DEVELOPMENT OF ASPHALTS AND PAVEMENTS
USING RECYCLED TIRE RUBBER

Phase I: Technical Feasibility

Final Report

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January 1998

Work Performed Under Contract No. DE-FC04-94AL99567

For

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Office of Industrial Technologies

Washington, D.C.

By

Texas Transportation Institute

College Station, Texas

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Texas A&M University
Research Foundation
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Department of Chemical Engineering

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PREFACE

This report documents the technical progress made on the DOE funded project "Development of Asphalts and Pavements Using Recycled Tire Rubber" for the time period covering September 1, 1994 through May 31, 1997. Cost sharing for this study is being supplied by the Texas Department of Transportation and industry. Bruce Cranford is the Program Manager for the DOE Office of Industrial Technologies. Ken Lucien is the Project Officer and M. Laurene Dubuque is the Contracting Officer, both for the DOE Albuquerque Operations Office. Frank Childs, the Project Technical Monitor, is on the staff of Scienteck, Inc., Idaho Falls, Idaho. Professors Jerry A. Bullin, Charles J. Glover, Richard R. Davison, and Raymond W. Flumerfelt, together with Cindy K. Estakhri of the Texas Transportation Institute are the Co-Principal Investigators. Other co-authors of this report are Travis Billiter, Jason Chipps, Vikas Sheth, Gerald Elphingstone, masters students Jay Chun and Heamo Koo, and technicians Clint Eckhardt and Scott Moffat.

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CHAPTER 1

INTRODUCTION AND SUMMARY

INTRODUCTION

Asphalt is a complex mixture of materials, the bottoms product of the crude oil barrel, that remains after the distillative removal of more profitable components. While its lower value has allowed it to go largely overlooked, the chemical engineering applications to asphalt are immense. The vast majority of automobile transportation surfaces are constructed with asphalt (nearly 95%) (Bullin 1993), and it has oxidative kinetics, mass transfer, thermodynamics, polymeric, strength and adhesion aspects that make it a uniquely complicated material, deserving of a study of multidisciplinary approach. It is important to realize that asphalt is not the perfect road binder, but it is the economical choice. Given the relatively lower value of these mixtures and the variety of crude oil sources, there is a great deal of variability in asphalt production, yet to say that asphalt is "produced" may be a misnomer. At minimum it is poorly engineered, like construction scraps discarded from the newly finished home.

As the number of varied uses of petroleum has increased, asphalt has become, more and more, a side product of a fuel and chemical production design; its production, variability and content is strongly determined by what source material the refinery has and what it cannot profitably use. This variability increases the complexity of understanding the material and inadvertently sets the refinery's profit motives against those of the transportation industry. Making asphalt better, then, is strongly constrained by the cost of the performance enhancing additives, or their value to the refiner, and by blend processing costs.

As budgetary limitations become an increasing emphasis of the federal and state governments, upgrading and renewal of the nation's highway systems will be a major challenge. Optimization of the asphalt production process is crucial, especially for the transportation industry. Not only will it have to deal with the oil companies' desires to maintain a high profit level, but it will also need to continually extend the life of the pavement. To this end a number of new asphalt testing and evaluation specifications, known as SuperPave, have been developed. This endeavor, part of the

Strategic Highway Research Program, is ambitious. Whether the reader may be familiar with the hot southern plains, the frigid northeastern hills, or the varied western extremes, there is no single asphalt to fit all of these conditions. Adapting asphalt production to this variability is the major challenge of the SuperPave program.

The SuperPave performance grading specifications provide a guide between statistical temperature realities and pavement needs and are a great start to categorizing a given asphalt for preferred use and for comparison with others. Their major benefit is a new standardization of testing that decreases the emphasis on such exacting and subjective tests as the ring and ball and the penetration test, but the means of improving the asphalt are not spelled out. Many approaches have been considered in recent years for treating and improving asphalts. The use of waste reducing recycling agents to soften and rejuvenate binder-aggregate mixes in use is already practiced in industry. The addition of asphaltenes to increase the upper grade, or the supercritical fractionation of a generic asphalt to produce tailorable recycling agents are other considerations. Another idea utilized is to alter the elastic properties of the asphalt binder allowing it to withstand stresses better, while maintaining the desired road shape. This concept of polymer modified asphalts, and more specifically crumb rubber modified asphalts (CRMA) is the main topic of this research work.

The utilization of polymer modifiers to improve asphalt performance has been studied for a number of years (Billiter 1996). In 1991 Congress enacted the Intermodal Surface Transportation Efficiency Act (ISTEA), which in part required some degree of implementation of tire rubber in the asphalt binder design. While the subsequent repeal of the tire rubber language in 1995 has led to government disinterest, resulting in the termination of this project, this endeavor is still well worth examination. Every year in the United States, about one tire is discarded for every U.S. citizen and as few as a third of them are recycled (Serumgard and Eastman, 1995). The objective of adding tire rubber or any other polymer modifier is to increase the resilience of the binder and allow it to withstand highway stresses and oxidative aging more easily, while still giving it the strength to hold its shape and position. At higher temperatures, i.e. hot days, the rutting effect is reduced compared to the original asphalt by increased viscosity contributions from the partially digested tire rubber solids (Billiter 1996). The elastic contribution of the added material would reduce thermal cracking at temperatures below freezing, and fatigue cracking is also benefitted by the higher elasticity at more

common daily temperatures (Billiter 1996, Bauer 1997). In this way the road surface can be more likely to last longer. Non-tire polymer modifiers may also be employed to widen the SuperPave grading span, because they inherently have the same desired elastic properties. The real challenge is to make sure that these objectives are realized without unfavorable side effects, such as settling, inconsistent mixing, compaction problems, and, of course, high cost.

The use of tire rubber as the polymer modifier is favored by the *waste nature* of tire rubber, where only the blend processing costs are a major factor. Because tire rubber is a *thermoset*, it cannot be melted and reformed into new tires, compared to other polymers that have also been used as modifiers. These materials are *thermoplastics*; they are more easily recycled into high value products, and thus carry a higher value. While reduction of road costs on a long term basis is an ideal goal, producing a workable material that improves performance at a reasonable cost is an important first step.

When designing and installing the polymer modified mix, maintaining high pavement quality must be key. The pavement must at least be appealing to the consumer in that it be installable and workable, and to the traveller in that it not fail prematurely or require constant repair. Then, after meeting these minimum requirements, because it is more expensive, the material must improve the road properties and lengthen the life-cycle of the road. Continued refinement would make the process desirable through life-cycle savings and improved performance. Then the added benefit of fewer waste tires would be a bonus, and not just an offsetting economic consideration.

SUMMARY

Approximately 285 million tires are being discarded every year. Of those, less than 100 million are being recycled. The excess tires not being recycled are placed in landfills and other waste sites, collecting moisture, breeding insects, and constituting a general nuisance. About 27 million tons of asphalt are used each year to construct and maintain most of the country's two million miles of roads (Takallou and Takallou, 1991). If all of the tire rubber wasted annually could be combined with asphalt in road construction, it would displace less than 6% of the total asphalt used each year, yet could save about 60 trillion BTUs of petroleum products annually, some of which might still be

catalytically converted to high value products. This suggests there is a great opportunity to solve a serious waste problem, save energy and materials, and improve asphalt roadway life and performance.

The use of tire rubber with various types of asphalt pavements has been demonstrated in recent years with promising results (Sainton, 1990). Unfortunately, the technology for using ground tire rubber was relatively undeveloped, and the results of using rubber-asphalt concrete have been very erratic. The Center for Asphalt and Materials Chemistry at Texas A&M University began this project in August, 1994, with support from the U.S. Department of Energy (DOE) and the Texas Department of Transportation (TxDOT) with the purpose of providing data needed to optimize the performance of rubber-asphalt concrete in an attempt to avoid failures of the past.

As originally established, this project consisted of three phases. The first phase of the overall project has been to implement the exploratory development. The duration of this phase was two years. Following Phase I, Phase III was to last for one year, during which time the finalization of blend and mix design and planning of test section implementation was to take place. During the final two years of the project, Phase IV would include the installation and monitoring of the test pavement sections. For the most part, the exploratory development was to continue into the fourth year of the project, early Phase IV. Due to the termination of support from the Department of Energy at the conclusion of the second year, the implementation of Phases III and IV under this project has been reduced and no reporting of those activities to DOE will be forthcoming. Phase I was extended in time to continue the gathering of information and its progress is contained herein.

Phase I was to develop asphalts and recycling agents tailored for compatibility with ground tire rubber in order to eliminate or reduce compatibility problems and to improve compaction properties. To accomplish this objective, this project has been divided into several tasks. The original proposed schedule for completion of all tasks is given in Table 1-1. Also included are the actual completion dates with regard to DOE. A number of tasks differ in their planned and actual completion dates, some due to the shortening of funding. The majority, however, are reactions to revised curing conditions, and due to the optimization process.

In order to achieve a workable asphalt rubber blend, the biggest drawbacks were found to be the heterogeneity of the sample, and the high viscosity at the hot mix conditions, where the binder and aggregate are combined and sent into the field for installation. To overcome this problem, the

Table 1-1: Proposed Schedule for Completion of Tasks

Task	Name	Original Completion Date	DOE Completion Date
1	Laboratory Testing and Evaluation		
1.1	Fractionate Asphalt Material	2/96	11/96
1.2	Reblending for Aromatic Asphalts	5/96	3/96
1.3	Verifying Optimal Curing Parameters	8/95	5/97
1.4	Aged Blends	10/96	5/97
2	Evaluating Mixture Characteristics		
2.1	Developing an Experiment Plan	11/95	12/95
2.2	Evaluating Compaction Characteristics of Mixtures	5/96	5/97
2.3	Evaluating Deformation and Failure of Compacted Mixtures	8/96	5/97
3	Adhesion Test Development		
3.1	Adhesion Tests	8/99	8/96
3.2	Water Susceptibility	8/99	8/96
4	Commercialization Plan - Scheduled for Phase III	8/99	None

production and use of low viscosity source materials was completed. These materials are described in Chapter 2. For Task 1.1, various asphalts were fractionated in a supercritical unit and Residuum Oil Supercritical Extractions (ROSE) fractions were utilized to produce highly aromatic material of various viscosities. Shell AC-20 was fractionated to produce a highly-aromatic, low asphaltene AC-5 asphalt and to also produce various highly-aromatic recycling agents. Also, various ROSE fractions were obtained from Murphy, Diamond Shamrock, Witco, and Fina. These were prepared as potential asphalts and recycling agents. The second portion of Chapter 2 concerns Reblending

for Aromatic Asphalts, Task 1.2. The supercritical fractions of the Shell AC-20 were characterized and blended to produce a large quantity of a highly-aromatic, low-asphaltene AC-5. A Sun 125 recycling agent was blended with a Murphy resin to produce a highly-aromatic, low-asphaltene AC-5. Also, Diamond Shamrock and Fina resins were characterized for possible use as components of highly-aromatic asphalts.

The remainder of Chapter 2 and the next two chapters involve Task 1.3, Verifying Optimal Curing Parameters. The ultimate goal of this portion of the research was to determine the optimal curing variables that result in an asphalt-rubber being flexible at low temperatures, resists rutting at road temperatures, and is compactible at high temperatures. This originally involved optimizing the following seven variables:

1. asphalt composition
2. curing shear rate
3. curing temperature
4. curing time
5. rubber content
6. rubber particle size
7. rubber type

The addition of tire rubber to an asphalt is accomplished on the batch scale by motorized stirring at varying rotation (shear) rates and temperatures. Energy is exchanged in the breaking of chemical bonds, while mechanical cleaving is also present. These differing concepts are important because tire rubber consists of polymer strands cross-linked at sulfur sites, formed from the vulcanization process; at least two distinct types of bonding exist. The breaking of sulfur bonds between polymer chains may be called devulcanization, while breaking the chains themselves is depolymerization. Depolymerization and devulcanization rates may differ over the wide variety of mixing conditions and therefore must be characterized and an optimal balance chosen. By using specialized mixing heads, the rubber can be chopped into pieces so that reaction and dissolution are accelerated, or can simply be well-mixed and allowed to dissolve without mechanically cleaving the material. Again, it is this dissolution that may favor either devulcanization or depolymerization in a selectivity that is thought to be temperature and shear dependent. This mixing strategy is applicable to an in-line mixing technique that can be employed in the industrial setting to accomplish scale-up. Rheological instruments such as the dynamic shear rheometer, and the bending beam rheometer are utilized to evaluate the blend results.

As research progressed, it became more evident that the accepted blending conditions were

insufficient to achieve acceptable results. Chapter 3 presents the low-cure efforts that led to this conclusion, while Chapter 2 may be considered a preliminary or exploratory examination of various curing variables. Chapter 4 focuses on the revised and improved blending methods that were developed from the knowledge gained in the efforts of Chapters 2 and 3. Both Chapters 3 and 4 comprise Task 1.3 on Table 1-1.

Another aspect of the asphalt-rubber blending process, apart from the installation and initial behavior aspects, is an analysis of the aging characteristics of the new material. In addition to the pressurized aging vessel, the utilization of atmospheric and pressurized oxidation chambers, and environmentally-controlled rooms allow the long term aging process to occur in a shorter period of time than road aging. Along with the rheological tests applied to the blends, Fourier Transform Infrared Spectroscopy is utilized in the study of carbonyl area for determining reaction kinetics. From such data, hardening susceptibilities, aging rates, and hardening rates were determined for the aged samples. An important qualitative analysis is gel permeation chromatography whose size-exclusion separation characterizes changes in molecular size distributions for varying blending and aging times. This portion of the effort, Task 1.4, is presented in Chapter 5. Chapters 2 through 5 are comprised of the activities performed under Task 1.

Task 2, Evaluating Mixture Characteristics, is considered in Chapters 6, 7 and 8. The main goal of this part of the project is to evaluate the modified binders in asphalt concrete mixtures. This chapter was divided into three subtasks, the first being Developing an Experiment Plan, Task 2.1. This plan was developed and implemented within the first year of this study. The second part of Task 2 presents progress made on Evaluating Compaction Characteristics of Mixtures, Task 2.2. The U.S. Army Corps of Engineers gyratory procedure (ASTM 3387) was used to evaluate the compaction characteristics of the materials. This is essentially an instrumented version of the Texas gyratory compactor and can be used to describe the progression of material changes throughout the compaction process. The procedure was designed to address both the compatibility and performance-related issues of mix designs such as rutting. This task was completed during the first year of the project and was discussed in the first annual report (Bullin, et al., 1996).

The next portion of this chapter concerns Evaluating Deformation and Failure of Compacted Mixtures, Task 2.3. A matrix of compacted materials, aged for various lengths of time, were tested

for deformation and failure using three test methods: (1) "non-destructive" sinusoidal frequency sweeps (fully reversed tension-compression), (2) creep and recovery, and (3) tensile strength to failure. The mixtures were categorized for the optimum combination of resistance to aging and permanent deformation/cracking. Detailed documentation of this work is presented in Chapters 6 through 8. Chapter 6 concerns the rheology of the binder blends employed and acts as an intermediary between tasks one and two. Here, aging, curing methods, and materials selection are evaluated in the rheological sense. Chapter 7 is concerned with the transient properties of the binder-aggregate mix, where behavior over time, in response to step change loads, is examined. Chapter 8 presents the dynamic reactions of the mixes and deals with sinusoidal loads at various frequencies

Chapter 9 details work accomplished involving Task 3, an Adhesion Test Development. The objective of this task is developing methods to measure the adhesive and cohesive strength of asphalt-rubber/aggregate systems. This chapter is divided into two parts. The first portion concentrates on describing the Adhesion Testing methods and apparatuses. The next section of this chapter concerns the results of these tests, Task 3.1, and those obtained from Water Susceptibility Tests (Task 3.2).

Task 4 is the Performance/Economic Update and Commercialization Plan. First-year work centered on finishing the DOE-OIT Projection Description which included completing a performance/economic analysis of the complete system. With the early termination of support from DOE, please refer to the first annual report as no additional commercialization planning is forthcoming.

CHAPTER 2

LABORATORY TESTING AND EVALUATION

The overall objective for this portion of the project was to formulate improved asphalts for use with ground tire rubber as well as improved recycling agents for recycling asphalt rubber (AR) concretes. In addition, parameters such as rubber type, rubber content, rubber particle size, mixing temperature, mixing time, and mixing shear rate were studied with these asphalts.

FRACTIONATE ASPHALT MATERIAL

The Supercritical (SC) fractionation apparatus design and operation is described by Davison et al. (1991, 1992) in detail under TxDOT studies 1155 and 1249. Modifications were made in the TxDOT Study 1314 (Davison et al., 1994). The unit operates at constant pressure above the critical pressure of the solvent. It separates heavy petroleum products into a maximum of four fractions per pass according to solubility in SC solvents. The temperatures of the separators determine the density of the solvent, thereby controlling the solvent power in each vessel. Components of the feed precipitate when no longer soluble in the solvent. The lightest, most-soluble materials are removed by decompression during solvent recovery. Please refer to Appendix A for more descriptive details of the supercritical fractionation apparatus.

Numerous runs were made in supercritically fractionating Shell AC-20. Enough Shell AC-20 was fractionated to produce a highly-aromatic, low-asphaltene AC-5 asphalt and several highly-aromatic recycling agents. Supercritical Asphalt, described in the blending study of Chapter 4, was the name given to the Separator 2 product of this in-house process. A Texaco AC-20 was also fractionated. Furthermore, various ROSE (residual oil supercritical extraction) fractions were obtained from Murphy, Diamond Shamrock, Witco, and Fina. The fractions represent both potential asphalts and recycling agents. The fractions were evaluated and characterized for use as asphalts or asphalt blending stocks. Fina Demex Resin and Supercritical Asphalt were employed in some of the blending studies under this project.

As a means of comparison, Corbett fractions were obtained for various asphalts. Although, these fractions were not produced by supercritical methods, the fractions obtained via Corbett fractionation were used as tools in understanding asphalt chemistry in general. Quantities of Corbett fractions (saturates, naphthene aromatics, polar aromatics, and asphaltenes) were produced. The composition of 6 asphalts/supercritical fractions are given in Table 2-1. Three asphalts were tested by Corbett fractionation: Exxon AC-5, Exxon AC-10, and Fina AC-10; and three supercritical fractions were also analyzed: Fina Demex Resin, Supercritical Asphalt, and Diamond Shamrock (DS) Resin.

