1 sec load/2.9 sec rest

Results:

Authors used both the VESYS permanent deformation and fatigue testing programs and the analysis program to estimate changes in pavement performance due to the use of polymer modified mixtures. The unmodified AC 5 mixtures were too soft to test at both 32 and 40 °C (120 and 140°F) and were eliminated from comparisons at these temperatures. Results indicated that polymer modification would result in a decrease in permanent deformation and an increase in the number of cycles to fatigue failure.

Resilient modulus testing indicated that polymer modification would reduce the temperature susceptibility of the mixtures, however, the polymer also increased the cold temperature stiffness.

King, G.W., King, H.W., Harders, O., Arand, W., Planche, J.

"Influence of Asphalt Grade and Polymer Concentration on Low Temperature Performance of Polymer Modified Asphalts," AAPT Vol. 62, 1993, pg. 1.

Materials:

40/50, 60/70, 80/100, 180/200 (Venezuela crude source)

SB (assumed referring to di block although not specified!); percentages referred to as x, 1.5x, 2x

Binder Tests:

Basics: Visc., R&B, ductility

Rheology: Parallel plate
Bending Beam

Direct Tension

Fraas Brittle Point

Mixture Testing:

Direct Tension (20, 5, -10, -25°C), 1 mm/min

Constrained Beam (TSRST), 10 °C/hr

Results:

Cold penetration results only showed a fair correlation to the constrained beam test ($R^2 = 0.69$). The correlation improved for the cold ductility and Fraas brittle point versus the constrained beam with r^2 of 0.73 and 0.85, respectively. Better results were obtained for the basic binder tests for no or low polymer contents.

Direct tension (unmodified binder only) was used to define the failure temperature as the temperature at which the sample achieves 1 percent strain at a load rate of 1 mm/min. The r^2 between the direct tension and the constrained beam was 0.83 although the authors noted that a poorer correlation should be expected when polymer modified asphalt cements are used.

The constrained beam test with the 40/50 pen asphalt cement showed an increase in cracking temperature with an increase in polymer concentration. The 60/70 through 180/200 pen asphalts showed a decrease in cracking temperature with an increase in polymer concentration. The decrease was about 4 and 8°C for the highest percent of polymer, respectively.

The bending beam rheometer results were correlated to the constrained beam test in two ways: 1) stiffness at 15°C, 60 seconds ($r^2 = 0.91$), and 2) bending beam results were determined at various temperatures and the critical cracking temperature was defined as the temperature at which the stiffness was 200 MPa ($r^2 = 0.96$). However, the critical cracking temperature calculated from the bending beam and from the constraint beam were not equivalent; the bending beam critical temperature was always higher. This difference was attributed to the faster load rate used in the bending beam than in the constrained beam test. An empirical relationship was developed:

$$Load_{Temp_{TSRST}} = 1.3\ Temp_{BBR} - 9.5$$

King, G.W., King, H.W., Harders, O., Chavenot, P., Planche, J.

"Influence of Asphalt Grade and Polymer Concentration on High Temperature Performance of Polymer Modified Asphalts," AAPT Vol. 61, 1992, pg. 29.

Materials:

40/50, 60/70, 80/100, 180/200 (Venezuela crude source)
SB (assumed referring to di block although not specified!); percentages referred to as x, 1.5x, 2x

Binder Tests:

Basics: Visc., R&B
Rheology: parallel plate

Mixture Testing:

Hamburg wheel tester, 104 and 122°F
LCPC wheel track

Results:

The tan delta values decreased with increasing polymer concentrations; the magnitude of the change was dependent upon the grade of base asphalt cement. For example, a 40/50 pen asphalt neat and modified with 1.5x percent SB had tan deltas of 6.74 and 1.86, respectively. For the 180/200 pen asphalt cement, tan delta was 4.44 and 2.66 for 1x and 2x polymer, respectively. Tan δ did not correlate with the mixture results from the wheel tester.

A comparison of rheology to mix performance indicated that binders with a G" greater than 8,500 Pa at 1 Hz, 60°C was equivalent to a rut depth of 5 mm or less after 30,000 cycles. For G" values less than 8,500 Pa, an empirical equation was developed to estimate rut depth (French wheel tester) from the binder rheology:

$$\textit{rut depth} = -27.36\,(\log G'') + 113.25$$

Lee, N.K., Hesp, S.A.N.

"Low Temperature Fracture Toughness of Polyethylene-Modified Asphalt Binders," TRB preprint 940185, 1994.

Materials:

PE, PE-chlorinated
SHRP AAN (Bow River 85/100)

Binder Testing:

TEM
Notched (5 mm) Bending Beam, -20°C, 3rd pt. loading (span 100 mm), constant rate of deformation of 0.01 mm/sec.

Results:

Toughness was defined as the energy expanded in fracturing a material. Material mechanisms that influence toughness include crack pinning, shear yielding (constant volume without intermolecular cohesion loss), and crazing (formation of fibers across the crack tip). The resistance of the material to crack propagation through crazing is solely a function of the molecular weight of the polymer which needs to be in excess of 20,000 g/mole.

The paper presented a fairly complicated equation for the calculation of K_{Ic}, the critical stress intensity factor (i.e., fracture toughness). This value was used to indicate that PE increased the fracture toughness about 25 and 50 percent at levels of 6 percent of unstabilized and stabilized PE, respectively. The fracture toughness was increased by about 100 percent for the chlorinated PE. Fracture toughness appeared to increase linearly with increasing polymer concentrations up to about 8 percent. A finer particle size distribution was linked to a higher toughness due to the crack pinning mechanism.

Lenoble, C.

"Rheology and Microstructure of Aged Polymer Modified Bitumens," ESSO SAF Research Centre, Mont Saint Aignon, Cedex-France (no date)

Materials:

Asphalt cement 80/100 and 100/40 (European grading?)
SBS - MW 120,000 at 3 and 5% concentrations
EVA - Melt flow index of 45, crystallinity of 16%, 7% concentration
EMA - Melt flow index of 5, crystallinity of 27%, 5% concentration

Binder Tests:

Basics - Penetration, R&B, RTFOT
Rheology - Parallel plate 0.1 to 2 rad/sec; -20 to 60°C
Direct Tension - 500 mm/min; 50 x 15 x 2 mm bar of asphalt cement; pulled to a maximum of 1,400% elongation
UV Florescence

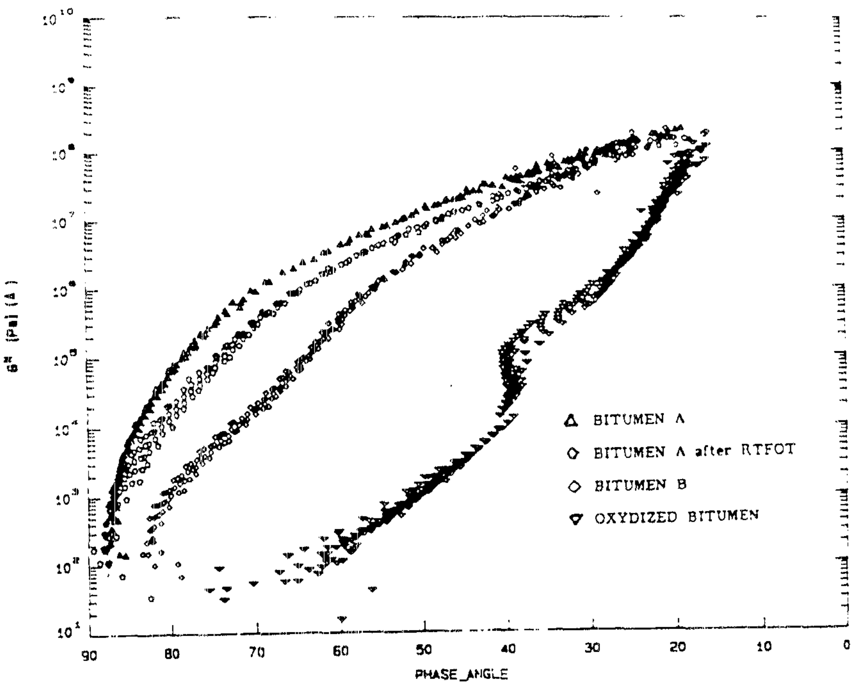
Results:

The authors used Black diagrams to present the rheological results. This is a graphical relationship between the phase angle (x axis) and the complex modulus (y axis) (Figure 1). A broadening of the Black diagram curves was interpreted as an indication of an increase in the asphaltene micelle interactions. With one of the binders classified as compatible with the SBS polymers, a positive effect of RTFOT aging was noted in the shape of the Black diagram curves; there was an increase in the viscoelastic characteristics and a decrease in the high temperature susceptibility. Using a polymer additive decreased the phase angle for a given complex modulus (G*); the same trend was seen after RTFOT.

The direct tension results indicated that the percent elongation increased from 50 to 1,400 percent after RTFOT for the SBS modified asphalt.

In the 80/100 asphalt cement, the SBS at a concentration level of 5 percent by weight, had an average particle size of about 10μm. In the 100/40 asphalt, the sizes were 20 and 100μm for 3 and 5 percent concentration levels. The larger particle size in the 100/40 was seen as an indication of poorer binder properties; these sizes were defined as a poor microstructure.

The use of either EVA or EMA resulted in heat-stabilized blends. At 7 percent, the EVA-asphalt cement blend appeared to be at the inversion point before aging; after aging the asphalt cement was obviously the continuous phase. At 5 percent, the EMA was well dispersed both before and after RTFOT.



Linde, S., Johansson, U.

"Thermo-Oxidative Degradation of Polymer Modified Bitumen," ASTM STP 1108, 1992.

Materials:

Swedish grades B180, B 85, 2HL (naphinic oil)
SBS (Cariflex TR1186, radial, and Cariflex TR1101, linear - Shell)
SEBS (Kraton G1652 - Shell)

Binder Tests:

Direct tension, -10°C (14°F), 50 mm/min (2 in/min)
SEC

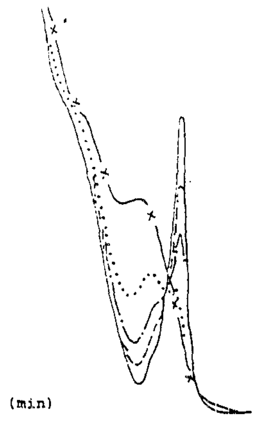
Results:

After 27 hours of aging a polymer modified binder at 200°C, the SBS had degraded to a lower molecular size. After aging, the original ductile behavior seen in the unaged modified binder during the direct tensile test showed a significant increase in the brittle behavior and a corresponding decrease in the percent elongation at failure. This trend was seen for both the linear and radial SBS polymers.

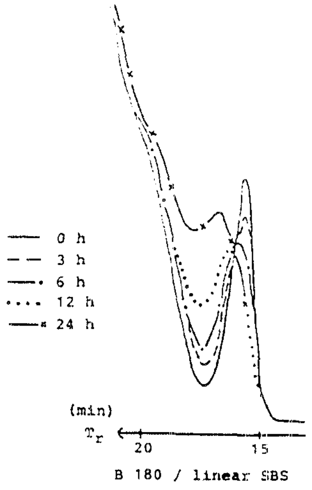
The SEBS modified asphalts showed a slight increase in the molecular weight of the asphalt cement but no change in the polymer after aging. However, there was a significant loss in the ability of the material to strain before failure; the percent elongation at failure decreased from 85 mm at 0 hours of aging to 10 mm after 27 hours. Authors felt that this was due to the aging of the asphalt cement and not the polymer, but no unmodified aging data was presented to substantiate this hypothesis.

The aging experiment was repeated, but in an inert atmosphere (i.e., no oxygen). These results showed no degradation of the polymer even after 27 hours of aging. This indicates that some polymers (e.g. SBS), like asphalt, are susceptible to oxidation-induced problems. When the polymers were mixed with the naphtinic oil, the polymer appeared to dissolve and oxidation degradation of the polymer was enhanced. The authors attributed the increased degradation to the exposure of more of the double bonds to oxygen due to the dissolved state of the polymer.

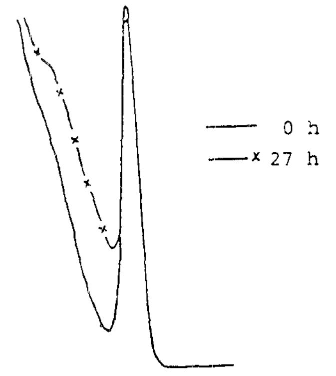
When the asphalt cement grade was increased for the same crude source asphalt, the compatibility of the asphalt with any given polymer was reduced.



B 180 / branched SBS
decreasing molecular mass ←



B 180 / linear SBS
decreasing molecular ma
←



decreasing molecular mass
←

B 180 / SEBS

Marvillet, J.

"Influence of Asphalt Composition on its Rheological Behavior", AAPT Vol. 44, 1975, pg. 416

Materials:

Misc. Asphalt Cements

Binder Tests:

GPC

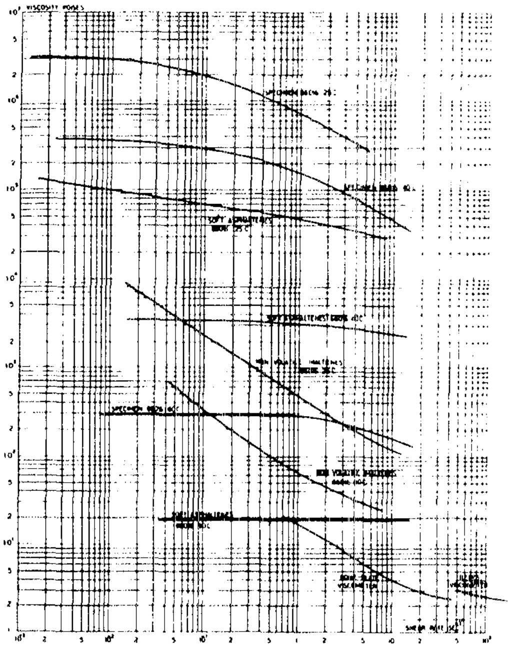
Rheology - Cone and Plate

Corbett separation

Vapor Pressure Osmometry (VPO)

Results:

An adaptation of the Corbett fractionation process which uses various solvents for selective extraction of asphalt cement components was evaluated. These results indicated that the maltenes (non-volatile fraction) were from 23 to 33.7 percent of the total asphalt cement for the materials studied. This percentage increased to 86 percent for flux oils. The number-average molecular weight (M_n) ranged from 420 (flux) to 720 (asphalt cement); the weight-average molecular weight (M_w) was about 720 for the asphalt. Soft asphaltenes were between 45.5 and 56 percent, and about 14 percent of the total oil for typical asphalt cements and flux oil, respectively. The M_n ranged from 540 (flux) to 855 (asphalts); M_w was about 930 (asphalt). The hard asphaltenes ranged from 14.25 to 22.2 percent of the total oil for typical asphalt cements; there were no hard asphaltenes in the flux oil. The M_n ranged from 3,340 to 3,350; M_w was between 9390 and 14,800 for asphalts. Figure 1 shows the viscosity versus shear rate for these various asphalt cement fractions.