Two of the supercritical fractions had the highest aromatic content: Fina Demex Resin and Supercritical Asphalt. The remaining supercritical fraction, the DS Demex Resin, has low asphaltenes but a very high saturate content. The three asphalts all had a lower aromatic content than the supercritical fractions, with the composition of the three being very similar.

Table 2-1: Chemical Composition of Several Asphalts and Supercritical Fractions

Asphalt	Chemical Composition			
	% Asphaltenes	% Polar Aromatics	% Napthene Aromatics	% Saturates
Exxon AC-5	10.80	31.11	45.52	12.57
Exxon AC-10	12.68	26.60	48.40	12.31
Fina AC-10	14.46	30.12	43.35	12.08
DS Demex Resin	4.13	34.14	46.26	15.47
Fina Demex Resin	3.00	38.18	49.65	9.19
Supercritical Asphalt	2.97	35.74	52.58	8.70

REBLEND FOR AROMATIC ASPHALTS

Several supercritical fractions, produced by the method in Appendix A, were used to obtain sufficient quantities of highly-aromatic low-asphaltene asphalts. The supercritical fractions

of the Shell AC-20 have been characterized and blended to produce a large quantity of a highly-aromatic low-asphaltene AC-5 supercritical asphalt. Furthermore, a Sun 125 recycling agent and a Murphy resin were blended to produce a highly-aromatic low-asphaltene AC-5. The supercritical asphalt and the Murphy/Sun asphalt both have an acceptable temperature susceptibility or performance grade span, which is the slope resulting from a plot of log viscosity (η^*) versus $1/(\text{Temperature})$.

Diamond Shamrock and Fina resins were characterized for possible use as components of highly-aromatic asphalts. The Fina resin has an acceptable temperature susceptibility and its viscosity of 285 poise at 60°C makes it well suited for use as an asphalt for blending with rubber. The Diamond Shamrock (DS) resin contained solvent which had to be removed before analysis. The DS resin, with a viscosity of 626.8 poise at 60°C and an acceptable temperature susceptibility, can be mixed with rubber to produce an acceptable binder. Chemical analysis for saturate, aromatic, and asphaltene content utilizing the Corbett column was performed on the Fina and DS resins with the results listed previously in Table 2-1.

DEVELOPMENT OF MICRODUCTILITY TEST FOR USE WITH ASPHALT-RUBBER BINDERS

The ductility of an asphalt-rubber binder is defined as the distance to which it will elongate before breaking when two ends of a specified geometry are pulled apart at a defined speed and temperature. It is a physical test that can be used to help characterize the performance properties of a binder. Although the significance of ductility for unaged binders is highly debatable, changes in ductility over a binder's service life appear to correlate with overall roadway performance (Hveem et al., 1963).

Several methods were used to test the ductility of a binder. Historically, the most widely used ductility method is the method specified in ASTM D113. The drawback to the current methods is that they require large sample sizes. For example, ASTM D113 requires a 1.0 cm thick "dogbone" briquette that is over 7.0 cm long. The total sample mass is close to 10 g. This method is particularly unsuitable when small amounts of material are available, as is the case with

laboratory aged samples or binder recovered from pavement samples. Another method is the recently-developed SHRP direct tension method as specified in AASHTO TP3. The direct tension test measures the low-temperature fracture properties of the asphalt binder. A dogbone-shaped specimen is tested at a constant rate of elongation of 1.0 mm/min at a specified temperature until it fractures. The stress and strain at failure are calculated using the initial cross-sectional area (A) and effective gauge length (L_e) of the specimen, the load at failure (P_f), and elongation at failure (ΔL_f). The Texas A&M Center for Asphalt and Materials Chemistry acquired a SHRP direct tension test apparatus in late 1996, and this instrument was used to verify or expand the SHRP performance grade specifications at low temperature.

Previously, ductility was measured with the micro-ductility instrument. This instrument and a micro-ductility test were developed in the 1960s by Hveem et al. (1963) to measure the ductility of a small amount of these materials. The apparatus and method developed by Hveem et al. and a modified version of their method are described below.

Experimental Method (Hveem et al.)

The apparatus and procedure used for the microductility experiment was developed in November, 1962 by California's Division of Highways. This test method (Calif. 349-A) is designed to measure ductility of a small sample (0.05 g) of bituminous material at $77^\circ \pm 1^\circ\text{F}$. Test specimens are liquified on a hot plate, thoroughly stirred, and then placed inside a two part brass mold of cylindrical geometry. This mold is allowed to cool to ambient conditions for 15 minutes. The mold forms a 0.069 inch diameter cylinder of asphalt binder and grips it at both ends. The mold is placed into a ductility machine designed to pull the mold halves apart along their axis. After the machine and mold have been immersed in a water bath for 10 minutes, the mold is placed into a holder. One end of the holder is attached to a motor. The motor is then activated and pulls the sample apart at a constant rate of 0.5 cm/min. As the test progresses, the original cylinder of asphalt-rubber binder stretches into a very thin thread and eventually breaks. The separation distance of the two mold halves is measured in millimeters and reported as the ductility. In addition to being able to measure the ductility using a small sample size, approximately 60-75% of the specimen can be recovered at the conclusion of the test, if necessary.

The biggest limitation of the equipment used by the Calif. 349-A method is the inability to measure the force required to generate the constant strain rate. Such force information could be used to create a stress-strain curve for the sample. Another limitation is the small size of the asphalt cylinder formed inside the mold. Aged binders will often fail before the molds separate a significant distance.

Modified Experimental Method

As described above, one limitation of the original method is the small size of the asphalt cylinder. To minimize this problem, molds with larger diameter holes were fabricated. The largest of the hole sizes is approximately twice that of the original mold. This only increases the sample mass required by a factor of four, so the apparatus is still capable of measuring the ductility of a material using much less than 1 g of sample. An additional benefit of using a larger hole size is the ability to perform the test at lower temperatures, where ductility is generally greatly reduced.

Application

The modified microductility apparatus was used to study bituminous materials without any addition of rubber. It was hoped that this test method would also yield useful information concerning asphalt-rubber binders. Because this method accommodates samples at relatively low temperatures (35-45°F), it may provide additional support for the low temperature benefits of rubber-modified binders.

VERIFY OPTIMAL PARAMETERS

The ultimate goal of the curing study was to determine the optimal curing variables that allow production of an asphalt-rubber that is flexible at low-temperature, resists rutting at road-temperatures, and is compactible at high-temperatures. This task was achieved by investigating one variable while holding the other variables constant. The verification of the optimal parameters involved the following seven variables:

1. asphalt composition	4. curing time	7. rubber type
2. curing shear rate	5. rubber content	
3. curing temperature	6. rubber particle size	

Blending work on these variables involved using the following materials and conditions:

- Nine asphalts:

1. ABL-2,	6. a laboratory-produced Fina
2. Exxon AC-5	AC-7
3. a laboratory-produced	7. Fina AC-10
Exxon / Sun AC-5	8. a Murphy / Sun AC-10
4. Exxon AC-10	9. laboratory-produced Supercritical
5. Fina Demex Resin	Asphalt
- Two rubber types: Rouse (RS) and Tire Gator (TG).
- Five rubber contents: 5, 10, 15, 18, and 20%.
- Three rubber mesh sizes: -10, -40, and -80 mesh.
- Variable curing times: Up to 60 hours.
- Five curing temperatures: 350, 375, 400, 450, and 500°F.
- Four curing shear rates: 500, 1550, 4000, and 8000 rpm.

The blending of the various asphalt-rubber binders occurred in the mixing apparatuses where each binder was contained and heated to the desired temperature within a holding tank and stirred with a mixer blade. While curing, nitrogen was introduced into the tank to create an oxygen-free blanket over the binder and thus prevent oxidation. More thorough descriptions of these curing mixers may be found in Appendix A. Furthermore, the effects of the above variables on the binder were investigated with the following analytical equipment (see Appendix A for equipment descriptions).

- Bending beam rheometer: To determine low temperature rheological properties: (10 to -22°F)
- Direct tension apparatus: To determine low temperature fracture properties: (10 to -22°F)
- Carri-Med rheometer: To determine intermediate temperature rheological properties.
- Brookfield rheometer: To determine high-temperature viscosities: (250-400°F)
- Fourier transform infrared spectrometer (FTIR): To determine carbonyl areas.
- Gel permeation chromatography: To determine molecular-size distributions.

- High pressure liquid chromatography: To determine chemical compositions.
- Whatman 42 test: To determine amount of THF soluble rubber as a result of curing.

A brief summary of the first year's findings are listed below with detailed discussion of each variable studied following.

- Asphalt composition: The compatibility of the asphalt and the rubber is definitely dependent upon the asphalt composition. Preliminary findings indicate that low-asphaltene highly-aromatic asphalts are the most compatible. Furthermore, high-asphaltene high-saturate asphalts are the least compatible.
- Rubber type: For Rouse (RS) and Tire Gator (TG) rubber of the same particle size, the Rouse rubber is better at improving the binder properties than the TG rubber. It is believed that this can be explained by the fact that for equivalent "labeled" mesh sizes, i.e. -10, -40, or -80 mesh, the distribution of the Rouse rubber is finer than the TG rubber.
- Rubber content: Generally, the properties of a binder were found to improve with increasing rubber content within the range tested, 0 to 20%. The viscosity at rutting temperature (140°F) increases, the creep stiffness at low-temperature (5°F) decreases, and the temperature susceptibility decreases, improvements in all, with rubber content. The negative aspect of increasing rubber content is that the high-temperature (375°F) viscosity increases with rubber content, leading to pavement compaction problems.
- Rubber particle size: Rubber with smaller particle size allows increased interaction with the asphalt, improving binder properties. It is theorized that this phenomenon is explained by the smaller rubber particles having more surface area per mass and volume than the larger rubber particles.
- Curing time: The binder properties improve with curing time within the range tested, 0-60 hours.
- Curing Temperature: The rate of asphalt-rubber interaction, and thus the rate of improvement in binder properties, increases with higher curing temperatures within

the range studied, 350-400°F.

- Curing shear rate: A higher shear rate increases the rate of asphalt-rubber interaction improving binder properties at a faster rate. The curing process is apparently mass-transfer limited because a higher shear rate allows greater dispersion, and thus better interaction, of the mixture.

Curing Temperature as a Variable

It was suspected that a higher curing temperature would allow a faster reaction rate between the asphalt and rubber when being cured. Figure 2-1 shows that a higher curing temperature produces a binder with a marginally higher viscosity at 60°C. Also, the binder cured at the higher temperature appeared to have a slightly lower creep stiffness at -15°C as evidenced in Figure 2-2. The role of curing time is also evident in these two figures and seems to be much more important.

The improvement in the binder's physical properties might be attributed to the additional amount of rubber going into the asphalt solution as a result of the higher curing temperature. Figure 2-3 represents the amount of initial rubber passing the Whatman 42 filter. More rubber dissolves in the asphalt when cured at a higher temperature. Note that in Figure 2-3 and similar figures to follow, the original rubber content of 5 or 10% is the maximum attainable, so the 48 hour curing samples indicate that 400°F curing is about twice as good as 350°F curing.

Curing Time as a Variable

By extending the amount of time a binder is cured, more rubber should go into solution with the asphalt. This was expected to improve intermediate- and low-temperature properties and reduce the high-temperature viscosity, all relative to the less-dissolved state.

Figure 2-4 shows a binder's temperature susceptibility, the slope of a $\ln \eta^*$ vs. $1/(\text{Temperature})$ correlation, decreases with an increase in curing time. In addition, the binder's high temperature viscosity decreases with increasing curing time. By Figures 2-2 and 2-5, for different source asphalts, extended curing lowers the creep stiffness of the binder. Again, these improvements in the binder's physical properties can be attributed to the additional amount of rubber that dissolves into the asphalt as a result of the extended curing time (Figures 2-3 and 2-6).

**Figure 2-1: Effect of Curing Temperature on Viscosity
10% TG-40 and 90% Fina AC-10**

**Figure 2-2: Effect of Curing Temperature on Low Temperature Data
10% TG-40 and 90% Fina AC-10**

Figure 2-3: Effect of Curing Temperature on the Solubility of Rubber 10% TG-40 and 90% Fina AC-10

Figure 2-4: Intermediate and High Temperature Data 10% TG-10 and 90% Exxon AC-5

Figure 2-5: Low Temperature Data
10% TG-10 and 90% Exxon AC-5

Figure 2-6: Solubility of Rubber in Asphalt
10% TG-10 and 90% Exxon AC-5

Rubber Amount as a Variable

To study the effects of the amount of rubber in a given binder, various samples were prepared using two different concentrations of rubber, 5 and 10%. All other curing parameters were held constant except for the amount of rubber in the binders.

Increasing the amount of rubber in a binder was expected to benefit some physical properties but hinder other properties. The low and intermediate temperature properties benefit with the addition of more rubber. Figure 2-7 shows that the binder cured with 10% rubber has a lower temperature susceptibility than the binder cured with less rubber. Consequently, at high temperatures, the binder with 10% rubber has a higher viscosity. Figure 2-8 reveals that the creep stiffness is lower for the binder containing the larger amount of rubber.

Rubber Particle Size as a Variable

The effect of mesh size on the curing process was evaluated by preparing binders using the various available mesh sizes. Theoretically, smaller rubber particles are much more easily dissolved in asphalt than larger rubber particles. The smaller graded rubber "reacts" or becomes entrained faster when cured with asphalt because of the increased surface area. Therefore, if better dissolution improves asphalt-rubber properties, then using smaller rubber particles benefits all physical properties of a binder: a lower creep stiffness at low temperatures, a lower temperature susceptibility in the intermediate temperature region, reduced viscosities at high temperatures (compared to the less-cured state) and reduced curing time.

Figure 2-9 shows that the temperature susceptibility is lowest for the binder cured with the smallest graded rubber, -80 mesh. This figure also reveals that the binder containing the -80 mesh rubber has lower viscosities at the higher temperatures. From Figure 2-10, it is evident that the same binder cured with the smaller graded rubber has a slightly lower creep stiffness. Again, these improved physical properties may be explained by the fact that the smaller graded rubber goes into the asphalt solution at a faster rate (see Figure 2-11).

Figure 2-7: Effect of Rubber Amount on Temperature Susceptibility 5 and 10% TG-40 with Fina AC-10

**Figure 2-8: Low Temperature Data
Fina AC-10 and TG Blends**

Figure 2-9: Effect of Particle Size on Temperature Susceptibility Exxon AC-5 and 10% Rouse Blends

Figure 2-10: Low Temperature Data Exxon AC-5 and RS Blends

**Figure 2-11: Effect of Particle Size on Solubility of Rubber
in Asphalt Exxon AC-5 and RS Blends**

Rubber Type as a Variable

Rubber used during experimentation was obtained from two sources. Tire Gator rubber (-10 and -40 meshes) was received from Granular Products located in Mexia, Texas, and Rouse rubber (-10, -40, and -80 meshes) from Vicksburg, Mississippi; a source comparison was performed. According to Figure 2-12, the binders cured with the Rouse rubber produced a slightly lower temperature susceptibility. Also, the binders with the Rouse rubber had lower viscosities than the Tire Gator rubber at high temperatures. Figure 2-13 shows that the creep stiffness for the binders cured with the Rouse rubber are lower than the ones prepared using the Tire Gator rubber. These differences in the binders' physical properties may be attributed to the amount of rubber going into solution after curing. Perhaps most significant, Figure 2-14 reveals that more rubber is dissolved in the asphalt for the binder cured with the Rouse rubber. Such results suggest that the Rouse rubber reacts better with asphalt than the Tire Gator rubber. For a given mesh size, the Rouse rubber has a finer gradation than the Tire Gator rubber. This finer

Figure 2-12: Effect of Rubber Type on Temperature Susceptibility Fina AC-10 with 10% TG-10 and RS-10

**Figure 2-13: Low Temperature Data
90% Fina AC-10 with 10% TG-10 and 10% RS-10**

**Figure 2-14: Effect of Rubber Type on the Solubility of
Rubber 90% Fina AC-10 with 10% TG -10 and 10% RS -10**

gradation of the Rouse rubber is thought to explain its increased "reactivity."

Mixing Speed as a Variable

In the first year, two blending speeds were used to cure the asphalt and rubber to see if an increased mixing speed attained improved binder physical properties at a faster rate. Binders were cured using mixing speeds of 500 or 1550 rpm.

Figure 2-15 shows that the temperature susceptibility for the binder cured for 2 hours at 1550 rpm is comparable to that of the binder cured for 24 hours at 500 rpm. The viscosities at high temperatures show a similar correlation. From Figure 2-16, it is evident that the creep stiffness for the binder cured for a short time at 1550 rpm is similar to that of the binder cured for a much longer time at 500 rpm. The solubility experiment, Figure 2-17, suggests that the rubber in the binder cured at a high mixing speed goes into the asphalt solution at a faster rate than the binder cured at a much slower mixing speed. From this it would appear that the curing time could

Figure 2-15: Effect of Mixing Speed on Temperature Susceptibility Fina AC-10 with 10% TG-10

Figure 2-16: Effect of Mixing Speed on Low Temperature Data 10% TG-10 and 90% Fina AC-10

**Figure 2-17: Effect of Mixing Speed on Solubility of Rubber
in Asphalt 10% TG-10 and 90% Fina AC-10**

be reduced by using higher mixing speeds. Note that this analysis does not eliminate curing time as a variable, as it compares short times and high shear rates to longer times and lower shear rates. If the curing were performed for equal times, then a more representative comparison may be made.

Asphalt Type as Variable

Again initially, numerous binders were prepared using two base asphalts: Fina AC-10, and Exxon AC-5. According to literature, a softer asphalt reacts with rubber at a faster rate. This was evident during experimentation. The binders prepared using the Exxon AC-5, which is the softer base asphalt, yielded superior physical properties when compared with the Fina AC-10. This effect is particularly apparent between the following Figures:

Figure 2-3, Fina AC-10 and Figure 2-11, Exxon AC-5: Whatman 42 digested rubber content.

Figure 2-4, Exxon AC-5 and 2-7, Fina AC-10: Temperature susceptibility slope.