Cone and plate results indicated that there was more than 1 order of magnitude decrease in the shear stress when the test temperature was increased from 45 to 60°C. The difference in shear stress decreased to 0.9 orders of magnitude for a temperature reduction from 45 to 25°C, and about 0.2 orders of magnitude from 25 to 15°C.

Little, D.N.

"Analysis of the Influence of LDPE Modified (Novophalt) Asphalt Concrete on Mixture Shear Strength and Creep Deformation Potential," ASTM STP 1108.

Materials:

AC 10 (Amoco, Trumbill, Atlantic)
AR 1000 (California Valley)
AC 5 (Texaco)
LDPE

Binder Tests:

Basics: viscosity, penetration index, R&B

Mixture Tests:

(Hveem compaction for large samples, Texas Gyratory for convention size)
Repeated axial creep (VESYS)
Diametral fatigue

Results:

The author described the total strain as:

$$Total\ \varepsilon = \frac{S}{S_e} + \frac{S}{S_{ve}} + \frac{S\,t}{3\eta}$$

Where S is the total mixture stiffness, S_e is the elastic component of stiffness, S_{ve} is the visco-elastic component of stiffness, t is the time, and η is the viscous component. Results indicated that LDPE increased ϵ_{ve} by about 100 percent; ϵ_η decreased by about 25 percent. This corresponded to about a 10°C rise in the softening point and an increase in the penetration index.

Mixture resistance to permanent deformation was evaluated with the calculation of octahedral shear stress and strain:

$$\tau_{oct} = \frac{2\sqrt{s}}{3\sin\phi}\left(\sigma_{oct}\sin\phi + c\cos\phi\right) \quad ; \quad \sigma_{oct} = \frac{\sigma_x + \sigma_y + \sigma_z}{3}$$

Conventional triaxial testing was used to determine C and ϕ. A modified ILLIPAVE program was used to calculate the octahedral shear stress and strain throughout the pavement layers. Results indicated that LDPE increased C from 100 to 250 percent; there was little change in ϕ.

Conventional creep testing showed that the axial strain at 40°C was reduced substantially at an LDPE concentration of 6 percent.

Fatigue testing was only briefly discussed; a series of regression equations were developed for both modified and unmodified mixtures.

Little, D.

"An Evaluation of Asphalt Additives to Reduce Permanent Deformation and Cracking in Asphalt Pavements: A Brief Synopsis of On-Going Research," AAPT Vol. 55, 1986, pg. 314

Materials:

AC-5, -10, -20 from Texaco Port Neches, Texas
AR 1000, 2000, 4000 from California San Joaquin Valley

Binder Tests:

Basics: Viscosity, R&B, penetration, ductility
Rostler Fractionation

Results:

General survey of all additives for asphalt cement including mineral fillers, etc. Under the rubber heading of additives, the author notes that an asphalt cement needs to have aromaticity but too much will prevent the reforming of the polymer structure on cooling.

Mayama, M., Yoshimo, M, Hasegawa, K.

"An Evaluation of Heavy Duty Binders in the Laboratory," ASTM STP 1108

Materials:
Ethylene ethyl acrylate (EEA) + SBR

Binder Tests:
Basics: Penetration, R&B, Viscosity

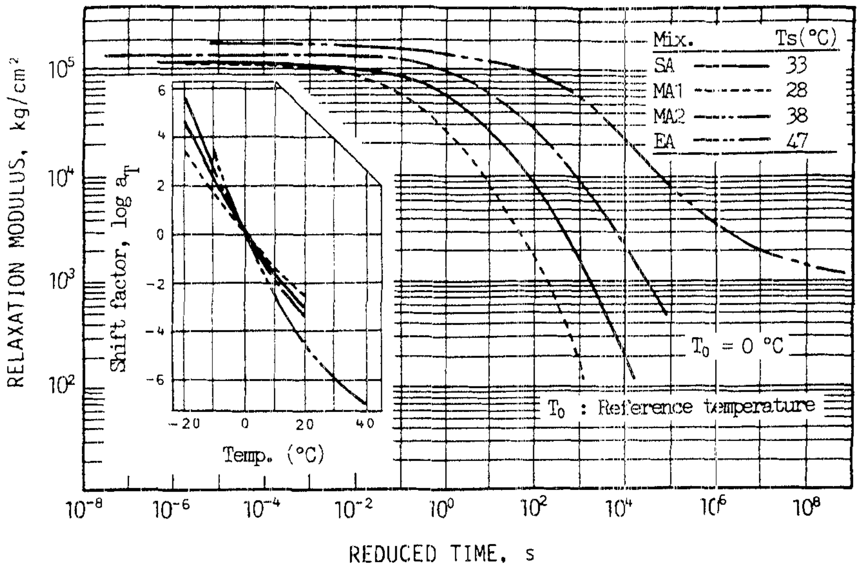
Mixture Tests:
Direct tensile - constant strain
Thermal contraction

Results:

The authors report the relaxation modulus master curve constructed using a shift factor of:

$$Log\ a_T = \frac{-C_1C_2\ (T - T_0)}{(C_2 + T - T_s)\ (C_2 + T_0 - T_s)}$$

Large values of Log a_T resulted in small changes in modulus due to time and/or temperature. When the EEA+SBR was used (code MA2), the relaxation modulus was increased for any given time compared to the neat asphalt (code SA).



Newcomb, D.E., Stroup-Gardiner, M., Epps, J.A.

"Laboratory and Field Studies of Polyolefin and Latex Modifiers for Asphalt Mixtures," ASTM STP 1108, 1992.

Materials:

Asphalt Cements:
  Lab: AC 5, AC 10, AC 20 (Marathon Oil, Michigan)
  Field: (Local Sources) 120/150 Michigan, AC 30 Alabama
Polymers:
  Polyolefins - ethylene acrylic acid copolymers

Binder Tests:

None

Mixture Tests:

Resilient modulus, 0.1 sec load/0.9 sec rest (assumed Poisson's ratio of 0.35); -12, 1, 25, and 40°C
Indirect tensile strength 50 mm/min (2 in/min), 25°C

Results:

An unmodified AC 10 had moduli similar to either an AC 5 modified with 5 percent P1 (a polyolefin with a melt flow rate of 600 dg/min) or an AC 5 modified with 5 percent P1 and 3 percent SBR latex respectively. A study to define the optimum order of combining the mixture components showed that the best results (i.e., highest moduli at 40°C) were obtained when the asphalt cement and the modifiers were pre-combined and then added to the aggregate.

The resilient modulus of the compacted mixture with either the P1 or P2 (a polyolefin with a melt flow rate of 2,600 dg/min) depended upon the compaction temperature. At a compaction temperature below about 116°C resulted in slightly higher moduli (about 25 percent) for mixtures with the lower melt flow rate polyolefin. Above 154 °C temperature, the higher melt flow rate polyolefin reduced the moduli slightly (about 25 percent); air voids were also reduced for the same compactive effort.