Initial Conclusions about Curing Asphalt with Rubber

The extent to which the rubber dissolves into the asphalt is very dependent upon the curing environment. Under the curing conditions initially studied, dissolving the rubber was found to improve the properties of a binder. The rubber dissolved faster with a higher curing temperature, a longer curing time, and a faster mixing speed. As a reasonable dissolution of rubber was desirable, the standard curing temperature of 350°F and curing time of 1 hour (Takallou and Takallou, 1991) was found to be lacking. Increasing temperature and curing time greatly increases the rate and progress of rubber degradation. Furthermore, the shear rate of mixing is a very important variable. Still, the conditions used were rather mild, except for the long curing times and there was room left to increase the curing temperature and speeds yet more to pursue better results. These three curing conditions comprise the "methods" by which the "material" is prepared and, given the variability of feedstocks, are logically more important in the overall study.

The chemical composition of the asphalt, the rubber type, fractional content, and mesh size were all determined to be important variables. Apparently, increasing the aromatic content of an asphalt increases the capacity for rubber and asphalt interaction. Faster reaction rates can also be obtained by using finer rubber gradation, with increased surface area per mass of the smaller particles allowing for faster reaction rates. This finding, coupled with the temperature, shear rate and curing time conclusions indicated that digestion during mixing is insufficient and should be a main concern for subsequent studies. Finally, the efforts of previous researchers were confirmed in that the benefits of adding tire rubber were directly related to the rubber content, over the range of content studied.

CHAPTER 3

PHYSICAL PROPERTIES OF LOW-CURE ASPHALT-RUBBER BINDER

There is little doubt that the proper use of crumb rubber in asphalt can improve performance. Some researchers (Chehovits et al. (1982), Estakhri et al. (1993), Roberts et al. (1989), and Stroup-Gardner et al. (1993)) have done thorough investigations, but none has considered the full range of variables that affect the cost and performance of asphalt rubber. The work presented in this chapter examines the full range of variables for the curing conditions of 1 hour at 450K (350°F), which are the curing conditions that are widely used in industry (Takallou and Takallou, 1991). This study is more structured than that of Chapter 2, and from it the effect of fewer variables may be discerned. Compared to the work of Chapter 4, these conditions should be defined as low-cure and are simulated in the laboratory by curing for 1 hour at 450K (350°F) with the Sears mixer at 50 rpm.

MATERIALS

Four asphalts were used in the study presented in this chapter. SHRP ABM-1 (a resampling of SHRP AAG-1) and SHRP ABL-2 (a resampling of SHRP AAK-2) were acquired from the SHRP Materials Reference Library. Diamond Shamrock (DS) AC-5 was acquired from a refinery in Texas. The final asphalt studied, Made AC-5, was produced in the laboratory by blending SHRP ABM-1 and Sun 125, a commercially-available highly-aromatic extending oil. The Sun 125 comprised 13% by weight of Made AC-5 and had a viscosity of 5.5 poise at 333K (140°F). Two of these asphalts, SHRP ABL-2 and DS AC-5 have good low temperature properties. Made AC-5 was produced to study the effect of adding a light aromatic fraction to an asphalt with poor low temperature properties.

Minus ten (-10) and minus forty (-40) mesh rubber were acquired from Granular Products, also known as Tire Gator, located in Mexia, Texas. Additionally, Minus 40 mesh rubber was acquired from Rouse Rubber located in Vicksburg, Mississippi.

EXPERIMENTAL DESIGN

The experimental design is shown in Table 3-1. As can be seen, this factorial includes 2 types of rubber, 4 asphalts, 2 rubber mesh sizes, and 4 rubber concentrations. Even so, the study does not include all curing variables, but is limited both in curing time and temperature to 1 hour and 450K (350°F), respectively. The asphalt rubber products were evaluated in terms of low temperature creep stiffness at 258K (5°F), intermediate temperature rheological properties (273 -363K, (32-194°F)), high temperature viscosities (>394K (>250°F)), and other structure and size based properties. Descriptions of these tests may be found in Appendix A.

Table 3-1: Experimental Design

Asphalt	Rubber Manufacturer	Rubber Mesh Size	Weight Percent Rubber
SHRP ABM-1	Rouse	-40	5%, 10%, 15%, 18%
	Tire Gator	-10	5%, 10%, 15%, 18%
		-40	5%, 10%, 15%, 18%
SHRP ABL-2	Rouse	-40	5%, 10%, 15%, 18%
	Tire Gator	-10	5%, 10%, 15%, 18%
		-40	5%, 10%, 15%, 18%
Diamond Shamrock (DS) AC-5	Rouse	-40	5%, 10%, 15%, 20%
	Tire Gator	-10	5%, 10%, 15%, 20%
		-40	5%, 10%, 15%, 20%
Made AC-5	Rouse	-40	5%, 10%, 15%, 20%
	Tire Gator	-10	5%, 10%, 15%, 20%
		-40	5%, 10%, 15%, 20%

RESULTS AND DISCUSSION

Low Temperature

Low temperature data are presented in Table 3-2 and are graphically arranged in Figures 3-1 through 3-4. Examining these data, it can be concluded that the addition of rubber had only positive effects on the low temperature rheological properties of the tested asphalts. The higher the rubber content, within the range studied, the greater the improvements in the low temperature properties. In addition, the smaller-mesh rubber particles improved the low temperature properties more than comparable amounts of larger mesh rubber. It is theorized that the smaller rubber particles are better able to interact with the asphalt because they have more surface area per unit mass than the larger rubber particles. Furthermore, the benefits obtained by adding rubber were greater for the neat asphalts with the worst low temperature properties, SHRP ABM-1 and Made AC-5.

Ground rubber from two sources were used with asphalt ABM-1 and ABL-2 in the bending beam experiments. Both of these rubbers were nominally -40 mesh, with the results for the ABM-1 being inconclusive since the Rouse rubber was better at improving the m-value, while the Tire Gator rubber was better at improving the creep stiffness. Neither rubber content nor particle size had much measurable effect in ABL-2, because the original stiffness of this asphalt is too low to make any improvements discernable.

The addition of the light, highly aromatic recycling agent to asphalt ABM-1 to produce Made AC-5 halved the 333K (140°F) viscosity, which alone would improve the 258K (5°F) stiffness. Interestingly, the effect of the rubber was also enhanced. Although in general, less benefit is expected for a more flexible material, the percent reduction in stiffness was greater with Made AC-5 than with ABM-1, and the m-value was also improved.

Table 3-2: Low-Temperature Data for Low-Cure Blends

Asphalt	Rubber Type and Mesh	Variable (S(t) has units of MPa)	Rubber Concentration				
			0%	5%	10%	15%	18%or 20%
SHRP ABM-1	RS -40	S(t) at 60 sec	1018	770	610	494	287
		m-value	0.24	0.28	0.29	0.30	0.34
	TG -40	S(t) at 60 sec	10189	719	468	441	214
		m-value	0.24	0.25	0.24	0.28	0.29
Made AC-5	TG -10	S(t) at 60 sec	620	578	321	192	71
		m-value	0.36	0.36	0.37	0.39	0.40
	TG -40	S(t) at 60 sec	620	401	285	144	
		m-value	0.36	0.37	0.41	0.46	
DS AC-5	TG -10	S(t) at 60 sec	180	144	123	84	70
		m-value	0.34	0.38	0.38	0.37	0.39
	TG -40	S(t) at 60 sec	180	121	83	64	40
		m-value	0.34	0.29	0.42	0.44	0.43
SHRP ABL-2	TG -10	S(t) at 60 sec	58	49	58	57	49
		m-value	0.55	0.45	0.45	0.38	0.35
	TG -40	S(t) at 60 sec	58	44	47	40	42
		m-value	0.55	0.39	0.51	0.45	0.40
	RS -40	S(t) at 60 sec	58	47	56	48	37
		m-value	0.55	0.42	0.32	0.45	0.41

Figure 3-1: Creep stiffness data for SHRP ABM-1 blends.

Figure 3-2: m-value data for SHRP ABM-1 blends.

Figure 3-3: Creep stiffness data for Made AC-5 blends.

Figure 3-4: m-value data for Made AC-5 blends.

Intermediate Temperature

Figures 3-5 through 3-7 present intermediate temperature data that are summarized in Table 3-3. The full range of η^* , δ , and temperature susceptibility (TS) values for the blends of this chapter are given in Table B-1 of Appendix B. From these data, it can be concluded that the addition of rubber greatly enhanced the intermediate temperature properties of the tested asphalt-rubber binders. The temperature susceptibilities reported in Tables 3-3 and B-1 are defined in terms of the Andrade equation (Andrade, 1930):

$$\ln \eta^* = C_0 - \frac{E_v}{RT} \quad (3-1)$$

where E_v is a viscosity activation energy and is a measure of temperature susceptibility. E_v/R is reported throughout this work and has units of K^{-1} . The temperature susceptibilities improved (E_v decreased) with increasing rubber content and the complex viscosities at rutting temperatures also increased. The temperature susceptibility seemed independent of the rubber particle size, but the larger -10 mesh particles increased the complex viscosity more than the smaller -40 mesh particles. Furthermore, for a given rubber content, particle size, and temperature of interest, the increase in the complex viscosity relative to the base asphalt was dependent upon the base asphalt.

The addition of the light aromatic Sun 125 to ABM-1 to produce Made AC-5 and subsequent rubber blending reduced the complex viscosity compared to the blends of ABM-1, but also improved the temperature susceptibility somewhat. However, it did not greatly enhance the effect of rubber as it did at low temperature, suggesting that the temperature susceptibility improvement is mostly influenced by the low temperature properties, Figures 3-5 and 3-7. On the other hand, ABL-2, which has excellent low temperature properties without rubber addition and also has the best temperature susceptibility without rubber, shows the most improvement after its addition. However, this improvement resulted from the considerable increase in complex viscosity at higher temperatures rather than a decrease at low temperature, Figure 3-6.

So the addition of rubber has been shown to improve properties at low and intermediate temperatures through reductions of stiffness and rutting, respectively. The ABL-2 asphalt-rubber blends had the lowest phase angle at 333K (140°F). In spite of the lack of complex viscosity reduction at 273K (32°F), the 258K (5°F) bending beam results are improved. Unfortunately, the high complex viscosity at 363K (194°F), Table B-1, is reflected in unacceptably high viscosities at hot-mix temperatures.

Figure 3-5: Complex viscosity data for SHRP ABM-1 blends.

Figure 3-6: Complex viscosity data for SHRP ABL-2 blends.

Figure 3-7: Complex viscosity data for Made AC-5 blends.

Table 3-3: Intermediate-Temperature Data for Low-Cure Blends

Asphalt	Rubber Type and Mesh	Various Variables (η^* (poise), G^* (dyne/cm ²) and δ^* at 333 K (140°F)	Rubber Concentration		
			0%	10%	18% or 20%
SHRP ABM-1	TG -10	η^* or G^* at 1.0 rad/sec	2,051	7,278	17,240
		δ^* at 1.0 rad/sec (degrees)	89.7	84.2	76.8
		TS, E_v/R , (K ⁻¹)	18,170	16,500	14,230
	TG -40	η^* or G^* at 1.0 rad/sec	2,051	7,028	15,190
		δ^* at 1.0 rad/sec (degrees)	89.7	82.0	72.7
		TS, E_v/R , (K ⁻¹)	18,170	16,370	14,280
Made AC-5	TG -10	η^* or G^* at 1.0 rad/sec	936	3,291	7,460
		δ^* at 1.0 rad/sec (degrees)	89.9	83.4	72.2
		TS, E_v/R , (K ⁻¹)	17,770	14,230	12,430
	TG -40	η^* or G^* at 1.0 rad/sec	936	2,639	4,824
		δ^* at 1.0 rad/sec (degrees)	89.9	81.3	72.0
		TS, E_v/R , (K ⁻¹)	17,770	15,250	13,740
DS AC-5	TG -10	η^* or G^* at 1.0 rad/sec	448	1,801	5,011
		δ^* at 1.0 rad/sec (degrees)	89.3	85.0	77.6
		TS, E_v/R , (K ⁻¹)	18,160	16,380	14,550
	TG -40	η^* or G^* at 1.0 rad/sec	448	1,542	3,811
		δ^* at 1.0 rad/sec (degrees)	89.3	84.9	76.1
		TS, E_v/R , (K ⁻¹)	18,160	16,470	14,010
SHRP ABL-2	TG -10	η^* or G^* at 1.0 rad/sec	1,645	7,306	35,220
		δ^* at 1.0 rad/sec (degrees)	87.7	81.0	68.2
		TS, E_v/R , (K ⁻¹)	14,650	13,210	10,610
	TG -40	η^* or G^* at 1.0 rad/sec	1,645	6,005	33,910
		δ^* at 1.0 rad/sec (degrees)	87.7	79.8	60.1
		TS, E_v/R , (K ⁻¹)	14,650	13,340	10,660

High Temperature

The data of Table 3-4 and Figures 3-8 and 3-9 show that the addition of the rubber increased the high temperature viscosity of the binder, with the viscosity increasing with increasing rubber content. The effect of particle size is quite asphalt dependent. In Figure 3-8 for ABM-1 blends, no distinction is apparent between rubber mesh sizes at 10% rubber, while 18% rubber shows a considerable difference. Additionally, adding rubber by ~10% increments increases the high temperature viscosity by nearly an order of magnitude for each increment. As shown by Figure 3-9, only Made AC-5 shows any particle size effect at 10% rubber, but at 18% and 20% rubber, the viscosity increase for both ABM-1 and Made AC-5 respectively is much larger for the -40 mesh rubber.

The addition of the light aromatic in Made AC-5 may not be beneficial at high temperature, as opposed to the intermediate rutting reduction effect. The neat, unblended ABM-1 material itself shows a low temperature susceptibility that is further lowered both by the addition of the light Sun 125 in Made AC-5 and by the addition of rubber. Unfortunately, a decreasing temperature susceptibility is not desirable in this range, especially with such high viscosities as the rubber blending creates. At these temperatures the material needs to deform readily both for the hot mix process, where aggregate is added, and more importantly, for the installation and compaction process where deformation of the material is essential. Because of "better" temperature susceptibility, Made AC-5 has approximately the same viscosity at high temperature as ABM-1, although at 333K (140°F) it is less than half as viscous as ABM-1. On the addition of 20%, -40 mesh rubber, however, Made AC-5 showed a viscosity of half that of the ABM-1 containing 18%, -40 mesh rubber. This result is not significant, however given that both blends surpassed the recommended SHRP SuperPave maximum by a factor of 10. In fact the only blends in this study that may be acceptable for use under that requirement would be the Made AC-5 with 10% TG-10, Figure 3-9. The typical approach in industry, however, is to use close to 20% rubber and this has been proven to be wholly unacceptable.

Table 3-4: High-Temperature Viscosities (poise) for Low-Cure Blends

Asphalt	Rubber Type and Mesh	Rubber Concentration	Temperature in K (°F)				
			422 (300)	433 (320)	444 (340)	455 (360)	467 (380)
SHRP ABM-1	TG -10	0%	2.50	2.25	1.50	1.25	1.00
		10%	13.5	12.5	8.5	6.75	5.75
		18%	100	87.5	75.0	62.5	42.5
	TG -40	0%	2.50	2.25	1.50	1.25	1.00
		10%	12.5	9.00	6.50	5.75	5.25
		18%	610	510	450	370	280
Made AC-5	TG -10	0%	2.25	1.50	1.25	1.00	0.88
		10%	9.00	4.25	3.50	2.00	1.50
		20%	220	130	95.0	80.0	57.5
	TG -40	0%	2.25	1.50	1.25	1.00	0.88
		10%	20.0	13.8	10.8	7.50	5.00
		20%		320	280	210	170
DS AC-5	TG -10	0%	2.50	1.75	1.50	1.25	1.00
		10%	7.75	6.50	5.00	4.00	2.50
		20%	74.0	65.0	61.0	56.0	50.0
	TG -40	0%	2.50	1.75	1.50	1.25	1.00
		10%	8.25	7.00	4.75	4.00	3.00
		20%	310	180	140	120	100
SHRP ABL-2	TG -10	0%	1.83	1.67	1.17	0.75	0.58
		10%	7.50	5.50	4.75	3.50	3.00
		18%	80.0	71.0	62.0	52.0	46.0
	TG -40	0%	1.83	1.67	1.17	0.75	0.58
		10%	7.75	5.75	5.00	4.25	3.50
		18%	320	195	150	135	110

Figure 3-8: High-temperature data for SHRP ABM-1 blends.

Figure 3-9: High-temperature data for Made AC-5 blends.

General Compatibility

This section shows that the rubber is becoming compatible with the asphalt medium, or "dissolving," during the curing process. The results for DS AC-5, Figures 3-10 and 3-11, were obtained with the refractive index detector; the results for SHRP ABM-1, Figures 3-12 and 3-13, were obtained with the intrinsic viscosity detector. The enormous difference between the two types of chromatographs shows the increase in sensitivity for high molecular weight materials, such as dissolved rubber, when using the intrinsic viscosity detector. Figures 3-14 and 3-15 are graphical illustrations of the Whatman 42 test for blends of ABM-1 and DS AC-5, respectively. All but Figure 3-11 compare data for two initial rubber percentages, while only Figure 3-10 lacks a comparison of the two mesh sizes. Figures 3-14 and 3-15 may be used as a comparison of asphalt materials as well.

Figures 3-10 through 3-13, should draw ones attention to the growths just before the main asphalt peak in the retention time region of 20 to 22 minutes. These represent the influx of rubber into the asphalt phase of the binder. The use of narrow polystyrene standards to assure proper column separation efficiency and repeatability indicates that a molecular weight of 190,000 has an elution time of 20.63 minutes while the size exclusion separation retains a 9,100 molecular weight polystyrene sample for 23.38 minutes. It must be noted that the asphalt and asphalt rubber eluded at 20.63 or 23.38 minutes does not specifically have a molecular weight of either 190,000 or 9,100, but that it is of the same *characteristic size* of linear polystyrene of that molecular weight.

Figures 3-10, 3-12, and 3-13 show that the higher the blended percent rubber, the higher the mass transfer of rubber into the asphalt phase. Figures 3-11 through 3-15 show that the smaller the particle size, the higher the mass transfer of rubber into the asphalt phase. In Figure 3-13, this conclusion is probably supported by the higher shoulder for the smaller particles in the retention time region of 21 to 23 minutes. Figures 3-14 and 3-15 show that the fraction of the total rubber "going into solution" decreases with increasing rubber content. This phenomenon may be thought of as mass transfer limiting, as the mass transfer coefficient decreases with increasing viscosity. Also, from the concave downward nature of the data at high rubber content, a saturation condition may be present, either in the experimental procedure, or in the asphalt itself, requiring more study.