A comparison of the laboratory, behind the paver, and core mixture test results indicated that all modified mixtures had greater moduli at 40°C than the unmodified mixtures. The moduli for the behind the pavers were greater than for the cores, although the trends between the mixtures were generally consistent.

Park, J.K., Bontoux, L.

"Thermodynamic Modeling of the Sorption of Organic Chemicals in Thermoplastics and Elastomers," Applied Polymer Science Vol. 47, 1993, pg 771-780.

Materials:

SBR
LDPE
PE, Neoprene,

Organic chemicals:	toluene, n-xylene, p-xylene, o-xylene, ethyl benzene (aromatic hydrocarbons), n-hexane and n-nonane (aliphatic hydrocarbons), o-chlorphenol (phenols), methanol (polar compounds), and 2-butanone (methyl ethyl ketone)

Results (Polymer Chemistry Related Only):

Sorption is generally used to describe the initial penetration and dispersion of penetrant molecules into the polymer matrix. Sorption includes measurements of adsorption, and absorption into the micro voids and cluster formations. Mass transfer behavior includes the concentration gradient-controlled diffusion, and relaxation-controlled swelling. Partition and diffusion coefficients can be developed to determine the rate of permeation of a solvent by a polymer. Relevant equations and descriptions of procedures are included in this paper.

Painter, P.C.

"The Characterization of Asphalt and Asphalt Recyclability," SHRP Report A-675, 1993.

Results:

A program developed by the author to estimate the solubility parameters and phase behavior for asphalt cements was developed. A calculated value of V_B as used in the Flory-Huggins equation for calculating the change in entropy was developed as the volume of repeat units containing just one oxygen atom. It was assumed that this was a measurement of the hydrogen bonding functional group.

The findings indicate that the hydrogen bonding provides only a secondary contribution to the total asphalt cement structure due to the low overall concentration of this group in the asphalt cement. The author indicates that a good estimate of the molecular weight is needed to et good results from the program; it is questionable if this is an obtainable number. There was an indication that high molecular weights resulted in phase separation of the neutral fractions.

Pinke, H., Merz, R.E., Bosniack, P.S.

"Asphalt Rheology: Experimental Determination of Dynamic Moduli at Low Temperatures," AAPT Vol. 49, 1980, pg. 64

Materials:

Not specified - typical paving grade binders and air blown asphalt cements
No modifiers

Binder Tests:

Rheology - Torsional Bar 0.1, 1, and 10 rad/sec.; 35 mm long x 10 mm wide x 5 mm thick; testing started at 0°C and then cooled at intervals of either 5 or 10°C until sample failed.

Results:

Authors reported the repeatability of the torsion bar test method to be less than +/- 10 percent in the worst case; most results had substantially less variability. One source of error noted was clamping problems; these problems were reduced by using a fixed geometry for the sample and set-up.

Faster frequencies resulted in a higher glass transition temperature (T_g) which was determined as the peak of the loss modulus (G") master curve. There were significant differences in the T_g for various the various asphalt cements used in this study. However the biggest difference was seen between the typical paving grade binders and air blown asphalt cements.

Rogge, D.F., Terrel, R.L.

"Polymer Modified Hot Mix Asphalt - Oregon's Experience", ASTM STP 1108, 1992

Materials:

SBR (1 project)
SBS (6 projects)
Eva (1 project)

Binder Tests:

Basics: Penetration 4, 25°C, viscosities

Mixture Tests:

Hveem mix design
Resilient modulus, 0.1 second load; 1 Hz
Diametral Fatigue, 0, 23°C
Index of retained modulus

Results:

Oregon used these test sections to establish a PBA specification based on the basic binder tests, before and after RTFOT. General guidelines for Oregon's procedure but no specific information on test results.

An initial EVA test section showed sever cracking. An investigation of the construction information showed that the mix temperature might have been too high. Subsequent work with a reduced mix temperature showed that EVA sections were performing satisfactorily.

Rowlett, R.D.

"A Methodology for Evaluation of Performance-Based Tests Using Asphalt Modifiers," AAPT Vol. 60, 1991.

Results:

Survey form were sent to state agencies; responses indicate that most respondents felt that polymers could play a role in most pavement distresses. This indicates a general acceptance of the potential benefits of polymer modifiers.

Sabia, R.

"On the Characterization of Non-Newtonian Flow," Journal of Applied Polymer Science, Vol. 7, 1963, pg. 347-355.

Results:

This author indicated that a higher moment of molecular weight is needed to characterize the zero shear viscosity from molecular weights for broad distribution polymers. An equation of flow with a variable exponent can be used to characterize polymers:

$$\ln \frac{\eta}{\eta_0} = \left(\frac{\eta}{\eta_0} - a\right) \ln \left[1 + (\gamma\tau)^b\right]$$

Where *a* is a function of the inverse of the flow index.

Schmidt, R.J.

"The Relationship of the Low Temperature Properties to the Cracking of Pavements," AAPT Vol. 35, 1966, pg. 263

Materials:

Not specified - used data reported in other researchers' projects

Binder Tests:

Dilatometery for measuring T_g
Basics
Fatigue - beam (test parameters not specified)

Results:

Data reported in a previous paper (same reference) were used to compare to the number of cycles to failure (reported by other researchers) and the number of thermal cracks per mile of pavement. In general, lower shift factors resulted in lower numbers of cycles to failure in laboratory prepared specimens (Figure 1). While there was a substantial relationship between the T_g and the number of thermal cracks/mile, there was little relationship between the standard viscosity measurement and thermal cracks/mile (Figure 2).

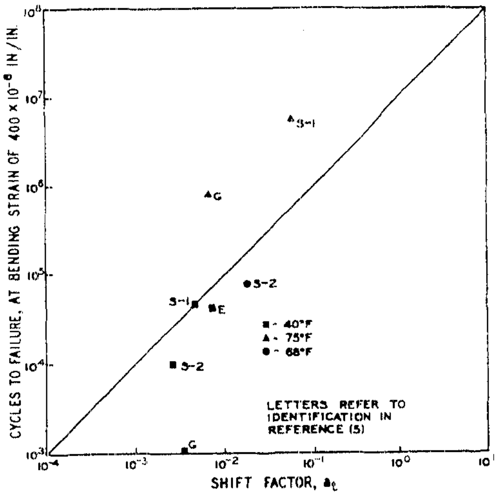


Figure 1.

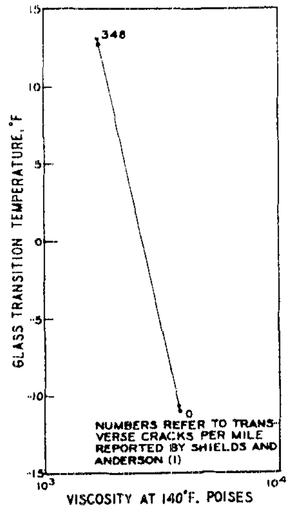


Figure 2.

Schmidt, R.J., Santucci, L.E.

"A Practical Method for Determining the Glass Transition Temperature of Asphalt and Calculation of Their Low Temperature Viscosity," AAPT Vol. 35, 1966, pg. 61

Materials:

Bureau of Public Roads library of asphalt cements (1954-1955)

Binder Tests:

Dilatometric Method for measuring glass transition temperature
Basic - viscosities, R&B, etc.

Results:

A dilatometric method was used to measure volume changes in asphalt cement due to changes in temperature (Figure 1). The authors noted that it was difficult to measure the volume change but results improved substantially when sufficient time was allowed for the volume change to stabilize.

The WLF constants C_1 and C_2 were found to be 17.44 and 92.88 for °F. These constants changed with shear rate (Table 1). The assumptions for using the WLF equation for shifting data included: 1) Newtonian behavior, 2) from T_g to T_g + 180°F, 3) high molecular weight materials at long times, and/or 4) correlation to the zero shear viscosity.

The T_g, and the viscosity at 60°C (140°F) (i.e., η_1 and T_1) were used to estimate the low temperature viscosity (η_2) from the equation:

$$\log \frac{\eta_1}{\eta_2} = \frac{C_1 (T_2 - T_g)}{C_2 + T_2 - T_g} - \frac{C_1 (T_1 - T_g)}{C_s + T_1 - T_g}$$

Table 1. Changes in WLF Constants with Shear Rate.

Shear Rate (1/sec)	C_1	C_2
0.001	24.80	188.3
0.05	34.94	461.0
0.1	38.42	555.7

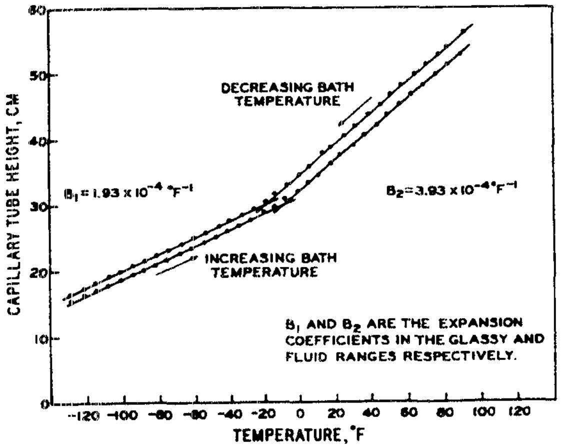


Figure 1.

Serfass, J., Joly, A., Samanos, J.

"SBS-Modified Asphalt for Surface Dressing - A Comparison Between Hot-Applied and Emulsified Binder," ASTM STP 1108, 1992., pg. 281

Materials:

SBS - linear, MW approx. 150.000
SBS - radial, MW approx. 250,000

Binder Tests:

R&B
Fraas Brittle Point

Results:

The softening point increased faster for the radial polymer than for the linear. The Fraas brittle point decreased with increasing concentration of polymer.

The authors defined compatibility as the colloidal instability index, I_c:

$$I_c = \frac{Asphaltenes + Saturates}{Resins + Aromatics}$$

Values of I_c below 0.13 were taken as an indication of good compatibility while values greater than 0.28 appeared to indicate incompatible blends.

Shell Chemical Company Supplier Literature

"Kraton Thermoplastic Rubber: Typical Properties 1992,"

Results:

Kraton 'D' series polymers have an unsaturated midblock (SBS); the 'G' series has a saturated midblock (SEBS). The physical crosslinking of the styrene blocks of the polymer as the modified asphalt cement cools down is supposed to be responsible for an increase in the modified binders tensile strength. Typical Kratons used in the modification of asphalt cement include the series: D1100, D1300, D1400, G1600, and G1700. The 1000 series are pure block copolymers, and the 4000 series are oil extended polymers.

Property	D1101	D1102	D1184	G1650	G1652	G1654 X	G1657
Tensile strength, psi	4,600	4,600	4,000	5,000	4,500	3,500	3,400
300% Modulus	400	400	800	800	700	900	350
% Elongation	880	880	820	500	500	700	750
Brookfield Viscosity (toluene, 25°C, cps	4,000	1,200	20,000	8,000	1,350	370	4,200
Melt Flow Index g/dmin	<1	6	<1	---	10	---	8
Architecture	Linear	Linear	Radial	Linear	Linear	Linear	Linear

Shell Chemical Company Supplier Literature

"Kraton Polymers: The Asphalt Modifier for America's Roads," SC: 1494 - 93, February, 1993

Materials: Kratons

Mixture Testing: Lottman
Permanent deformation (Niso)

Results:

Functional groups added to the backbone of the copolymer were considered to increase the adhesive strength of the binder. Lottman conditioning of compacted samples indicated original and wet tensile strengths for the Kraton modified asphalt were both significantly higher than either the unmodified, 0.5 percent Pavebond, or 1 percent lime modified mixtures. However, if the reader calculates the retained strength ratios, the same mixtures show 81, 80, 86, and 91 percent, respectively. This would indicate that the polymers function in increasing the viscosity is most likely responsible for the increase in tensile strengths.

At some concentration, the modified asphalt cement begins to act as an asphalt extended polymer due to the polymer swell. Research indicated that anywhere from 2 to 24 hours of high shear mixing is needed to obtain the maximum swollen polymer matrix.

If a polymer network is formed, the low temperature properties of the binder will assume that of the polymer rather than the asphalt cement; it was assumed that the polymer properties would absorb more of the thermal stress buildup than the unmodified asphalt cement. The polymer network would also provide more elastic response at warmer temperatures.

Results indicated that for mixtures with an AC 5, AC 20, and an AC 5 + 6% Kraton, the Niso values were 25,300, 54,600, and 118,00 cycles, respectively. This corresponded to a cracking temperature of -22.4, -11.4, and -61.6°C.

Shida, M., Cancio, L.V.

"Prediction of High Density Polyethylene Processing Behavior from Rheology Measurements," Polymer Engineering and Science, Vol. 11, No. 2, 1971, pg. 124-128

Materials: HDPE

Results:

The zero shear viscosity is a function of the molecular weight of the polymer. The shape of the flow curve was dependent upon the molecular weight distribution (MWD). On a comparison basis, the viscosity at high shear rates of one polymer will be higher than that for another polymer if the first sample has a narrower MWD. The flow index, n, will be smaller for polymers with less shear sensitivity.

Shuler, T.S., Hanson,D., McKeen, R.G.

"Design and Construction of Asphalt Concrete Using Polymer Modified Asphalt Binders," ASTM STP 1108, 1992

Materials:

120/150 Pen Navajo refinery in Artesia, NM.
3, 6% SBS (Kraton D4463X - Shell; X means extender oil - SBS: oil = 47:53)
2, 4% EVA (Elvax 150W- Dupont)
3, 6% Styrelf process (Elf)

Binder Tests:

Basics: Viscosities, R&B
Rotational recovery
Forced ductility
Schweyer apparent viscosity

Mixture Tests:

Marshall mix design
Resilient modulus (no info on load/rest), -12, 25, 40°C
Moisture conditioning (ASTM D4867)

Results:

Field test sections were placed in northern New Mexico. During construction, problems with air quality were noted when the polymer with the extender oil was used (i.e., smoke). There was also a residue on the oil cooler of the paving machine. Early results indicated no difference between any of the sections.

Laboratory results indicated that at the lower polymer concentrations, the modulus was similar for all materials at the cold test temperatures; modified mixtures were all stiffer at the warm test temperature. The results were mixed at the higher concentrations of polymers. Six percent of the Kraton D4463X had lower moduli at cold temperatures and similar to unmodified at the warm temperature (not mentioned but might possibly be a function of the extender oil softening the neat asphalt cement). The 4 percent of the Elvax 150W had a higher moduli at the cold temperature and was similar to the unmodified mixtures at warm temperatures. The 6 percent of the styrelf had similar cold temperature and lower warm temperature moduli.