Figure 3-10: GPC data for DS AC-5, TG-40 mesh blends.

Figure 3-11: GPC data for DS AC-5, 20 percent blends.

Figure 3-12: GPC data for SHRP ABM-1, TG -40 blends.

Figure 3-13: GPC data for SHRP ABM-1, TG -10 and TG -40 blends.

Figure 3-14: Rubber dissolution data for SHRP ABM-1 blends.

Figure 3-15: Rubber dissolution data for DS AC-5 blends.

The dissolved rubber molecules represented by the data in Figures 3-10 through 3-13 are all smaller than 0.45 microns, 4500 Å, because each sample was prepared for GPC injection with a filter that has a pore membrane size of 0.45 µm. While the sizes of the fresh rubber particles may range from 400 to 2000 µm before curing, some are apparently reduced to less than 4,500 Å during the curing and GPC preparation processes. Furthermore as the GPC preparation process is the same for all samples, the rubber almost certainly is being "devulcanized and depolymerized" during the curing process. Understanding this phenomenon is essential, because the extent to which the advantages of rubber can be realized, depends on optimizing this rubber degradation.

Apparently, this phenomenon has been known for years in the reclaiming industry, and Franta (1989) says, "Reclaiming is a procedure in which scrap rubber or vulcanized waste is converted, using mechanical and thermal energy, into a state in which it can be mixed, processed and vulcanized again. The principle of the process is devulcanization. It is assumed that breakage of the network takes place, with further shortening of the chains and the simultaneous formation of new double bonds, which enhances revulcanization". Furthermore, to aid in the reclamation of styrene-butadiene rubbers, oils or reclaiming reagents must be utilized. Interestingly enough, a thermomechanical reclamation process, the Lancaster-Banbury Process, utilizes asphalt as a reclaiming agent, with Franta (1989) saying, "According to the original proposal (U.S.A., 1939), the material was mixed, with addition of reclaiming oils and asphalt, for about 30-40 minutes in an ordinary Banbury Mixer. The temperature was maintained below 150°C ...". The process described is very similar to the curing process employed in this work except that the authors used much lower amounts of thermal and mechanical energy; and their objectives were not the same. Because the devulcanization of the rubber is a mass transfer process as well as a chemical reaction and the Lancaster-Banbury Process utilizes a large amount of mechanical energy, the curing process is dependent upon the shear rate of agitation. In fact the degree of curing is almost certainly a function of shear rate, curing temperature, particle size, and asphalt composition. There are data in the literature (Oliver, 1979) that indicate that, when curing at high temperature, the viscosity first increases and eventually begins to decrease.

LOW-CURE CONCLUSIONS

In this chapter the accepted curing conditions for asphalt-rubber have been utilized not only to evaluate their effectiveness, but also to examine the variety of materials that may be used in the blending process. Of the four asphalts studied, three of them ABM-1, ABL-2, and Made AC-5 (made from ABM-1), are available from the SHRP materials library to examine the repeatability of the results presented herein. The use of asphalt materials of varying properties was undertaken to determine the measure of improvement that could be realized. The variation of rubber sources allowed for a comparison of materials, while mesh size and rubber content deviations provided blend properties.

The addition of ground tire rubber considerably enhances the low temperature properties of asphalt. The effect is particularly good in asphalts that originally have a high degree of stiffness. At intermediate temperature, the complex viscosity is considerably increased by rubber addition which should increase rutting resistance. The increase is greater for -10 mesh than for -40 mesh material. Temperature susceptibility is considerably improved by rubber addition, but there is little effect of particle size. Unfortunately, high temperature viscosities are greatly increased by rubber addition and this is particularly problematic in the installation phase. At higher rubber concentrations, the -40 mesh material has a greater effect than the -10 mesh material.

Many of these effects are asphalt dependent. For instance in the softer ABL-2, rubber had the largest effect on the 333K (140°F) complex viscosity and phase angle δ , while low temperature properties were hardly affected. On the other hand, ABM-1 and Made AC-5 were greatly improved at low temperatures and, while enhanced at intermediate temperatures, were not improved as much as ABL-2. The addition of light aromatics to ABM-1 generally improved its properties.

From this study two conclusions may be drawn, and they may be at least partially conflicting. First, the wide variation in asphalt-rubber interactions underscores the importance of considering this fact in choosing an asphalt for use with ground tire rubber. And perhaps more important, the change of properties as an asphalt cures and the degree of rubber dissolution is a powerful argument that the 1-hour curing time at 450K (350°F) and relatively low shear conditions used in this study and

generally used in the field, are not optimum.

CHAPTER 4

PHYSICAL PROPERTIES OF HIGH-CURE ASPHALT-RUBBER BINDER

Currently, the standard industry wet process uses a curing time of about one hour at about 450K (350°F) in a low-shear rate environment to produce asphalt-rubber binder (Takallou and Takallou, 1991). The blends discussed in Chapter 3 were produced with these curing conditions. The results of Chapter 3 showed that adding rubber to asphalt was beneficial, with the rubber improving the low-temperature creep stiffness at 258K (5°F), the temperature susceptibility in the 273-363K (32-194°F) temperature region, increasing G^* and η^* at 333K (140°F) and 1.0 rad/sec, and decreasing δ at 333K (140°F) and 1.0 rad/sec. However, the results of Chapter 3 also showed that the addition of rubber greatly increased the viscosity in the compaction temperature region of 422-467K (300-380°F), which can cause compaction problems during pavement placement. Allison (1967b) reported that engineers blamed the compaction problems of asphalt-rubber on undissolved crumb rubber, which they believed had no beneficial effect. Additionally, the engineers reported that improper compaction led to early road failure. High compaction viscosities also can lead to high air void content for dense-graded mixes (Jimenez, 1982). This is detrimental, because Linden et al. (1989) reported a correlation between compaction and performance.

In a follow-up paper, Billiter et al. (1996) showed that by extending the curing time and increasing the curing temperature and rate of mixing, the high temperature viscosity could be significantly reduced from the value obtained by curing at 450K (350°F) and a low-shear rate for 1 hour. They also found that the low- and intermediate-temperature rheological properties of a binder could also be improved by using longer curing times, higher temperatures, and higher shear-rates, as detailed in Chapter 2. This was explained by the devulcanization and depolymerization of the rubber during the curing process. Other authors; Franta (1989), and Zanzotta and Kennepohl (1996), have similarly discussed the devulcanization and depolymerization of rubber in the presence of asphalt and application of temperature and shear. Additionally, Flanigan (1995) discussed the complete incorporation of the rubber into the asphalt using air and Warner (1995) discussed numerous other methods of devulcanizing thermoset rubber.

While depolymerizing and devulcanizing of the rubber leads to the rubber losing some of its elasticity, it also allows the asphalt to digest the polymer and produces a more homogeneous product with better compaction properties and less tendency to settle. Basically, such a binder would eliminate many of the problems now associated with asphalt-rubber pavement. However, the extended curing times used by Chapter 2 and Billiter et al. (1996), up to 60 hours, will not be acceptable to the paving industry. One way to lower the curing time is by using higher temperatures and higher shear rates. Obviously, the determination of the optimal curing environment, one which uses curing times agreeable to industry personnel, will require a study of the variables of curing time, curing temperature, and shear rate of mixing. This work is an attempt to determine the optimal combination of these variables relative to binder properties.

MATERIALS

Five asphalts, as described in Tables 4-1 and 4-2, were used in this study. Exxon/Sun AC-5 and Fina AC-5 were house blends produced in the laboratory by blending the listed components prior to the addition of rubber. Fina AC-5 and Exxon/Sun AC-5 were produced to study the effect of asphalt composition on the curing process. Supercritical (SC) Asphalt was produced in the laboratory by supercritically fractionating a Shell AC-20 into 4 fractions. SC Asphalt was the fraction from the second stage of the unit. The asphalts produced in this study were compared to Neste-Wright Liquefied Tire Rubber 10 (LTR10), a commercially available asphalt-rubber binder which uses rubber at the 10% level and supposedly uses Exxon AC-10 as its base asphalt. Neste-Wright LTR10 is advertised as being homogeneous and, therefore, indistinguishable from asphalt to the road contractors. Asphalt rubber materials from the company are currently being used in sealcoat applications.

The compositions of these asphalts are listed in Table 4-2. The compositions of Fina Demex Resin, Exxon AC-10, and SC Asphalt were obtained by Corbett analysis (1969). The composition of Fina AC-5 was obtained by performing Corbett analysis on the asphalts that constitute these two asphalts and then calculating the composition by a mass balance and assuming that the Corbett compositions are additive. The composition of Exxon/Sun AC-5 was obtained by a mass balance using the Corbett analysis of Exxon AC-10 and the advertised composition of Sun 125.

Table 4-1: Specification of Asphalts Studied

Asphalt Name	Laboratory Modifications	Resultant η^* (dPa·s (poise)) at 333K & 1.0 rad/sec
Exxon AC-10	None	952.0
Exxon / Sun AC-5	94 % Exxon AC-10 and 6% Sun 125 commercial recycling agent: [$\eta^* = 5.5$ dPa·s (poise)]	561.0
Fina Demex Resin	None	238.6
Fina AC-5	50 % Fina AC-10 and 50% Fina Demex Resin	507.9
SC Asphalt	Supercritical fractionation of a Shell AC-20	369.0

Table 4-2: Compositions of the Asphalts Studied

Asphalt	% Asphaltenes	% Polar Aromatics	% Naphthene Aromatics	% Saturates
Fina Demex Resin	3.00	38.18	49.65	9.19
Fina AC-5	8.73	34.15	46.50	10.64
Exxon AC-10	12.68	26.60	48.41	12.31
Exxon/Sun AC-5	11.93	25.81	49.76	12.50
SC Asphalt	2.97	35.74	52.58	8.70

Minus ten (-10) and minus forty (-40) mesh rubber were again acquired from Granular Products, also known as Tire Gator (TG), located in Mexia, Texas. The TG -40 mesh rubber was made from tire buffings. The TG -10 mesh rubber was made from whole tires and the polymer make-ups of these two sources may vary slightly.

EXPERIMENTAL DESIGN

Table 4-3 shows the combinations of curing temperature, mixer speed, weight percent rubber, rubber mesh size, and asphalt that were used to produce the 14 blends that were investigated in this study. All the asphalt-rubber blends of this chapter were produced with the Silverson L4RT high shear laboratory mixer. The total curing time was 6.5 hours for all of the blends, with samples being taken at 0.5, 1.0, 1.5, 2.5, 3.5, 5.0, and 6.5 hours. The asphalt-rubber binders were evaluated in terms of high-temperature viscosities ($>394\text{K}$ ($>250^\circ\text{F}$)), high-temperature settling (375K (215°F)), intermediate-temperature rheological properties ($273\text{--}363\text{K}$ ($32\text{--}194^\circ\text{F}$)), low-temperature creep stiffness (249K (-11°F)), rubber dissolution, molecular weight distribution, and FTIR.

Table 4-3: Experimental Design

Curing Date	Asphalt	Weight Percent Rubber	Mesh Size	Silverson Mixer Speed (rpm)	Curing Temperature
3/3/96	Fina Demex Resin	10	-10	4000	505K (450°F)
3/7/96	Fina Demex Resin	10	-10	4000	533K (500°F)
3/8/96	Fina Demex Resin	10	-10	8000	533K (500°F)
3/9/96	Fina Demex Resin	10	-40	4000	533K (500°F)
3/13/96	Fina Demex Resin	20	-10	4000	533K (500°F)
3/10/96	Fina AC-5	10	-10	4000	533K (500°F)
2/5/96	Exxon AC-10	10	-10	4000	505K (450°F)
2/13/96	Exxon AC-10	10	-10	4000	533K (500°F)
2/23/96	Exxon AC-10	10	-10	8000	533K (500°F)
2/24/96	Exxon AC-10	10	-40	4000	533K (500°F)
2/29/96	Exxon AC-10	20	-10	4000	533K (500°F)
2/27/96	Exxon / Sun AC-5	10	-10	4000	533K (500°F)
3/18/96	Supercritical (SC) Asphalt	10	-10	4000	505K (450°F)
3/19/96	SC Asphalt	10	-10	4000	533K (500°F)

RESULTS AND DISCUSSION

As discussed in this chapter's introduction, previous results and those in the literature suggest the dissolution or entrainment of rubber in the asphalt medium is desirable for binder properties. Consequently, the primary objective of this study was to examine the variables of curing time, curing temperature, and shear rate of mixing in hopes of determining the fastest and therefore, most economical way of dissolving rubber in asphalt. The elevation of both curing temperature and mixing shear were selected as variables, while curing time was also elevated from the single hour of the Chapter 3 studies, but decreased from the up to 60 hour times undertaken in Chapter 2. The variables of asphalt composition, mesh size, and rubber content also remain important.

The η^* , δ , and temperature susceptibility (TS) values of the Silverson blends are presented in Table B-2 of Appendix B. The η^* and δ values in Table B-2 of Appendix B are reported at 1.0 rad/sec and have units of poise and delta, respectively. The temperature susceptibility (TS) in Table B-2 of Appendix B is E_v/R and has units of K^{-1} . The percentage of crumb passing a Whatman 42 filter for the Silverson blends is presented in Table B-3 of Appendix B.

Curing Temperature

The rate at which the rubber dissolved into the asphalt and the type of asphalt-rubber reaction were dependent on the curing temperature. As seen in Chapter 2, Billiter et al. (1996) found that the rate of rubber dissolution increased with temperature in the range of 450-478K (350-400°F). In this study, temperatures higher than previously examined were used, 505K (450°F) and 533K (500°F). As shown in Figures 4-1 through 4-3, the rate at which the rubber dissolved into the asphalt was much faster at 533K (500°F) than at 505K (450°F). This assumes that the amount of rubber dissolving is proportional to the amount of rubber passing a Whatman 42 paper filter. This is not perfectly true for the high-shear and high-temperature results. The rubber contains about 30% carbon black, so the high percentages passing the filter must include some of the carbon black. Some of the rate increase can be explained by the lower asphalt viscosity at the higher temperature allowing for more mass transfer between the rubber and the asphalt. However, the majority of the increased rate is probably due to the rubber-asphalt reaction, which like any chemical reaction, is very dependent upon temperature. The rubber-asphalt reaction is one of devulcanization and depolymerization in

which breaking of the cross-linking network and further shortening of the main chains takes place (Franta, 1989). The difference in type of asphalt-rubber reaction can be seen by comparing two blends of Exxon AC-10, identical in nature except for the curing temperature. Figures 4-4 and 4-5 refer to blends at 450°F and 500°F, respectively. These data, produced by size exclusion chromatography, are measurements of intrinsic viscosity, as described in Appendix A. Here a distinction may be made between types of bond cleaving, devulcanization versus depolymerization. At 505K (450°F) the rubber appears to be mostly devulcanizing during the curing process, Figure 4-4. Note the magnitude of the initial and smaller peak does not decrease substantially over the curing period. This may be consistent with the long chain polymer strands being separated from one another by cleaving at the sulfur bond sites. As time passes, note the trough between peaks becomes more shallow. Some depolymerization, defined as the breaking of backbone of the main chain, may also be occurring with curing time. Devulcanization is believed to be more prevalent because the sulfur-sulfur crosslinks tend to be less stable to thermal and chemical attack than carbon-carbon crosslinks (Reich and Stivala, 1971). The devulcanized rubber is believed to be represented by the massive peak in the retention time region 20 to 22 minutes.

Figure 4-1: Rubber dissolution data for Exxon AC-10 blends.

Figure 4-2: Rubber dissolution data for Fina Demex Resin blends.

Figure 4-3: Rubber dissolution data for Supercritical Asphalt blends.

Figure 4-4: GPC data for 10/90, TG -10WT/Exxon AC-10, 505K, 4000 rpm.

Figure 4-5: GPC data for 10/90, TG -10WT/Exxon AC-10, 533K, 4000 rpm.

Because the separations illustrated on the chromatographs are based on size exclusion, it is important to note that molecular weights of differing materials that are eluted at the same retention time may differ, but that these materials will have the same characteristic molecular size. Linear polystyrene takes up more space than highly crosslinked materials of the same molecular weight. With this in mind, the linear polystyrene molecular weight distribution in the region of the initial peak varies from approximately 190,000 at 20.6 minutes to 37,900 at 21.5 minutes. The depolymerized material is believed to be represented by the material in the retention time region of 21.5 to 24 minutes, Figure 4-5. The linear polystyrene molecular weight distribution in this region varies from approximately 37,900 at 21.46 minutes to 5,970 at 24.37 minutes. The appearance of material in this molecular weight range almost certainly confirms that considerable breakage of the main polymer chain is occurring. At 533K (500°F) the devulcanization reaction, and especially the depolymerization reaction, is occurring at a much faster rate, Figure 4-5. It would appear from comparing Figures 4-4 and 4-5 that the curing temperature was not hot enough at 505K (450°F) to adequately depolymerize the rubber. In Figure 4-5, the large peak between 20 to 22 minutes is the highest at 0.5 hours of curing, the minimum sampling time. This peak decreases appreciably with curing time as the devulcanized rubber is depolymerized to produce smaller molecular weight material; the trough region is almost eliminated for the 6.5 hour sample and the existence of two distinct peaks is blurred. Interestingly, the devulcanization of the rubber does not stop after 0.5 hours, but continues as shown by rubber dissolution analysis, Figure 4-1, which shows that rubber continues to be dissolved into the asphalt phase of the solution with curing time. Apparently, the mass transfer between the rubber and asphalt (devulcanization) is initially fast (perhaps carbon black influence here) and then slows with respect to the depolymerization reaction. The difference between the rate and type of asphalt-rubber reaction at 505K (450°F) and 533K (500°F) was asphalt dependent, but for the asphalts studied, the above description applies, with devulcanization and some depolymerization occurring at 505K (450°F) and the depolymerization of the rubber being much greater at 533K (500°F) than 505K (450°F). Figures 4-6 and 4-7, for Fina Demex Resin, and Figures 4-8 and 4-9, for SC Asphalt, show this temperature effect.