Sisko, A.W., Brunstrum, L.C.

"Relation of Asphalt Rheology Properties to Pavement Durability," NCHRP Report 67, 1969

Materials:

Bureau of Public Roads library of asphalt cements (1954-1955)

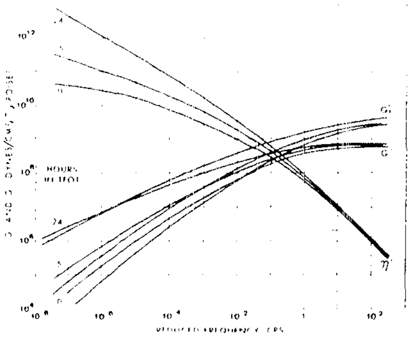
Binder Tests:

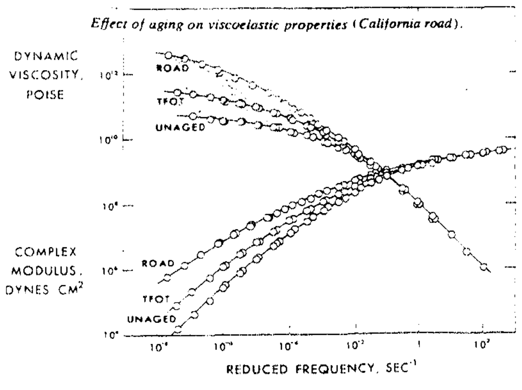
Rheology - parallel plates
Basic - viscosities, R&B, etc.

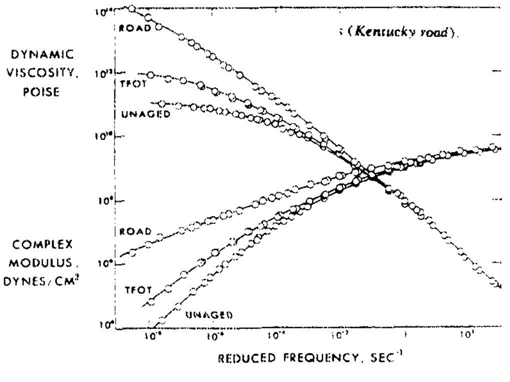
Results:

Researchers found that the WLF constants C_1 and C_2 (i.e., shift factors for master curve) were 28.6 and 292, respectively, for °K. Some changes in the shift factors were noted with asphalt cement aging. Dynamic testing at higher frequencies ($>10^2$) showed that both the complex modulus and viscosity were reasonably uniform with most values between 5 to 7 x 10^9 dyne/cm^2 and 1 to 2 x 10^5 Poises, respectively. These values were constant regardless of aging, and asphalt cement grade. At lower frequencies, there was a significance difference between grades, and aged and unaged materials.

Changes due to aging were much less than changes due to different asphalt cements. Both the complex modulus and viscosities were higher for the recovered roadway binder than for the thin film oven aged binder. The authors indicated that aging changes were due to the development of a gel structure with the asphaltenes acting as nucleating agents. These conclusions were based on: 1) aged binder did not flow back into cut surface, 2) penetration and softening point relationships changed, 3) there was a large increase in the complex viscosity for small changes in the molecular weight, 4) the WLF constants changed, and 5) large complex viscosity changes were seen without large changes in the glass transition temperature.




Effect of aging on viscoelastic properties (California road).


(Kentucky road).

Swager, B.

"Viscosity Measurements of Polymer Modified Asphalts," ASTM STP 1108, 1992.

Materials:

SBR (AC20R from Asphalt Supply)
SBS (AC10P from Fina Oil)
EVA (AR 400HP from Conoco)
SB (AC20R from Conoco)
Neoprene (PMAC 20 from Elf)

Binder Tests:

Basics: Viscosity (60°C)
Cannon Manning tube sizes 11, 12, 13
Asphalt Institute tube sizes 100, 200, 400

Results:

The authors evaluated the use of conventional viscosity tubes with polymer modified binders. They concluded that the use of the straight-walled Asphalt Institute tubes were preferable for modified binders. However, the use of these tubes with unmodified asphalts could increase the viscosity measurements by as much as 20 percent when compared to the standard Cannon Manning tubes.

Tappeiner, W., Male, A.G.

"Enhancement of Asphalt Concrete Mixtures through the Addition of Recycled Polyethylene," Novophalt America literature (no date)

Materials:

AC 10, Ac 20
SBR latex
SBS
5-6% LDPE
EVA

Binder Tests:

Basics: Visc., R&B, Penetrations (4, 25°C), Fraas brittle point

Mixture Tests:

Static axial creep
Diametral fatigue
Wheel track, 40 - 60°C (method not specified - but since Georgia did the testing, assume the Georgia wheel tracking device was used).

Results:

The general influence of LDPE on basic binder properties was shown as about a 300 to 400 percent increase in viscosity, and a 50 and between 20 to 30 percent decrease in penetration values at 25 and 4°C, respectively. The softening point was increased by about 10°C while the Fraas was not significantly altered (findings reported but data not included).

Static creep tests indicated that the slope, m, of the axial strain versus time relationship decreased with increasing percentage of LDPE: $m = 0.41$ for unmodified AC 20, and 0.33, and 0.17, for 4.3, and 5 percent, respectively.

Various comparisons were presented in the figures, however, no information on other polymers (e.g. percent, type, etc.) was included. General comparisons indicated that rut depths after 8,000 cycles, 100 psi, and 105°F were 0.20, 0.12, 0.14, 0.08 and 0.05 inches for an unmodified AC 30, SBS, SBR latex, EVA, and LDPE, respectively. Fatigue testing at 25°C showed that at 40 psi stress level, the numbers of cycles to failure were 4,000, 14,000, and 27,000 for an unmodified AC 10, an unmodified AC 20, and an LDPE modified AC 10, respectively. At a stress level of 70 psi, all mixtures failed by between 1,000 and 4,000 cycles.

Tayebali, A.A., Goodrich, J.L., Sousa, J.B., Monismith, C.L.

"Relationship Between Modified Asphalt Binder Rheology and Binder-Aggregate Mixture Permanent Deformation Response," AAPT Vol. 60 1991

Materials:

6, 8, 12% SBS (Kraton K4460 - 50% Kraton 1101 and 50% extender oil)
20% Microfil 8 (pelletized carbon black)

Watsonville aggregate 3/4-inch max.
  2 compactive efforts
  3 AC contents (opt. of 4.8% +/- 0.6%)

Binder Tests:

Rheology: (Assumed parallel plate - not specifically defines)

Mixture Tests:

Axial static, 100 and 200 kPa (15 an 30 psi) axial with 100 kPa (15 psi) confining
  40 and 60°C (104 and 140°F)
Axial dynamic, 0.1 second load time, 1 Hz

Results:

A reduction in the loss tangent with increasing percentage of the K4460 polymer was noted. However, no difference was noted in the creep strain or modulus between the AR 2000, AR 2000 modified with 12 percent K4460, and the AR 2000 modified with 20 percent of the Microfil 8. Without a confining pressure, the average plastic strains were significantly lower either of the modified asphalts; the K4460 and Microfil 8 results were similar. With 15 psi confining pressure, the AR 2000 and the K4460 modified AR 2000 had similar strains while the Microfil 8 modified AR 2000 was still significantly lower.