Figure 4-6: GPC data for 10/90, TG -10WT/FNDMRS, 505K, 4000 rpm.

Figure 4-7: GPC data for 10/90, TG -10WT/FNDMRS, 533K, 4000 rpm.

Figure 4-8: GPC data for 10/90, TG -10WT/SC Asphalt, 505K, 4000 rpm.

Figure 4-9: GPC data for 10/90, TG -10WT/SC Asphalt, 533K, 4000 rpm.

Figure 4-10: GPC data for Neste-Wright LTR10 and Exxon AC-10 blends.

Figure 4-10 compares the molecular weight distributions of the Exxon AC-10 blends cured for 6.5 hours at both 533K (500°F) and 505K (450°F) with Neste-Wright LTR10, a commercially available asphalt rubber binder which supposedly also uses Exxon AC-10 as its base asphalt. Figure 4-10 almost certainly verifies that LTR10 is Exxon asphalt based, if not Exxon AC-10 based, because the molecular weight distribution of LTR10 is very similar to the molecular weight distribution of Exxon AC-10. The advertised benefit of using Neste-Wright LTR10 is that it is a homogeneous material that, to the field personnel, is indistinguishable from asphalt. The homogeneity of the material produced in this study is close to the homogeneity of Neste-Wright LTR10, far closer, in fact than any of the materials produced in previous studies, Figures 3-12 and 3-13. However, homogeneity is only one binder property and there is surely a trade off in other binder properties because the complete degradation and therefore, elimination of the elasticity of the rubber, cannot be totally desirable.

The settling properties of some of the blends are given in Table 4-4. The Neste-Wright LTR10 had the best settling properties as measured by the complex viscosity ratio and the phase angle ratio. The complex viscosity ratio is the complex viscosity of the sample from the settling tester divided by complex viscosity of the original perfectly mixed sample. Similarly, the phase angle ratio is the phase angle of the sample from the settling tester divided by the phase angle of the original perfectly mixed sample. Obviously, the undissolved rubber particles and undissolved carbon black settle to the bottom of the tester and therefore, the viscosity ratio is greater than one and the phase angle is less than one in all cases. For the samples in Table 4-4, a trend is apparent between the decreasing difference in settling ratio values from top to bottom, and the increasing rubber passing the Whatman 42 paper filter. For example, the LTR10 had both the best settling properties and the highest percentage of rubber dissolved, 99.99%. Increasing the curing temperature from 505K (450°F) to 533K (500°F) greatly improved the settling properties of the blend. These results are explained by the increased devulcanization and depolymerization that occurs at the higher temperature, 533K (500°F).

There was also an improvement in high-temperature viscosity with curing temperature, Table 4-5. The high-temperature viscosity was lower for the blends produced at 533K (500°F), however even the viscosity of the blend produced at 505K (450°F) is comparable to the base asphalt viscosity. The lower viscosity at the higher curing temperature can most likely be explained by the faster rate of rubber devulcanization and depolymerization at the higher curing temperature. This phenomenon can be explained qualitatively by imagining the rubber particles as rigid spheres and applying an equation derived by Einstein for the viscosity of a dilute suspension of rigid spheres:

$$\eta = \eta_s (1 + 2.5 \phi) \quad (4.1)$$

where η is the viscosity of the solution, η_s is the viscosity of the solvent, and ϕ is the volume fraction of the spheres (Rosen, 1993). Obviously, the higher the percent rubber the higher the effective ϕ and thus, higher viscosity. Furthermore, the decrease in high-temperature viscosity with curing temperature has to be caused by the rubber particles being reduced in size, thus lowering the effective ϕ , because the viscosity of the asphalt, η_s , is definitely increasing with curing time.

Table 4-4: Viscosity and Delta Ratios

Sample Details	Layer	At 333K (140°F) & 1.0 rad/sec		η^* Ratio	δ Ratio
		η^* (poise)	δ (degrees)		
Exxon AC-10 10 % TG -10 4000 rpm 505K 450°F 6.5 hours	Tank	1,768	85.60		
	Top	1,336	86.72	0.756	1.013
	Middle	1,498	85.62	0.847	1.000
	Bottom	4,986	80.33	2.820	0.938
Exxon AC-10 10 % TG -10 4000 rpm 533K 500°F 6.5 hours	Tank	1,414	85.21		
	Top	1,152	86.81	0.815	1.019
	Middle	1,269	85.49	0.897	1.003
	Bottom	2,047	82.47	1.448	0.968
Exxon AC-10 10 % TG -40 4000 rpm 533K 500°F 6.5 hours	Tank	1,249	86.74		
	Top	1,231	86.93	0.986	1.002
	Middle	1,276	86.84	1.022	1.001
	Bottom	1,337	86.20	1.070	0.994
Exxon AC-10 10 % TG -10 8000 rpm 533K 500°F 6.5 hours	Tank	1,355	86.55		
	Top	1,349	86.61	0.996	1.001
	Middle	1,368	86.55	1.010	1.000
	Bottom	1,425	86.50	1.052	0.999
Neste-Wright LTR10 Commercial Material	Tank	433.3	88.72		
	Top	428.3	88.85	0.988	1.002
	Middle	436.3	88.79	1.007	1.001
	Bottom	441.6	88.68	1.019	1.000
Fina Demex Resin 10 % TG -10 8000 rpm 533K 500°F 6.5 hours	Tank	326.9	87.73		
	Top	315.8	87.78	0.966	1.001
	Middle	338.7	87.69	1.036	1.000
	Bottom	339.8	87.70	1.039	1.000

Table 4-5: High-Temperature Viscosity Data

Sample Details	High-Temperature Viscosity, η (poise)					
	394K (250°F)	422K (300°F)	433K (320°F)	444K (340°F)	455K (360°F)	467K (380°F)
Exxon AC-10, Tank	7.20	2.60	1.87	1.15	0.85	0.68
Exxon AC-10 10 % TG -10 4000 rpm 505K 450°F 6.5 hours	15.93	5.72	3.45	2.84	1.87	1.70
Exxon AC-10 10 % TG -10 4000 rpm 533K 500°F 6.5 hours	13.38	4.75	2.52	2.18	1.70	0.90
Exxon AC-10 10 % TG -10 8000 rpm 533K 500°F 6.5 hours	16.50	7.12	3.97	2.90	1.80	1.42
Exxon AC-10 10 % TG -40 4000 rpm 533K 500°F 6.5 hours	13.83	4.42	3.17	1.93	1.50	1.00
Exxon / Sun AC-5 10 % TG -10 4000 rpm 533K 500°F 6.5 hours	13.13	5.20	3.45	1.89	1.35	1.03
Exxon AC-10 20 % TG -10 4000 rpm 533K 500°F 6.5 hours	45.85	10.35	7.43	5.58	5.58	3.38
SC Asphalt 10 % TG -10 4000 rpm 533K 500°F 6.5 hours	6.80	3.18	3.15	2.05	1.58	1.40

Table 4-5: High-Temperature Viscosity Data (Continued)

Sample Details	High-Temperature Viscosity, η (poise)					
	394K (250°F)	422K (300°F)	433K (320°F)	444K (340°F)	455K (360°F)	467K (380°F)
Fina Resin, Tank	3.38	1.00	0.65	0.60	0.43	0.25
Fina Demex Resin 10 % TG -10 4000 rpm 505K 450°F 6.5 hours	15.75	4.27	3.42	2.25	1.98	1.35
Fina Demex Resin 10 % TG -10 4000 rpm 533K 500°F 6.5 hours	8.83	3.40	1.70	1.38	0.93	0.78
Fina Demex Resin 10 % TG -10 8000 rpm 533K 500°F 6.5 hours	8.68	2.45	1.75	1.18	0.89	0.74
Fina Demex Resin 10 % TG -40 4000 rpm 533K 500°F 6.5 hours	7.65	2.60	1.78	1.43	1.03	0.98
Fina AC-5 10 % TG -10 4000 rpm 533K 500°F 6.5 hours	9.48	3.68	1.98	1.34	0.91	0.73
Fina Demex Resin 20 % TG -10 4000 rpm 533K 500°F 6.5 hours	16.48	6.43	4.48	3.05	2.48	1.90
SC Asphalt 10 % TG -10 4000 rpm 505K 450°F 6.5 hours	9.28	5.03	3.03	2.23	1.73	1.28

Table 4-6: High-Temperature Viscosity Data with Respect to Curing Time

Sample Details	Curing Time (hours)	High-Temperature Viscosity, η (poise)					
		394K (250°F)	422K (300°F)	433K (320°F)	444K (340°F)	455K (360°F)	467K (380°F)
Exxon AC-10 10 % TG -10 8000 rpm 533K 500°F	1.0	15.75	4.70	3.23	2.53	1.77	1.20
	3.5	12.60	4.07	3.65	1.73	1.35	1.02
	6.5	9.33	4.30	3.10	2.40	1.28	1.13
Fina Demex Resin 10 % TG -10 8000 rpm 533K 500°F	1.0	9.82	3.33	1.97	1.63	1.10	0.85
	3.5	8.10	2.60	1.48	1.00	0.80	0.63
	6.5	8.68	2.45	1.75	1.18	0.69	0.74

The high-temperature viscosities of the blends cured at 8000 rpm and 533K (500°F) did not decrease with curing time. The data in Table 4-6 might be interpreted to suggest that the high-temperature viscosity went through a minimum at 3.5 hours. However, most likely the viscosity declined to a minimum and then leveled off with curing time. The viscosity minimum of the data in Table 4-6 is probably within the noise of the data, especially at the extreme highest temperatures.

Figures 4-1, 4-2, and 4-3 show that the rate of dissolution slowed with curing time. They also show that the extent to which the rubber dissolved into the asphalt was definitely dependent upon the curing conditions. For the majority of blends, their complex viscosity and phase angle at 333K (140°F) and 1.0 rad/sec, and temperature susceptibility for the 273K-363K (32-194°F) region arrived at near constant values within a curing time of 6.5 hours. However, Figures 4-11, 4-12, and 4-13 show that these values for the complex viscosity of the binders were highly dependent on curing conditions, as were the values for phase angle in Figures 4-14 through 4-16 and, to some extent, temperature susceptibility in Figures 4-17 through 4-19. These binder properties were most certainly being determined by the amount and state of the undissolved rubber and dispersed carbon black as well as by the molecular weight distribution of the devulcanized and depolymerized rubber.

Figure 4-11: Complex viscosity data for Exxon AC-10 blends.

Figure 4-12: Complex viscosity data for Fina Demex Resin blends.

Figure 4-13: Complex viscosity data for Supercritical Asphalt blends.

Figure 4-14: Phase angle data for Exxon AC-10 blends.

Figure 4-15: Phase angle data for Fina Demex Resin blends.

Figure 4-16: Phase angle data for Supercritical Asphalt blends.

Figure 4-17: TS data for Exxon AC-10 blends.

Figure 4-18: TS data for Fina Demex Resin blends.

Figure 4-19: TS data for Supercritical Asphalt blends.

For each asphalt type, most blends cured at 533K (500°F) had a lower phase angle and were therefore more elastic than the blend cured at 505K (450°F), Figures 4-14, 4-15, and 4-16. The results for temperature susceptibility with respect to curing temperature, Figures 4-17 through 4-19, however, were inconclusive. Again, in this work the temperature susceptibility is defined in terms of the Andrade equation, Equation 3-1. The complex viscosity of a binder was lower when cured at 533K (500°F), Figures 4-11, 4-12, and 4-13. Generally, the complex viscosity decreased with curing time until stabilizing at a near constant value. This contradicts the findings of Chapter 2, where the complex viscosity was found to increase with curing time. As stated previously, the complex viscosity was dependent on the curing variables, and the much higher temperatures and higher shear rates used in this study, as opposed to Chapter 2, probably explains the difference in results. Interestingly enough and yet perhaps anomalously, the complex viscosity of the blend of 3/18/96; a 10% TG -10, SC Asphalt cured at 505K (450°F) and 4000 rpm, increased from the 0.5 hour to 1.0 hour curing times, Figure 4-13. Furthermore, the curing conditions of this blend were the least severe

curing conditions employed in this study and therefore, closest to the conditions used by Chapter 2 and Billiter et al. (1996), where complex viscosity increases with curing time were more common. Oliver (1979) determined that elastic recovery goes through a maximum with respect to curing time. Oliver reported this phenomenon occurred at a curing temperature of 513K (464°F). Although a maximum in elasticity, a minimum in phase angle, did not occur for Exxon AC-10 blends, Figure 4-14, it did occur for Fina Demex Resin and SC Asphalt blends produced at 533K (500°F), Figures 4-15 and 4-16.

The low-temperature properties of the Silverson blends as measured at 249K (-11°F) are presented in Table 4-7. The creep stiffness of the Exxon AC-10 blend cured at 505K (450°F), the blend of 2/5/96, decreased and thus improved with curing time, Figure 4-20. This result agrees with the results of Billiter et al. (1996), who used curing temperatures of 450 to 478K (350 to 400°F). However, the creep stiffness of the other Exxon AC-10 blends, all cured at 533K (500°F), increased with curing time, Figure 4-20. Although the creep stiffness increased with curing time, the creep stiffness at 6.5 hours is still lower and, therefore, better than the creep stiffness of the base asphalt, Exxon AC-10, Table 4-8.

Figure 4-20: Creep stiffness data for Exxon AC-10 blends.

Table 4-7: Low-Temperature Data for the Silverson Blends

Sample Details	Bending Beam Test Temp = 249K (-11°F)					
	1.0 hour		3.5 hour		6.5 hour	
	S (MPa)	m-value	S (MPa)	m-value	S (MPa)	m-value
Exxon AC-10 10 % TG -10 4000 rpm 505K 450°F	332.7	0.327	318.6	0.334	298.8	0.340
Exxon AC-10 10 % TG -10 4000 rpm 533K 500°F	328.1	0.353	326.5	0.345	444.7	0.341
Exxon AC-10 10 % TG -10 8000 rpm 533K 500°F	461.5	0.487	499.0	0.468	559.3	0.528
Exxon AC-10 10 % TG -40 4000 rpm 533K 500°F	293.1	0.356	332.2	0.339	371.5	0.327
Exxon / Sun AC-5 10 % TG -10 4000 rpm 533K 500°F	264.7	0.399	292.4	0.402	316.6	0.354
Exxon AC-10 20 % TG -10 4000 rpm 533K 500°F	135.1	0.392	175.9	0.410	231.7	0.397
Fina Demex Resin 10 % TG -10 8000 rpm 533K 500°F	541.9	0.521	615.9	0.529	647.3	0.510
Fina Demex Resin 10 % TG -40 4000 rpm 533K 500°F	363.6	0.344	374.7	0.327	395.4	0.331

Table 4-8: Low-Temperature Data for the Unaged Asphalts

Asphalt	BBR Test Temp. = 258K (5°F)		BBR Test Temp. = 249K (-11°F)	
	S (MPa)	m-value	S (MPa)	m-value
Fina Demex Resin, Tank	160.9	0.607	1306.0	0.673
Exxon AC-10, Tank	146.4	0.565	842.9	0.552
Neste-Wright LTR10, Tank	31.5	0.625	196.0	0.417

Mixer Speed

From the results of Chapter 2, the a second important influence in curing asphalt rubber was mixing speed. Although the data were rather limited, the results seemed very promising. For Fina Demex Resin, Figure 4-2, increasing the mixer speed increased the rate at which the rubber dissolved into the asphalt. For Exxon AC-10, Figure 4-1, the amount of rubber dissolving was not substantially affected by mixing speed, with the curing variable of rubber mesh size having a larger effect. The difference in results can most likely be explained by the difference in molecular weights of the asphalts, with the lighter molecular weight material being better able to accept and absorb the rubbery material, through both saturation and mass transfer advantages.

The phase angle, δ , at 333K (140°F) was the highest at the higher mixing speed of 8000 rpm, Figures 4-14 and 4-15. The temperature susceptibility, Figures 4-17 and 4-18, was highest for the higher shear rate of 8000 rpm. The complex viscosity at 333K (140°F) was lower at the higher mixing speed of 8000 rpm, Figures 4-11 and 4-12. This, combined with the fact that higher temperature also gave a lower complex viscosity, indicates that the more severe the curing environment, i.e., the higher the curing temperature and shear rate, the lower the complex viscosity, Table 4-9. Interestingly, following this trend the very homogeneous Neste-Wright LTR10 had a complex viscosity and phase angle of 433.3 poise and 88.72°, respectively, while its base asphalt, Exxon AC-10, had a complex viscosity and phase angle of 952.0 poise and 89.95°, all measured at 333K (140°F) and 1.0 rad/sec. Perhaps, the producers of Neste-Wright LTR10 have reduced the rubber to a point where the remaining material is less viscous than the original asphalt, or perhaps an AC-5 was really used.

Table 4-9: Viscosity Increase Ratios

Sample Details	η^* (poise) at 333K & 1.0 rad/sec		Viscosity Increase Ratio
	Base Asphalt, Neat	6.5 hours	
Fina Demex Resin - 10 % TG -10 4000 rpm - 505K 450°F - 6.5 hours	238.6	482.9	2.024
Fina Demex Resin - 10 % TG -10 4000 rpm - 533K 500°F - 6.5 hours	238.6	372.8	1.562
Fina Demex Resin - 10 % TG -10 8000 rpm - 533K 500°F - 6.5 hours	238.6	348.3	1.460
Fina Demex Resin - 10 % TG -40 4000 rpm - 533K 500°F - 6.5 hours	238.6	327.9	1.374
Fina AC-5 - 10 % TG -10 4000 rpm - 533K 500°F - 6.5 hours	507.9	684.5	1.348
Fina Demex Resin - 20 % TG -10 4000 rpm - 533K 500°F - 6.5 hours	238.6	454.0	1.903
Exxon AC-10 - 10 % TG -10 4000 rpm - 505K 450°F - 6.5 hours	952.0	1,694	1.779
Exxon AC-10 - 10 % TG -10 4000 rpm - 533K 500°F - 6.5 hours	952.0	1,414	1.485
Exxon AC-10 - 10 % TG -10 8000 rpm - 533K 500°F - 6.5 hours	952.0	1,276	1.340
Exxon AC-10 - 10 % TG -40 4000 rpm - 533K 500°F - 6.5 hours	952.0	1,212	1.273
Exxon / Sun AC-5 - 10 % TG -10 4000 rpm - 533K 500°F - 6.5 hours	561.0	906.0	1.615
Exxon AC-10 - 20 % TG -10 4000 rpm - 533K 500°F - 6.5 hours	952.0	1,807	1.898
SC Asphalt - 10 % TG -10 4000 rpm - 505K 450°F - 6.5 hours	369.0	1,374	3.724
SC Asphalt - 10 % TG -10 4000 rpm - 533K 500°F - 6.5 hours	369.0	1,223	3.314

The blends produced at 8000 rpm and the blends produced at 4000 rpm had similar high-temperature viscosities, Table 4-5. Furthermore, increasing the blending speed greatly improved the settling properties of a blend, Table 4-4. Using a blending speed of 8000 rpm and 533K (500°F) allowed the production of asphalt-rubber binder with settling properties almost as good as Neste-Wright LTR10. The viscosity ratios with respect to curing time of the blends produced at 8000 rpm and 533K (500°F) are presented in Table 4-10. As would be expected, the settling properties of a binder improved with curing time, i.e., with the dissolving of the rubber.

Interestingly enough, even with the severe degradation of the rubber by the extreme curing conditions, the low-temperature creep stiffness of the 8000 rpm blend improved relative to the base asphalt, Tables 4-6 and 4-7. Apparently enough of the devulcanized and depolymerized rubber is still in polymer form to improve the elasticity of the binder. Nonetheless, the most severe curing conditions, 533K (500°F) and 8000 rpm, produced the binder with the worst (highest) creep stiffness values, Table 4-7 and Figure 4-20. The Neste-Wright LTR10 had better low-temperature properties than any of the 10% Exxon AC-10 blends, Tables 4-7 and 4-6. Theoretically, the Neste-Wright LTR10 should have the worst low-temperature properties because it had the highest extent of curing. Again, either Neste-Wright is producing LTR10 with a process vastly different from the process used in this study, or the source material is an AC-5 with inherently better low temperature properties.

Table 4-10: Viscosity Ratio Data with Respect to Curing Time

Sample Details	Layer	η^* Ratio (η^* at 333K and 1.0 rad/sec)		
		0.5 hours	2.5 hours	6.5 hours
Exxon AC-10 - 10 % TG -10 8000 rpm - 533K 500°F	Top	0.6535	0.7983	0.996
	Middle	0.6821	0.8235	1.010
	Bottom	2.6414	2.2378	1.052
Fina Demex Resin - 10 % TG -10 8000 rpm - 533K 500°F	Top	0.5597	0.6865	0.966
	Middle	0.6270	0.7307	1.036
	Bottom	3.1827	1.1221	1.039

Asphalt Composition

For the asphalts studied, the extent and rate of rubber dissolution were asphalt dependent. With respect to their ability to dissolve the rubber during the curing process, the asphalts were ranked in the following order: Fina Demex Resin, SC Asphalt, Fina AC-5, Exxon/Sun AC-5, and Exxon AC-10, Figures 4-1, 4-2, and 4-3. The lower the saturate and asphaltene content, the better an asphalt was at dissolving rubber, Table 4-2. As discussed previously, the dissolving of the rubber is believed to be a devulcanization process. Apparently, the devulcanization process is faster when light molecular weight, highly aromatic fractions are used. This is reasonable because the extending oils used in the rubber processing industry are such light molecular weight, highly aromatic oils and their miscibility with rubber diminishes in the order aromatic > naphthenic > paraffinic (Blackley, 1983). In fact, paraffinic oils have such limited miscibility that they tend to "sweat out" of the rubber. The increased interaction of the lighter molecular weight fractions is thought to be a diffusion phenomenon, in which the lighter molecular weight fractions can more quickly diffuse into the swollen rubber particles and interact to dissolve them. Obviously, the lower the asphaltene content, the lower the molecular weight and viscosity of the asphalt and thus, the better the diffusion characteristics of the asphalt.

It is of further interest to compare the chromatograms in Figures 4-5, 4-7, and 4-9. Exxon AC-10, which had the slowest devulcanization rate, appears to have the faster depolymerization rate as indicated by the material in the retention time region of 21.5 to 24 minutes, Figure 4-5. Exxon AC-10 has the largest percentage of asphaltenes, Table 4-2, and probably also has more heavy polar aromatics than the other asphalts studied. The asphaltenes and polar aromatics, while being hindrances with respect to diffusion into the rubber molecules, are apparently able to use the polar groups present on their structures to chemically interact and break the backbone of the devulcanized rubber. The SC Asphalt has a slightly higher depolymerization rate than Fina Demex Resin as indicated by Figures 4-9 and 4-7, respectively. Although they have very similar Corbett compositions, SC Asphalt, 360.0 poise at 333K, is more viscous than Fina Demex Resin, 238.6 poise at 333K, which would indicate that it is comprised of higher molecular weight material. Most likely the SC Asphalt has more heavy polar aromatics than the Fina Demex Resin. Exxon/Sun AC-5, produced by combining 94% Exxon AC-10 and 6% Sun 125, apparently was not chemically different

enough from Exxon AC-10, since no difference in the devulcanization/depolymerization rates could be seen using the intrinsic viscosity detector. However, Fina AC-5, produced by combining Fina Demex Resin and Fina AC-10 in a 50/50 ratio, behaved quite differently from Fina Demex Resin. The heavier components of Fina AC-5 improved its ability to depolymerize the rubber relative to Fina Demex Resin, Figure 4-21.

The increase in complex viscosity that occurred with the addition of rubber and curing seemed more dependent upon blending conditions than source asphalt, Table 4-9. The viscosity increase ratio is the complex viscosity at 333K (140°F) after 6.5 hours of curing divided by the complex viscosity at 333K (140°F) of the unaged base asphalt. For Fina Demex Resin blends and Exxon AC-10 blends, the viscosity increase ratio ranged from 1.374 to 2.024 and from 1.273 to 1.898, respectively, and comparing these blends shows relatively good agreement with respect to curing level. For SC Asphalt the viscosity increase ratios were 3.724 and 3.314, well above the other asphalts. Adding light molecular weight material (Sun AC-5) to Exxon AC-10 caused the viscosity increase ratio of Exxon/Sun AC-5 to increase to 1.615 from 1.485, and adding the heavy molecular weight material, Fina AC-10, to Fina Demex Resin caused the viscosity ratio of Fina AC-5 to decrease from 1.562 to 1.348. Apparently, the light, low-molecular weight material was better able to interact with the rubber in such a way as to increase the complex viscosity of the binder. Billiter et al. (1996) reported similar findings. The high-temperature viscosities of the Fina Demex Resin blends were lower than the high-temperature viscosities of the Exxon AC-10 blends, but the percent increase in viscosity relative to the tank asphalt viscosity was higher for the Fina Demex Resin Blends, Table 4-5.

The asphalt composition was very important to the low-temperature properties of a binder. Each asphalt had its own temperature susceptibility with respect to creep stiffness, Table 4-8. Interestingly, the lighter Fina Demex Resin had a worse, higher temperature susceptibility than the heavier Exxon AC-10. Although the Exxon AC-10 had more asphaltenes and saturates than the Fina Demex Resin, Table 4-2, visual inspection of the Corbett fractions showed that the Fina Demex Resin had waxier saturates than the Exxon AC-10. Apparently, the wax content of the saturates is more important to the low-temperature properties of an asphalt than the saturate content itself, the asphaltene content, the 333K (140°F) viscosity, or the molecular weight of an asphalt.

Figure 4-21: Comparison of GPC data for Fina blends.

Mesh Size

Relative to mesh size there was a difference in binder properties, but the difference was no more than the difference encountered by changing any other curing variable. The amount of rubber dissolving relative to mesh size was asphalt dependent. For the amount of rubber dissolving in Fina Demex Resin, there was no significant difference between the -40 mesh and -10 mesh particles, Figure 4-2. This contrasts Exxon AC-10, where there was an appreciable difference between the -40 mesh and -10 mesh particles, with the -40 mesh particles dissolving faster, Figure 4-1. This is most likely a diffusion phenomenon, where Fina Demex Resin, being of much lower molecular weight, can penetrate throughout the larger -10 mesh particles as thoroughly as it can the -40 mesh particles. Apparently, for low-molecular weight materials like Fina Demex Resin, the diffusion into the rubber during the curing process is not the limiting factor relative to dissolving rubber. Interestingly enough, the variable of shear rate had much more effect on the rubber dissolution ability of Fina Demex Resin than Exxon AC-10.

The complex viscosity of a -40 mesh blend produced at 4000 rpm and 533K (500°F) was very comparable to a -10 mesh blend produced at 8000 rpm and 533K (500°F), with the complex viscosity of the -40 mesh blends being slightly lower, Figures 4-11 and 4-12. As measured by the viscosity increase ratio, the -40 mesh particles were more beneficial than the -10 mesh particles in maintaining a low complex viscosity, Table 4-9. The phase angle and the temperature susceptibility of the -40 mesh blends fell in the ranges of the phase angle and the temperature susceptibility of the -10 mesh blends, Figures 4-14, 4-15, 4-17, and 4-18. The high-temperature viscosities of the -40 mesh blends were very similar to -10 mesh blends, Table 4-5. On the other hand, the -40 mesh blend had much better settling properties than the -10 mesh blend, Table 4-4. At low-temperature, the -40 and -10 blends had very similar creep stiffness values, Table 4-7 and Figure 4-20.

Overall, these results indicate that the high-shear and high-temperature curing conditions used in this study negate the advantages the -40 mesh particles have over the -10 mesh particles at low-cure conditions. Furthermore, the minimal benefits of using the -40 mesh particles at the high-cure conditions are not enough to justify the extra expense of the -40 mesh particles, which cost approximately twice as much as the -10 mesh particles.

Rubber Content

While more rubber was present in the 20% blends and more material passed the Whatman 42 test, the percentage passing the Whatman 42 filter was lower, relative to the 10% rubber level, Figure 4-1 and 4-2. Nonetheless, the rubber still dissolved faster for the 20% blend cured at 533K (500°F) than for the 10% blend cured at 505K (450°F). This is an indicator of the importance of curing temperature on the curing process. The amount of mass being transferred into the asphalt phase of the mixture, as measured by the intrinsic viscosity detector, increased at the 20% rubber content level, Figure 4-22. The devulcanization and depolymerization reactions also occurred at the 20% rubber content level, Figure 4-22.

Figure 4-22: GPC data for 20/80, TG -10WT/Exxon AC-10, 533K, 4000 rpm.

For the Exxon AC-10 and Fina Demex Resin blends, the increased rubber content increased the complex viscosity, Figures 4-11 and 4-12, respectively. In Figure 4-12, the complex viscosity of the 10% Fina AC-5 blend is higher than the 20% Fina Demex Resin blend. This can be explained by the much higher complex viscosity of Fina AC-5. The viscosity increase ratio for the 20% Fina Demex Resin blend, 1.903, is much higher than the ratio for the 10% Fina AC-5 blend, 1.348, Table 4-9. The high-temperature viscosity was higher at the 20% rubber level, Table 4-5. The phase angle of the 20% rubber level blends was lower than the corresponding 10% rubber level blends, Figures 4-14 and 4-15. The phase angle at the 20% rubber content level generally increased with curing time, Figures 4-14 and 4-15. Similarly, the temperature susceptibility of the 20% rubber level blend was lower than the temperature susceptibility of the corresponding 10% rubber level blend, Figures 4-17 and 4-18. The temperature susceptibility of the 20% blend also increased with curing time, Figures 4-17 and 4-18. At low temperature, 249K (-11°F), the creep stiffness was lower for the 20% Exxon AC-10 blend than any of the 10% Exxon AC-10 blends, Table 4-7 and Figure 4-20. Obviously, the

higher the content of the rubber, the more elastic the properties of the asphalt-rubber binder. The high temperature viscosity for the 20% Exxon AC-10 blend, Table 4-5, is certainly the highest of all, but the Fina Demex Resin with 20% rubber is not unreasonable.

SHRP Superpave Results

The specifications of the SHRP Superpave Performance Grading are outlined by the Asphalt Institute (1995). The individual test elements are described in Appendix A, and Figure A-1 illustrates the combined test procedure, which follows. The full Performance Grade process begins with the original binder or binder blend. This material is evaluated by using the dynamic shear rheometer (DSR) to determine $G^*/\sin \delta$ and by also using the Brookfield rotational viscometer to determine the high temperature viscosity. Next, the material is aged in the Rolling Thin Film Oven Test (RTFOT). From this short term aged sample, the DSR is again used to evaluate $G^*/\sin \delta$, then the material may be aged for the long term in the Pressurized Aging Vessel (PAV). The DSR is employed a third time to evaluate the fatigue criterion through $G^* \sin \delta$. The PAV aged sample is evaluated at low temperatures by the bending beam rheometer and, optionally, the direct tension test.

The high cure blends prepared using the Silverson mixer, along with their source materials, were evaluated by performance grade testing, and the results of this testing are provided in Table 4-11. When the objective is to widen the SHRP grade span, it can be seen that the Exxon AC-10 neat asphalt, which fell just short of an upper rating of 58 can easily be raised to the 58 rating, and in the case of the 505K (450°F) blend, to nearly 64. This is due to the increase in limiting viscosity that the addition of rubber provides at intermediate temperatures. Additionally, the neat AC-10 failed the BBR test at -18°C and only by direct tension was the low temperature -28 rating obtained. All of the Exxon samples easily obtain the -28 rating by passing at -18°C, while the addition of either 20% rubber or the Sun recycling agent allowed for the -34 rating. The Fina Demex Resin blends are shown to be less desirable, except in colder climates, due to the rutting potential. They did not significantly improve the material at the top of the span and only incrementally at the bottom. These results, especially from the Exxon AC-10 blends, would indicate that the curing conditions are too harsh and need to be scaled back slightly. Addition of a few percent more rubber, combined with curing nearer to 505K (450°F), can achieve a 64-34 with reasonable ease.

Table 4-11: SHRP Superpave Results for Silverson Blends

Source Asphalt	Rubber Type	Rubber Content	Curing Temp K (°F)	Speed of Mixing (rpm)	SHRP Grade
Exxon AC-10	Neat				52 ¹ -28 ²
Exxon AC-10	TG-10	10%	533 (500)	4000	58-28
Exxon AC-10	TG-40b	10%	533 (500)	4000	58-28
Exxon AC-10	TG-10	20%	533 (500)	4000	58-34 ²
Exxon AC-10	TG-10	10%	505 (450)	4000	58 ³ -28
Exxon AC-10	TG-10	10%	533 (500)	8000	58-28
• Exxon / Sun AC-5	TG-10	10%	533 (500)	4000	52 ¹ -34
• Neste Wright LTR-10	???	10%	???	???	52-34
Fina Demex Resin	Neat				46-28 ²
Fina Demex Resin	TG-10	10%	533 (500)	4000	46-28
Fina Demex Resin	TG-40b	10%	533 (500)	4000	46-28
Fina Demex Resin	TG-10	20%	533 (500)	4000	46-34 ²
Fina Demex Resin	TG-10	10%	505 (450)	4000	46-28
Fina Demex Resin	TG-10	10%	533 (500)	8000	46-28
Fina AC-5	TG-10	10%	533 (500)	4000	52-28 ²
Supercritical Asphalt	TG-10	10%	533 (500)	4000	58-22

• - Compare These Two ¹ - Almost 58 ² - By Direct Tension ³ - Almost 64

CONCLUSIONS

The implications of these results are that homogeneous, compactible, truly elastic asphalt-rubber binders can be produced using high-shear and high-temperature curing conditions. These high-cure binders are homogeneous, non-settling, and have a non-detrimental viscosity at hot-mix temperatures, while still being more viscous and elastic at rutting temperatures and less stiff at cold temperatures than the base asphalt. Furthermore, the asphalt and rubber likely would be combined at the refinery, where quality control and the economics of the process can be maximized.

CHAPTER 5

AGING PROPERTIES OF ASPHALT-RUBBER BINDER

The binder properties of unaged or tank asphalt-rubber were discussed in the previous three chapters. To select the optimal binder to utilize in a roadway, the tank properties must be known. However, to have a road that will last a long time, the aging characteristics of the asphalt-rubber binder must also be known. This chapter presents the results of the aging studies done under Task 1.4, Age Rubber Blends.

For asphalts, it is known that oxidative aging is one of the major causes of roadway failure. The oxygen present in the atmosphere diffuses into the pavement and reacts with the asphalt. This reaction produces asphaltenes which increase the viscosity of the binder. Subsequently, the binder becomes brittle and cracks because of mechanical and thermal loading.

It is believed that asphalt-rubber binder behaves in a similar way when oxidized, but besides Shih et al. (1996), there have been no studies to determine the effect of the rubber on the aging properties of the binder. Furthermore, there have been no attempts to determine how the extent of curing affects the aging properties of an asphalt-rubber binder. Surely, undissolved rubber molecules affect the aging process of a binder differently than devulcanized and depolymerized rubber molecules. Much work has been done to understand the oxidative aging properties of asphalt binder. In fact, numerous aging tests exist for evaluating asphalt binders, including the SHRP aging test which specifies the use of air at a pressure of 20 atm and a temperature of 363, 373, or 383K (194, 212, or 230°F). However, the use of elevated temperature and pressure to evaluate and rank asphalts and then apply these ranks to roadway conditions, assumes that all asphalts possess the same activation energy and reaction order. Extending this already questionable assumption to heterogeneous asphalt-rubber, which is a combination of two vastly different materials, is highly problematic.

There seems to be no definitive studies that determine how the rubber and the extent of curing affect the aging properties of asphalts, or the feasibility of an asphalt-rubber aging test. These are important determinations, for if rubber is to be used in asphalt-rubber binder to build quality roads, the effect of the rubber and the extent of curing have to be known and an aging test to accurately and

practically predict the performance of asphalt-rubber has to be available. In this work, the determination of how the rubber and the extent of curing affect the oxidation of asphalt-rubber binder, and the feasibility of an asphalt-rubber aging test are attempted.