Terrel, R.L., Waters, J.L.

"Modified Asphalt Pavement Material, the European Experience," AAPT Vol. 55, 1986

Materials:
General modifiers

Binder Tests:
None

Mixture Tests:
Dynamic Modulus, 10 Hz.
Loaded Wheel Tracking Test
Fatigue Testing - Trapezoid, 30 Hz., 10°C (50°F), Failure was defined as a 50 percent decrease in modulus

Results:

The authors identified the tentative SHRP classification of modifiers for asphalt cement as: 1) mineral fillers, 2) rubbers (SBS, SBR), 3) plastics (EVA, PE), 4) oxidants (Manganese, metal salts), 5) anti-oxidants (lead compounds, carbon, calcium salts), and 6) hydrocarbons (aromatic oils, extender oils). The rubber categories were further separated into natural latex, synthetic latex, block co-polymers, and reclaimed rubber.

The authors suggest that a continuous polymer lattice network can only form if the polymer swells sufficiently due to the effect of the maltene fractions. The absorption of this asphalt cement fraction by the polymer can cause a colloidal imbalance in the asphalt cement by making the aromatic and polar aromatic oils insoluble. This in turn can lead to the flocculation of the asphaltenes. The authors indicated that the ability of the styrene domains to dissolve at high temperatures and re-link as the temperature drops was considered an important hypothesis. The butadiene portion of the SBS should not be dissolved by the maltene oils and would therefore not be dissolved. Due to the low concentrations of polymers used in the modification of asphalt cement, either the polymer is swollen by the oils or the asphaltenes in the asphalt cement are swollen by the remaining oils.

Limited mix test results presented in this paper showed similar complex modulus (G*) versus temperature relationships. Modified asphalt cements had a higher tensile strain for a given number of fatigue cycles (i.e., a higher number of cycles to failure for a given strain level). The rut depth from the loaded wheel tester was reduced by about 50 percent for modified mixtures.

Standard European procedures for design modified binders and asphalt concrete mixtures are currently under development. The Central Laboratory of the Public Works Division (LCPC) defines a series of tests to be conducted by LCPC for informational purposes only (i.e., no specifications). Binder testing includes Fraas, R&B, penetration, and sliding plate viscosity for both unaged and RTFOT materials. A balance rheometer is used to determine G*. Other tests include torsional recovery, and tensile strength. Mixture testing includes a gyratory design, the determination of G*, fatigue, and wheel tracking tests.

Veaga, C., Bathiato, G., LaBellle, G.

"Asphalt Cement Improvement: The Influence of a Carboxylated SBR Elastomer Investigated by Means of Viscoelastic Parameters," AAPT Vol. 44, 1975, pg. 366

Materials:

Asphalt Cements: 85/100, 60/80, 40/50 pen
SBR - Elastra 104 (Enichem)

Binder Tests:

Rheology - binder cylinder (7.5 cm diameter by 15 cm)
Creep - Dynamic and Static with strains limited to about $100\mu\epsilon$; -10, 0, and 10°C (14, 32, and 50°F)

Results:

There was a significant increase in the complex viscosity (η^*) when the SBR was added although there were no signs of a network formation. Both 5 and 10 percent levels of SBR with the 60/80 pen asphalt cement significantly increased the asphalt stiffness over all temperatures (70 - 150°C). Only the stiffness for the 10 percent level of SBR was still higher at the 10°C test temperature.

Youtcheff, J.

"In Road in Characterizing Asphalts," Center for Applied Energy Research, University of Kentucky, Vol.2, No. 3, 1991.

Materials:

Asphalt cements only (SHRP AAD, AAK, AAM)

Binder Tests:

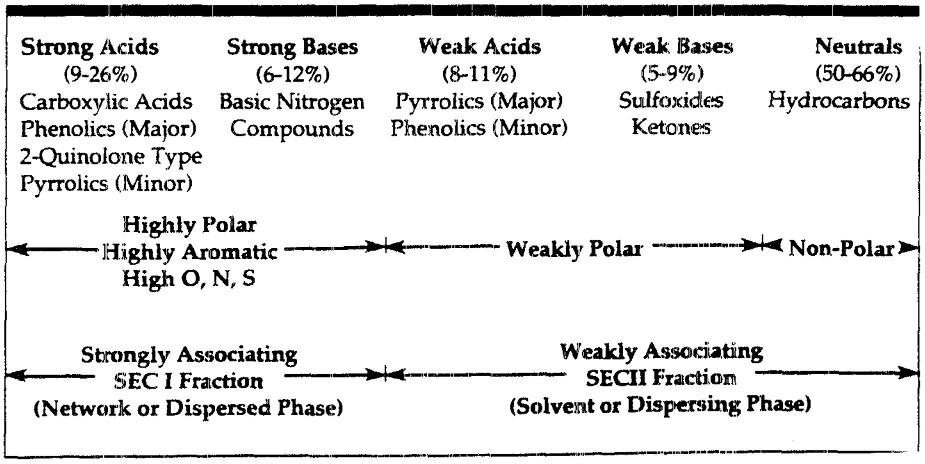
IEC
SEC

Results:

The typical molecular weight range for asphalt cements is between 700 and 1,000 daltons. The high molecular weight portion of the asphalt cement is the strong acid fraction which is friable at room temperature. The removal of the strong acids from the asphalt cement resulted in a decrease in the viscosity by several orders of magnitude.

IEC results indicated that the AAM asphalt was a solvent de-asphalted asphalt which consists of high molecular weight neutral components. The author felt that this suggested that the physical properties of the AAM asphalt were dominated by the large molecular size and not associations between smaller molecules.

The author felt that the SEC results supported a model of asphalt that was a bi-continuous system which consisted of a matrix of weakly associated polar and aromatic molecules dispersed in a relatively non-polar solvent phase. The asphalt properties should then be explained by the degree of association and the dispersing ability of the solvent phase. The dispersing ability of the solvent phase should either inhibit or accentuate molecular associations.



Strong Acids	**Strong Bases**	**Weak Acids**	**Weak Bases**	**Neutrals**
(9-26%)	(6-12%)	(8-11%)	(5-9%)	(50-66%)
Carboxylic Acids Phenolics (Major) 2-Quinolone Type Pyrrolics (Minor)	Basic Nitrogen Compounds	Pyrrolics (Major) Phenolics (Minor)	Sulfoxides Ketones	Hydrocarbons

Highly Polar Highly Aromatic High O, N, S ←→ **Weakly Polar** ←→ **Non-Polar**

Strongly Associating SEC I Fraction (Network or Dispersed Phase) ←→ **Weakly Associating SECII Fraction (Solvent or Dispersing Phase)**

Youcheff, J.

Products of the SHRP Asphalt Program: Advances and Applications of an Enhanced Understanding of Asphalt Binders," as yet unpublished paper, June, 1994.

Binder Testing: NMR wide line; Dynamic shear rheometer (parallel plate); Vapor pressure osmometry (VPO); SEC; IEC; Fractionation -n-heptane, iso-octane

Results:

IEC was used to separate the strong acids (SA), weak acids (WA), strong bases (SB), weak bases (WB), and neutrals. The neutrals were found to be more than 50 percent of the asphalt cement. The strong acids and neutrals were found to be the most correlated with other information. Some separation of selected asphalts for the amphoterics (fractions with both acid and base properties) were also conducted.