EXPERIMENTAL DESIGN

The aging of the asphalt-rubber blends was carried out in five phases. The pressures, the gas utilized, and the temperatures that were used for each phase of this study are listed in Table 5-1. The various asphalts and asphalt-rubber blends that were used in each phase of this study are listed in Table 5-2. Both Tables 5-1 and 5-2 show, in parentheses, the chapter of this report in which the indicated blends may be found; for example, Phase I aging concerned the materials described in Chapter 3. The η^* and δ values of the unaged Phase 3 and Phase 4 blends at temperatures from 273K (32°F) to 363K (194°F) are presented in Table C-1 of Appendix C. The η^* and δ values of the unaged Phase 5 blends at temperatures from 273K (32°F) to 363K (194°F) are presented in Table B-2 of Appendix B. The temperature susceptibility (TS) is E_a/R and has units of K^{-1} . It is defined in Chapter 3 and obtained by Equation 3-1.

Table 5-1: Pressure, Gas, and Temperatures for Each Phase of Aging

Phase and (Blending Chapter)	Pressure and Gas	Temperatures
1 - (3)	3.4 atm N ₂	367K (200°F)
2 - (3)	20 atm O ₂	355K and 367K (180 and 200°F)
3 - (2)	1 atm Air	333K and 372K (140 and 210°F)
4 - (2)	1 atm Air	333K, 353K, 358K, and 363K (140°F, 176°F, 185°F, and 194°F)
5 - (4)	1 atm Air	353K, 358K, and 363K (176°F, 185°F, and 194°F)

Table 5-2: Asphalts and Asphalt-Rubber Blends Used in Each Aging Phase

Phase and (Blending Chapter)	Asphalt	Percent Rubber and Mesh Size	Curing Temp	Curing Speed	Curing Time
1 (3)	Diamond Shamrock (DS) AC-5	0%			
		10% TG -40 20% TG -40	450K (350°F)	Sears 500 rpm	1 hour
	SHRP ABM-1	0%			
		10% RS -40 18% RS -40	450K (350°F)	Sears 500 rpm	1 hour
2 (3)	Diamond Shamrock (DS) AC-5	0%			
		20% TG -10 20% TG -40	450K (350°F)	Sears 500 rpm	1 hour
	SHRP ABM-1	0%			
		5% TG -40 10% TG -40 15% TG -40 18% TG -40 18% TG -10 18% RS -40	450K (350°F)	Sears 500 rpm	1 hour
		0%			
		5% TG -40 10% TG -40	450K (350°F)	Sears 500 rpm	1 hour
	SHRP AAA-1 FRACTION	0%			
		5% TG -40 10% TG -40 15% TG -40	450K (350°F)	Sears 500 rpm	1 hour
3 (2)	Exxon AC-5 Exxon AC-10 Fina AC-10	0%			
		5% TG -40 10%TG -40 5% RS -40 10% RS-40	464K (375°F)	Sears 500 rpm	12 hour
4 (2)	Exxon AC-5 Exxon AC-10 Fina AC-10 Fina Demex Resin	0%			
		10% TG-40 20% TG-40	464K (375°F)	Sears 1550 rpm	6 hour

Table 5-2: Asphalts and Asphalt-Rubber Blends Used in Each Aging Phase (Continued)

Phase and (Blending Chapter)	Asphalt	Percent Rubber and Mesh Size	Curing Temp	Silverson Curing Speed	Curing Time
5 (4)	Exxon AC-10	0%			6.5 hours
		10% TG -10	505K (450°F)	Silverson 4000 rpm	
		10% TG -10	533K (500°F)	Silverson 8000 rpm	
		10% TG -10			
		10% TG -40			
		20% TG -10		Silverson 4000 rpm	
	Exxon / Sun AC-5	10% TG -10			
	Fina Demex Resin	0%			6.5 hours
		10% TG -10	505K (450°F)	Silverson 4000 rpm	
		10% TG -10	533K (500°F)	Silverson 8000 rpm	
		10% TG -10			
		10% TG -40			
		20% TG -40		Silverson 4000 rpm	
	Fina AC-5	10% TG -10			
	Supercritical (SC) Asphalt	0%			6.5 hours
		10% TG -10	505K (450°F)	Silverson 4000 rpm	
		10% TG -10	533K (500°F)		
	Neste Wright Liquefied Tire Rubber 10 (LTR10) (A Commercially Available Asphalt-Rubber That is Exxon AC-10 Based)				

RESULTS AND DISCUSSION

Phase 1 Results

Asphalt and asphalt-rubber are known to behave differently when mixed at high-temperature under a nitrogen blanket. Under these conditions, asphalt-rubber cures. That is, the rubber is swelled, disintegrated, dissolved, and/or reduced in molecular size. From the last two chapters, it is known that the physical properties of the asphalt-rubber binder are changed substantially by this process. However, the physical properties of an asphalt do not change under these conditions.

The samples in Phase 1 were POV-aged at 367K (200°F) with 3.4 atm of pure nitrogen. This environment was chosen to determine if asphalt-rubber would cure at high-temperature under nitrogen without mixing. If the asphalt-rubber did behave differently than asphalt under Phase 1 conditions, then the development of a high-temperature asphalt-rubber aging test would be drastically complicated.

The asphalts and asphalt-rubber blends listed under Phase 1 in Table 5-2 were placed in the POV under nitrogen for up to 5 days. The measured values of the carbonyl area, CA, the complex viscosity, η^* , and the phase angle, δ , are presented in Table C-2 of Appendix C. The relative changes in CA, η^* , and δ with aging time are presented in Table 5-3. The relative changes of CA and η^* with aging time for the asphalt-rubber blends appear to be no greater than the relative changes of CA and η^* with aging time for the asphalts. The measured values of η^* and CA are presented in Figures 5-1 and 5-2. For both the asphalts and the asphalt-rubbers, there do not appear to be any significant changes in CA and η^* with aging time and the small negative trend in δ is most likely within the scatter of the data. The measured values of δ are presented in Figure 5-3.

GPC analyses were also performed to determine if there was some interaction between the asphalt and the rubber during aging. Figures 5-4, 5-5, and 5-6 are GPC chromatograms representing the molecular weight distribution of the SHRP ABM-1 blends as measured by the RI detector. SHRP ABM-1 did not age under nitrogen, Figure 5-4. As noted in Chapter 4, during the curing process, the rubber is devulcanized and depolymerized as it is transferred into the asphalt phase of the binder. In Figures 5-5 and 5-6, these phenomena are represented by the peak in the molecular weight distribution of the tank samples in the 20 to 25 minute retention time region. However, the lack of peak growth in Figures 5-5 and 5-6 with aging time indicates that the rubber and ABM-1 do not cure

Table 5-3: Relative Changes in CA, η^* , and δ for Phase 1 Blends

Sears Blend	Days	$(CA - CA_{\text{tank}})/CA_{\text{tank}}$	$(\eta^* - \eta^*_{\text{tank}})/\eta^*_{\text{tank}}$	$(\delta - \delta_{\text{tank}})/\delta_{\text{tank}}$
Diamond Shamrock (DS) AC-5	1	-0.085	0.177	0.000
	2	-0.106	0.195	-0.003
	3	-0.001	0.363	-0.027
	4	0.143	0.024	-0.003
	5	-0.052	0.096	-0.004
10% TG -40 Diamond Shamrock (DS) AC-5 500 rpm, 1 hour 450K (350°F), N ₂	1	0.072	0.085	-0.001
	2	-0.028	0.138	-0.009
	3	0.049	0.020	-0.003
	4	0.155	-0.006	0.014
	5	0.208	0.436	-0.041
18% TG -40 Diamond Shamrock (DS) AC-5 500 rpm, 1 hour 450K (350°F), N ₂	1	-0.030	0.129	-0.028
	2	-0.235	0.143	-0.047
	3	0.183	0.422	-0.064
	4	0.259	0.259	-0.034
	5	0.193	0.097	-0.027
SHRP ABM-1	1	-0.012	0.066	-0.011
	2	-0.070	0.083	-0.003
	3	-0.031	0.111	-0.014
	4	0.125	0.080	-0.005
	5	0.081	0.011	-0.002
10% RS -40 SHRP ABM-1 500 rpm, 1 hour 450K (350°F), N ₂	1	0.169	-0.025	-0.004
	2	0.101	-0.019	-0.007
	3	0.022	0.051	-0.021
	4	0.197	0.036	-0.012
	5	0.205	-0.077	-0.012
18% RS -40 SHRP ABM-1 500 rpm, 1 hour 450K (350°F), N ₂	1	0.311	0.002	-0.001
	2	-0.027	0.142	-0.030
	3	-0.029	-0.030	-0.020
	4	-0.017	0.051	-0.013
	5	0.162	-0.024	-0.015

Figure 5-1: Viscosity data for nitrogen-aged samples.

Figure 5-2: Carbonyl data for nitrogen-aged samples.

Figure 5-3: Phase angle data for nitrogen-aged samples.

Figure 5-4: GPC (RI) data for nitrogen-aged SHRP ABM-1.

Figure 5-5: GPC (RI) data for nitrogen-aged 10/90, RS -40/SHRP ABM-1 blend.

Figure 5-6: GPC (RI) data for nitrogen-aged 18/82, RS -40/SHRP ABM-1 blend.

with high-temperature aging under nitrogen, as was also true of Diamond Shamrock blends.

Examining all measured properties, CA, η^* , δ , and molecular weight distribution, allows the conclusion that asphalt-rubber binder does not cure at high-temperature under nitrogen without mixing. This fact supports the idea of developing an asphalt-rubber aging test, because it will not be necessary to separate the oxidation from the curing when analyzing high-temperature aging data.

Phase 2 Results

Numerous authors have used carbonyl content to correlate changing physical properties with asphalt oxidation (Martin et al., 1990; Lau et al., 1992; Liu et al., 1996). The rate of change of any physical property with carbonyl formation is asphalt dependent. Nonetheless, carbonyl area is an excellent surrogate for oxidative aging and because of its ability to correlate to physical properties, an excellent predictor of the changes in physical properties with oxidation. These attributes can be partly explained by the fact that for each asphalt there is a linear relationship between carbonyl growth and oxygen increase (Liu et al., 1996).

Lau et al. (1992) used high pressure oxygen, 20 atm, and high temperatures, 333 to 366K (140 to 200°F), to age five asphalts. Lau et al. (1992) aged asphalts under these conditions and found that the rate of carbonyl formation becomes constant or linear, Equation 5-1, after an initial, more rapid rate region:

$$CA = CA_0 + r_{CA} t \quad (5-1)$$

where CA is the Carbonyl Area, r_{CA} is the constant reaction rate after an initial jump, and CA_0 is the intercept of the constant rate aging line. By aging at multiple temperatures, Equation 5-2 becomes useful in calculating the activation energy, E :

$$r_{CA} = A' \exp \left[-\frac{E}{RT} \right] \quad (5-2)$$

where A' is the frequency factor, E is the activation energy, R is the universal gas constant, and T is the absolute aging temperature.

Additionally, Lau et al. (1992) reported that for asphalts, there is a linear relationship between $\ln \eta^*$ and carbonyl content, Equation 5-3:

$$\ln \eta_0^* = \ln m + (HS)(CA) \quad (5-3)$$

where η_0^* is the zero-shear complex viscosity, m is the intercept, and HS is the hardening susceptibility. It was shown that hardening susceptibility is a characteristic property that is unique to each asphalt and that is also independent of aging temperature. Note that for asphalt rubber, the complex viscosity does not converge to a limiting value at zero-shear. Thus, complex viscosity data, η^* , are reported at 1.0 rad/sec.

Liu (1996) extended the work of Lau et al. (1992) by examining the effect of both pressure and temperature on the asphalt aging process. It was determined that the asphalt aging rate could, as in classic kinetics, be expressed as Equation 5-4:

$$r_{CA} = A P^\alpha \exp\left[-\frac{E}{RT}\right] \quad (5-4)$$

where P is the aging pressure and α is the reaction order with respect to oxygen pressure. Equation 5-4 was also linearized to a more useful form, Equation 5-5:

$$\ln r_{CA} = \ln A + \alpha * \ln P - \frac{E}{RT} \quad (5-5)$$

This equation was used to perform multivariable regression of r_{CA} as a function of both temperature and pressure. From this analysis it was determined that the Arrhenius-type parameters; A , α , and E , are asphalt dependent. Ten asphalts were studied and the ranges of E and α were established to be 83.3 to 100.7 KJ/mol and 0.33 to 0.58, respectively. From these results it was concluded that any attempt to use relative asphalt-aging rates at elevated temperatures and pressures, and to assume they represent relative rates at road conditions could be highly misleading (Liu 1996).

As described in Table 5-1, the samples in Phase 2 were POV-aged at 355 or 367K (180 or 200°F) with 20 atm of pure oxygen. If the results were similar to the findings of Lau et al. (1992) and Liu (1996) for asphalts, then the development of an accelerated, high-pressure aging test for asphalt-rubber binder would seem feasible.

The first round of samples aged under 20 atm oxygen were the SHRP ABM-1, 18% rubber blends with TG -10, RS -40, and TG -40 rubber, and the Diamond Shamrock AC-5, 20% rubber blends with TG -10 and TG -40 rubber, Table 5-2. It was believed that aging large rubber concentration blends would best show the effect of rubber on the aging process. On the other hand, it was realized that the 18% and 20% rubber blends are hard to analyze in the laboratory because of their large rubber concentrations. Various mesh sizes were used to study the effect of mesh size on the aging process. The CA , η^* , and δ values for the 20 atm oxygen-aged 18% and 20% blends are presented in Table C-3 of Appendix C.

The aging of the 18% SHRP ABM-1 and 20% Diamond Shamrock blends yielded some interesting results. At both 355 and 367K (180 and 200°F), the aging rate was increased by the presence of rubber. The slope of the constant-rate regression line, Equation 5-1, is the aging rate, r_{CA} , while the intercept is defined as the initial jump, CA_0 . The increase in aging rate, over the neat asphalt, is shown for the SHRP ABM-1 blends in Figures 5-7 and 5-8. The aging rates for both the SHRP ABM-1 and Diamond Shamrock blends are presented in Table 5-4. The rubber also increased the aging rate of Diamond Shamrock AC-5. It is theorized that the rubber acts as a catalyst for the oxidation of the binder and causes the overall oxidation rate to increase. Nonetheless, for the SHRP ABM-1 and Diamond Shamrock asphalt-rubber blends, the rate of carbonyl formation becomes constant after an initial, more rapid rate region, but is still higher than the unblended asphalt. Furthermore, the intercepts of the aging equations, CA_0 , for SHRP ABM-1 asphalt at 355 and 367K (180 and 200°F) are in agreement at $CA_0=2.25$, Figures 5-7 and 5-8. Similarly, the intercepts of the aging equations, CA_0 , for the SHRP ABM-1 blends at 355 and 367K (180 and 200°F) agree within the noise of the data. The intercepts for both the SHRP ABM-1 and Diamond Shamrock blends are presented in Table 5-5. The intercepts of the Diamond Shamrock blends were also independent of aging temperature. These results agree with Lau et al. (1992) for asphalts aged under similar conditions.

Figure 5-7: Aging rate plot for SHRP ABM-1 blends aged at 355K.

Figure 5-8: Aging rate plot for SHRP ABM-1 blends aged at 367K.

Table 5-4: Hardening Rates (HR), Aging Rates (AR), and Hardening Susceptibilities (HS) for Phase 2 Blends Aged under 20 atm Oxygen

Sears Blend	Aging Temperature	Hardening Rate (1/day)	Aging Rate (CA/day)	Hardening Susceptibility (1/CA)	
Diamond Shamrock (DS) AC-5	355K (180°F)	2.794e-1	6.737e-2	3.779	3.590
	367K (200°F)	6.576e-1	1.857e-1	3.392	
20% TG -10 DS AC-5 500 rpm, 1 hour 450K (350°F), N ₂	355K (180°F)	1.816e-1	8.691e-2	2.033	
	367K (200°F)	6.644e-1	2.457e-1	2.619	
20% TG -40 DS AC-5 500 rpm, 1 hour 450K (350°F), N ₂	355K (180°F)	1.993e-1	8.340e-2	2.374	
	367K (200°F)	6.243e-1	2.174e-1	2.838	
SHRP ABM-1	355K (180°F)	1.733e-1	1.236e-1	1.343	1.250
	367K (200°F)	3.920e-1	3.188e-1	1.189	
18% TG -10 SHRP ABM-1 500 rpm, 1 hour 450K (350°F), N ₂	355K (180°F)	5.105e-2	1.441e-1	3.344e-1	
	367K (200°F)	1.991e-1	3.364e-1	5.584e-1	
18% TG -40 SHRP ABM-1 500 rpm, 1 hour 450K (350°F), N ₂	355K (180°F)	7.454e-2	1.257e-1	5.355e-1	
	367K (200°F)	2.437e-1	3.747e-1	5.999e-1	
18% RS -40 SHRP ABM-1 500 rpm, 1 hour 450K (350°F), N ₂	355K (180°F)	5.923e-2	1.615e-1	3.529e-1	
	367K (200°F)	1.582e-1	3.758e-1	3.431e-1	
5% TG -40 SHRP ABM-1 500 rpm, 1 hour 450K (350°F), N ₂	355K (180°F)	1.008e-1	1.376e-1	7.274e-1	
	367K (200°F)	1.835e-1	3.109e-1	5.835e-1	
10% TG -10 SHRP ABM-1 500 rpm, 1 hour 450K (350°F), N ₂	355K (180°F)	7.653e-2	1.490e-1	5.049e-1	
	367K (200°F)	1.330e-1	3.456e-1	3.694e-1	

Table 5-4: Hardening Rates (HR), Aging Rates (AR), and Hardening Susceptibilities (HS) for Phase 2 Blends Aged under 20 atm Oxygen (Continued)

Sears Blend	Aging Temperature	Hardening Rate (1/day)	Aging Rate (CA/day)	Hardening Susceptibility (1/CA)	
15% TG -40 SHRP ABM-1 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	4.242e-2	1.656e-1	2.566e-1	
	367K (200°F)	4.723e-2	3.508e-1	1.245e-1	
SHRP ABM-1 Fraction	355K (180°F)	8.880e-2	1.316e-1	6.763e-1	5.091e-1
	367K (200°F)	1.243e-1	2.842e-1	4.475e-1	
5% TG -40 ABM-1 Fraction 500 rpm, 1 hours 450K (350°F) N ₂	355K (180°F)	6.866e-2	1.319e-1	5.138e-1	
	367K (200°F)	9.848e-2	3.027e-1	3.027e-1	
10% TG -40 ABM-1 Fraction 500 rpm, 1 hours 450K (350°F) N ₂	355K (180°F)	3.933e-2	1.450e-1	2.670e-1	
	367K (200°F)	5.008e-2	3.169e-1	1.549e-1	
SHRP AAA-1 Fraction	355K (180°F)	3.829e-1	2.192e-1	1.741	1.632
	367K (200°F)	8.430e-1	5.350e-1	1.577	
5% TG -40 AAA-1 Fraction 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	2.969e-1	1.994e-1	1.468	
	367K (200°F)	1.043	6.344e-1	1.656	
10% TG -40 AAA-1 Fraction 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	1.776e-1	1.799e-1	1.003	
	367K (200°F)	1.144	9.009e-1	1.294	
15% TG -40 AAA-1 Fraction 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	9.474e-2	1.448e-1	6.428e-1	
	367K (200°F)	1.041	1.023	1.043	