The SEC was divided into sections I and II with SEC I being friable at room temperature and SEC II being somewhat fluid. The SEC I fraction was between 10 and 31 percent of the whole asphalt. The percentage of SEC I was similar to that for the strong acids plus strong bases. The molecular weight for the SEC I was much higher than for the SEC II fraction; it was also more aromatic and had more heteroatoms. The properties of the individual fractions (amphoterics and SEC I) were not necessarily representative of the whole asphalt. The properties appear to depend on the polarity and structure of the undisturbed asphalt cement.

The M_n from VPO measures fractions for associated complexes and as such, could produce errors in estimating the true molecular weight.

The addition of n-alkanes and monofunctional species tended to act as plasticizers while the addition of bifunctional species acted as stiffening agents. Both observations increased with the increasing percentages of additives. The functional groups had a large effect on the T_g.

NMR spin-spin relaxation times (T_2) from pulsed adaptation of standard wide line NMR techniques were found to correlate with rheological properties. Tan δ calculated from the free induction decay (FID) versus the rheometer tan δ matched well.

Phase behavior was modeled with a computer program. This program was used to both estimate the solubility parameters and develop phase behavior diagrams. The accuracy of the program to estimate the solubility parameter was $\pm$ 0.6 (cal cm^{-3})$^{1/2}$; this is a large error in the estimate. Program predicted phase separation behavior below 140°C for the SHRP AAG strong acids and neutrals at higher concentrations. However, since the SA fraction is only between 10 and 31 percent of the whole asphalt cement, temperatures would have to be -100 and 20°C, respectively, for two phase behavior of these fractions. Solubility parameters for both the whole asphalt, SA, and neutral fractions are shown below.

SHRP Asphalt Cement	Whole Bitumen		Strong Acids		Neutrals	
	δ	M_n	δ	M_n	δ	M_n
AAD	9.07	700	11.32	2,500	9.04	510
AAG	9.34	710	10.82	1,080	9.67	590
AAK	9.35	860	11.42	2,780	9.60	590
AAM	9.03	1,300	11.67	3,040	8.99	1,140

Zanzotto, L., Foley, D.P., Watson, R.D., Juergens, C.

"On Some Practical Aspects of Using Polymer Asphalt in Hot Mix," CTAA Proceedings, Vol. 34, 1989

Materials:
SBS

Binder Tests:
GPC (Detailed procedure given in Appendix)
Kinematic viscosity at 135°C
Aging accomplished in large cylindrical storage tank, horizontally oriented, and equipped with 2 mixers.

Field Studies:
Several case histories documented. Covers general construction information.

Results:

Authors' indicate that the goal for an effective modified asphalt cement is to have the polymer dispersed in the asphalt rather than dissolved. Most of the work was centered on the length of storage time of a modified asphalt; relationships between the molecular weight distributions and storage time were developed for binders with and without an antioxidant. Typical results are shown in Figure 1. These results indicated that the polymer peak evident in the GPC results at short storage times began to disappear as the storage time increased. This was accompanied by a corresponding increase in viscosity. The authors' hypothesize that this is the result of crosslinking although no proof is given.

The use of ASTM 2042 was identified as being used to evaluate the compatibility of asphalts and modifiers, however, no letter in front of the number was given for test method; not sure which method was being referenced. δ_{AC} listed as approximately 8.3.

Several general case histories of the construction of polymer modified test sections were included in this paper. No major difficulties in constructing the modified sections were noted.

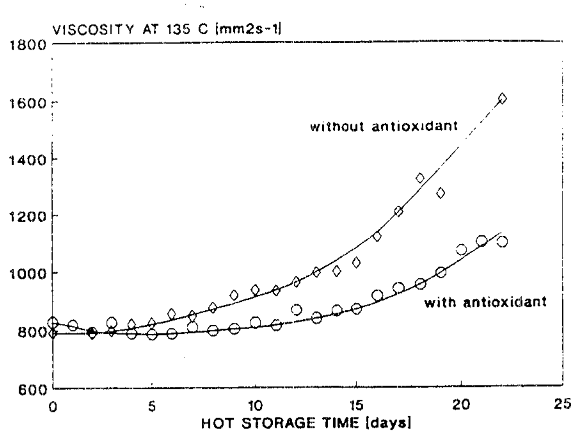


Figure 4: Kinematic viscosity vs time of hot storage of polymer asphalt without and with antioxidant

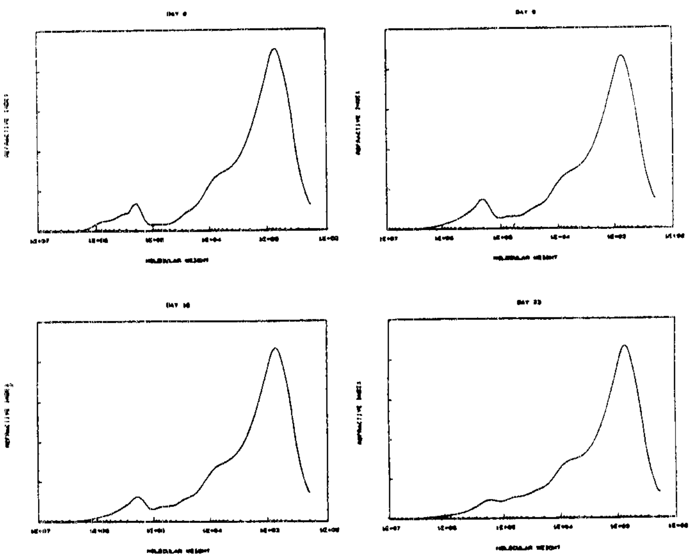


Figure 5: GPC chromatograms of hot stored polymer asphalt (without antioxidant)

Zanzotto, L., Foley, D., Rodier, C.E., Watson, R.D.

"Modified Asphalts - Are You Really Coming?", CTAA Proceedings, Vol. 32, 1987

Materials:

General:

Binder Tests:

Basics: Penetration, R&B
Rheology: Parallel Plate

Results:

General informational background: Plastomers contribute to the cohesive properties; a higher percentage than is typically used in block copolymer. Elastomeric polymers expand the temperature range of acceptable behavior by increasing elasticity which in turn leads to increased resistance to fatigue. Thermoplastic block co-polymer add strength at high temperatures because of their two-phase structure. These materials form physical rather than chemical crosslinks which means that they are easily dispersed in asphalt cement at high temperatures and reform crosslinks as the binder cools; it is this property that helps improve the low temperature properties.

Polymers and naphthenes compete for the available aromatics and asphaltenes; an insufficient supply of these should result in an unstable, coarse dispersion. The authors feel that the polymer should create a secondary network in the maltenic phase of the asphalt cement if it is to provide effective polymer modification. The authors indicated that compability between the polymer and the asphalt cement is defined by the morphology and resistance to phase separation during extended hot storage.

An optimal polymer concentration should occur around 7 to 10 percent by weight of asphalt cement. However, this range of concentrations is usually cost prohibitive for normal construction projects. Therefore, typical concentrations used in the construction of test sections is usually between 3 and 6 percent.

Actual data presented in the paper but compares materials in terms of PMA I through IV without defining the type or level of polymer modification. Therefore, a discussion of results not included in this review.

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