Table 5-5: Intercepts of the Hardening Rate (HR), Aging Rate (AR), and Hardening Susceptibility (HS) Equations for Phase 2 Blends Aged under 20 atm Oxygen

Sears Blend	Aging Temperature	Intercept of HR eq., (η^*) _o (poise)	Intercept of AR eq., CA _o	Intercept of HS eq., m (poise)	
Diamond Shamrock (DS) AC-5	355K (180°F)	2,278	1.085	42.69	58.26
	367K (200°F)	2,508	1.039	80.20	
20%, TG -10 DS AC-5 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	9,825	1.006	1,314	
	367K (200°F)	4,483	9.921e-1	355.2	
20%, TG -40 DS AC-5 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	4,453	9.765e-1	442.6	
	367K (200°F)	3,761	1.070	184.7	
SHRP ABM-1	355K (180°F)	10,870	2.252	556.3	693.1
	367K (200°F)	10,940	2.250	776.5	
18% TG -10 SHRP ABM-1 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	34,080	2.005	17,780	
	367K (200°F)	22,610	2.316	6,417	
18% TG -40 SHRP ABM-1 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	22,280	2.169	7,334	
	367K (200°F)	17,550	2.192	4,987	
18% RS -40 SHRP ABM-1 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	24,200	1.907	12,540	
	367K (200°F)	21,680	2.128	11,410	
5% TG -40 SHRP ABM-1 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	14,890	2.493	2,438	
	367K (200°F)	14,510	2.422	3,557	
10% TG -40 SHRP ABM-1 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	17,200	2.393	5,176	
	367K (200°F)	15,940	2.318	6,896	

Table 5-5: Intercepts of the Hardening Rate (HR), Aging Rate (AR), and Hardening Susceptibility (HS) Equations for Phase 2 Blends Aged under 20 atm Oxygen (Continued)

Sears Blend	Aging Temperature	Intercept of HR eq., (η^*) ₀ (poise)	Intercept of AR eq., CA ₀	Intercept of HS eq., m (poise)	
15% TG -40 SHRP ABM-1 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	23,050	2.316	12,722	
	367K (200°F)	21,940	2.304	16,674	
SHRP ABM-1 Fraction	355K (180°F)	2,281	1.859	648.1	929.8
	367K (200°F)	2,257	1.767	1,014	
5% TG -40 SHRP ABM-1 Fraction 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	2,513	1.868	967.9	
	367K (200°F)	2,913	1.772	1,744	
10% TG -40 SHRP ABM-1 Fraction 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	2,799	1.809	1,733	
	367K (200°F)	2,805	1.760	2,143	
SHRP AAA-1 Fraction	355K (180°F)	332.7	4.513e-1	152.8	190.9
	367K (200°F)	380.9	3.418e-1	221.6	
5%, TG -40 SHRP AAA-1 Fraction 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	417.7	4.410e-1	224.3	
	367K (200°F)	210.7	9.425e-2	176.0	
10%, TG -40 SHRP AAA-1 Fraction 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	733.4	5.071e-1	433.6	
	367K (200°F)	176.6	-4.154e-1	280.7	
15%, TG -40 SHRP AAA-1 Fraction 500 rpm, 1 hour 450K (350°F) N ₂	355K (180°F)	1,314	6.534e-1	872.4	
	367K (200°F)	263.8	-5.896e-1	446.5	

The energy of the oxidization reaction is most likely devulcanizing and depolymerizing the rubber, since the hardening rate, the slope of a $\ln \eta^*$ versus time (t) plot, is lowered by the presence of the rubber, Figures 5-9 and 5-10. The hardening rate equation is:

$$\ln \eta^* = \ln (\eta^*)_0 + HR t \quad (5-6)$$

where η^* is the carbonyl content, HR is the constant hardening rate, and $(\eta^*)_0$ is the intercept of the constant rate hardening line at time zero. The effect of the rubber on the hardening rate of the SHRP ABM-1 asphalt is exceptional, with the hardening rate being reduced by more than one-half for two of the three asphalt-rubber blends, Table 5-4. Figures 5-9 and 5-10 also show that while the viscosity of the asphalt-rubber binder is initially much higher than the asphalt, 6.3 to 8.8 times higher at 18% rubber content depending on mesh size, with high-pressure oxygen POV-aging, the viscosity of the asphalt quickly catches up to and may exceed the viscosity of the asphalt-rubber blends. This phenomenon was present at both 355 and 367K (180 and 200°F) for SHRP ABM-1 and can be explained by the improved hardening rate with the addition of rubber and the lowering of the initial viscosity jump with the addition of rubber. The viscosity jump occurs in an initial rapid hardening period, a period before $\ln \eta^*$ becomes constant with time. The initial viscosity jump is present in Figures 5-9 and 5-10 and all other hardening plots in this work. Comparing the equations presented in Figures 5-9 and 5-10 shows that the intercept of the hardening rate equation, $(\eta^*)_0$, is independent of aging temperature for the SHRP ABM-1 asphalt and is not independent of aging temperature for the SHRP ABM-1 asphalt-rubber blends. For the blends, $(\eta^*)_0$ is lower at the higher aging temperature, Table 5-5. These results are a very good indicator that at 20 atm oxygen and the temperatures used, 355 and 367K (180 and 200°F), the oxygen prefers to react with rubber. Apparently, the energy of the reaction goes toward attacking and cutting up the rubber molecules instead of hardening the asphalt. The reaction of liquid polar aromatics proceeding to solid asphaltenes may be lessened by the presence of rubber resulting in fewer liquid phase materials being removed, thus the lower hardening rate.

Figure 5-9: Hardening rate plot for SHRP ABM-1 blends aged at 355K.

Figure 5-10: Hardening rate plot for SHRP ABM-1 blends aged at 367K.

For Diamond Shamrock, the rubber is not as exceptional at improving the hardening rate, Table 5-4, with the rubber lowering the hardening rate at 355K (180°F), Figure 5-11, but not lowering the hardening rate at 367K (200°F), Figure 5-12. However, note that in Figure 5-12 the initial increase in viscosity was much higher for the asphalt, with the asphalt increasing by a factor of 8.2 with one day of aging, whereas for one day of aging the viscosity of the asphalt-rubber blends increased by only a factor of 1.6 and 2.0, for TG -10 and TG -40, respectively. Thus, overall the rubber improved the hardening characteristics of Diamond Shamrock AC-5. Furthermore, $(\eta^*)_0$ is approximately the same at the two aging temperatures for Diamond Shamrock, but is quite different at the two aging temperatures for the Diamond Shamrock blends, Table 5-5. For the blends, $(\eta^*)_0$ is lower at the higher aging temperature.

The hardening rate can be linked to the aging rate by Equation 5-7:

$$\frac{\partial \ln \eta^*}{\partial t} = \frac{\partial \ln \eta^*}{\partial CA} \frac{\partial CA}{\partial t} \quad (5-7)$$

The term on the left-hand side is the hardening rate (HR), the first term on the right-hand side is the hardening susceptibility (HS), and the second term on the right-hand side is the aging rate. The aging rate is given by Equation 5-2. Substituting these variables into Equation 5-7 yields:

$$HR = HS r_{CA} = HS A' \exp \left(-\frac{E}{RT} \right) \quad (5-8)$$

Taking the natural logarithm of both sides of Equation 5-8 gives:

$$\ln HR = \ln HS + \ln A' - \frac{E}{RT} \quad (5-9)$$

Because the HS of an asphalt is independent of aging temperature, a plot of $\ln HR$ versus T^{-1} will yield a viscosity-based activation energy, E_{vis} .

Figure 5-11: Hardening rate plot for DS AC-5 blends aged at 355K.

Figure 5-12: Hardening rate plot for DS AC-5 blends aged at 367K.

However, for asphalt-rubber blends aged at high-pressure oxygen, a plot of $\ln HR$ versus T^{-1} will not be linear because the hardening susceptibility was determined to be dependent on temperature. Figure 5-13 is a hardening susceptibility plot for the 18% TG -10, SHRP ABM-1 blend that was aged at 355 or 367K (180 or 200°F). Agreeing with findings of Lau et al. (1992), the asphalt, SHRP ABM-1, data points for both temperatures lie on a single line. However, for the 18% TG -10, SHRP ABM-1 blend, the data points from the material aged at 355K (180°F) lie on a distinctly separate line than the data points from the material aged at 367K (200°F), and the slopes, HS, of those lines also differ. Just looking at the numerical values of the hardening susceptibilities of the 18% and 20% asphalt-rubber binders can be deceiving because the hardening susceptibilities for the 367K (200°F) data and the 355K (180°F) data are reasonably close, Table 5-4. Furthermore, for 18% and 20% blends, the intercept of the hardening susceptibility equation, m in Equation 5-3, is also dependent on the temperature, Table 5-5. Using rubber at the 18% and 20% level was beneficial in that it improved the hardening susceptibility of the asphalts, Table 5-4. The fact that the relationship in Equation 5-5 is not linear for asphalt-rubber complicates the development of a high-pressure, accelerated aging test for asphalt-rubber binder.

The results of the high-pressure aging for the 18% SHRP ABM-1 and 20% Diamond Shamrock blends were inconclusive with respect to mesh size. Relative to aging rate, hardening rate, and hardening susceptibility the effect on the mesh size was random, Table 5-4. The effect of rubber source also was random. Because the only obvious difference in the rubber sources is mesh size distribution, for a given mesh size the Rouse rubber was found to have a finer gradation than the Tire Gator, this result agrees with the findings with respect to mesh size.

The second round of samples aged under oxygen were the SHRP ABM-1, TG -40 mesh blends at the 5%, 10%, and 15% rubber level, the SHRP ABM-1 Fraction, TG -40 mesh blends at the 5% and 10% rubber level, and the SHRP AAA-1 Fraction, TG -40 mesh blends at the 5%, 10%, and 15% rubber level, Table 5-2. The CA, η^* , and δ values for these blends are presented in Table C-3 of Appendix C. It was believed that aging a range of rubber concentrations would show the effect of rubber concentration on the aging process. The SHRP ABM-1 and SHRP ABM-1 Fractions were chosen to determine the effect of molecular weight distribution and asphalt composition on the asphalt-rubber aging process.

Figure 5-13: Hardening susceptibility plot for SHRP ABM-1 blend.

The SHRP ABM-1 and SHRP ABM-1 Fraction blends behaved similarly with respect to the properties of hardening rate, aging rate, and hardening susceptibility, Table 5-4. With increasing rubber content, the hardening rate decreased, Figures 5-14 and 5-15, the aging rate increased marginally, Figures 5-16 and 5-17, and the hardening susceptibility (HS) decreased, Figures 5-18 and 5-19. These results agree with the results from the 18% and 20% rubber level SHRP ABM-1 and Diamond Shamrock blends in that the rubber was beneficial for the hardening rate and the hardening susceptibility and detrimental to the aging rate of an asphalt. Furthermore, these results agree with the earlier high-pressure results in that the intercept of the aging rate, CA_0 , was independent of aging temperature for both the asphalts and the asphalt-rubber blends, Table 5-5. On the other hand, contrary to the earlier high-temperature results, the intercept of the hardening rate, $(\eta^*)_0$, for an asphalt-rubber blend was not conclusively dependent on temperature, Table 5-5.

The extent to which the rubber affected binder properties was asphalt dependent. At both aging temperatures, the hardening rate for the SHRP ABM-1 Fraction was lower than the hardening rate for the SHRP ABM-1 asphalt, Table 5-4. Figure 5-14 through 5-19 pertain to ABM-1 based

materials aged at 355K (180°F). The even numbered figures illustrate SHRP ABM-1 and blends, while the odd numbered ones represent the ABM-1 fraction results. Figures 5-14 and 5-15 give the hardening rates at 355K (180°F). The improved hardening rate is probably due to the fact that the SHRP ABM-1 Fraction was produced from the SHRP ABM-1 asphalt by removing most of the asphaltenes and saturates during the supercritical fractionation process. The hardening characteristics of such supercritical fractions have been found to be superior relative to their base asphalt (Jemison et al., 1992). Figures 5-16 and 5-17 provide the reaction rate constants and carbonyl growth trends for the ABM-1 based materials. Figures 5-18 and 5-19 combine hardening and aging to obtain the hardening susceptibility, HS, as defined in Equation 5-3. The minimal amount of material formed in the 22 to 26 minute retention time region in Figure 5-20 shows that the SHRP ABM-1 Fraction does not produce appreciable amounts of large molecular weight material, asphaltenes, when oxidized, while the SHRP ABM-1 asphalt does produce asphaltenes, Figure 5-21.

For a given rubber amount, the rubber was more beneficial to the hardening rate of the SHRP ABM-1 asphalt. That is, the percent improvement in hardening rate was greater for the SHRP ABM-1 blends than for the SHRP ABM-1 Fraction blends, Table 5-4. With aging, under high-pressure oxygen, the flux of mass into the asphalt phase of the binder, represented by the growth in the 20 to 25 minute retention time region, is much more prevalent for the SHRP ABM-1 blend than the SHRP ABM-1 Fraction blend, Figures 5-22 and 5-23, respectively. Apparently, the SHRP ABM-1 asphalt interacts better with the rubber during the aging process than the SHRP ABM-1 Fraction. The higher interaction of the SHRP ABM-1 asphalt is most likely explained by the presence of the asphaltenes and heavy polar aromatics not found in the SHRP ABM-1 Fraction. It is theorized that these large molecular weight molecules are able to use the polar groups present on their structures to help devulcanize and depolymerize the rubber during the aging process. This phenomenon helps explain the increased effect of the rubber on the hardening rate of the SHRP ABM-1 blends. However, note that for a given rubber level, the SHRP ABM-1 Fraction blend still had a lower hardening susceptibility. That is, although adding rubber was beneficial for the hardening rate, it was less beneficial in the fraction than in the source material, at least when aging at elevated POV temperatures.

Figure 5-14: Hardening rate plot for SHRP ABM-1 blends aged at 355K.

Figure 5-15: Hardening rate plot for SHRP ABM-1 Fraction blends aged at 355K.

Figure 5-16: Aging rate plot for SHRP ABM-1 blends aged at 355K.

Figure 5-17: Aging rate plot for SHRP ABM-1 Fraction blends aged at 355K.

Figure 5-18: Hardening susceptibility plot for SHRP ABM-1 blends aged at 355K.

Figure 5-19: HS plot for SHRP ABM-1 Fraction blends aged at 355K.

Figure 5-20: GPC (RI) data for SHRP ABM-1 Fraction aged at 367K.

Figure 5-21: GPC (RI) data for SHRP ABM-1 aged at 355K.

Figure 5-22: GPC (RI) data for 10/90, TG -40/SHRP ABM-1 aged at 367K.

Figure 5-23: GPC (RI) data for 10/90, TG -40/SHRP ABM-1 Fraction aged at 367K.

Interestingly, while SHRP ABM-1 interacts better in *aging*, the lower molecular weight SHRP ABM-1 fraction is better at interacting with the rubber during *curing*, as indicated by the massive increase in viscosity during the curing process, Figures 5-14 and 5-15 (at time = 0). For example, at the 10% rubber level, the ratio of asphalt-rubber complex viscosity to asphalt complex viscosity, both before aging, is 10.64 for the SHRP ABM-1 Fraction and 2.92 for the SHRP ABM-1 asphalt, again Figures 5-14 and 5-15. This phenomenon is surely explained by diffusion, with the lower molecular weight material being better able to diffuse into the rubber, and thus, also interact with the rubber to dissolve it. This phenomenon also can be seen by comparing the molecular weight distributions of the tank samples in Figure 5-22 and Figure 5-23. It shows that in the 20 to 25 minute retention time region, the region where dissolved rubber appears, the SHRP ABM-1 Fraction has a much more significant rubber shoulder at the initial cure condition, and therefore performed better than the SHRP ABM-1 with respect to curing.

The addition of rubber increased the aging rate of the SHRP ABM-1 while an incremental increase was found for the SHRP ABM-1 Fraction, Figures 5-16 and 5-17. It may seem contrary to previous results, but the aging rate and the hardening rate may fluctuate independently. The selection of the optimum binder incorporates a compromise of these and other variables. The higher the rubber content, within the range studied, the higher the aging rate, Table 5-4. As with the 18% and 20% blends, the rubber acted as a catalyst for the oxidation of the binder. Interestingly, the increase in aging rate for a SHRP ABM-1 and SHRP ABM-1 Fraction blend was not definitively dependent on the base asphalt at the temperatures studied, 355 and 367K (180 and 200°F).

The addition of rubber improved the hardening susceptibility of both the SHRP ABM-1 and SHRP ABM-1 Fraction, Figures 5-18 and 5-19. The higher the rubber content, within the range studied, the lower the hardening susceptibility, Table 5-4. Because the hardening susceptibility is $\partial(\ln\eta^*)/\partial CA$, the decrease in hardening susceptibility with increasing rubber content is a strong indicator that the oxygen is attacking the solid rubber and possibly cutting it up instead of forming asphaltenes from the liquid polar aromatics. The rubber was more beneficial to the SHRP ABM-1 asphalt, with a given rubber concentration lowering the hardening susceptibility by a larger percentage than in the comparable SHRP ABM-1 Fraction blend, due mainly to the ABM-1 fraction's lower hardening susceptibility.

The SHRP AAA-1 Fraction blends behaved quite differently from the other asphalts studied. Like the other asphalts studied at 355K (180°F), the hardening rate of SHRP AAA-1 Fraction decreased with increasing rubber content and the hardening susceptibility of SHRP AAA-1 Fraction also decreased with increasing rubber content, Table 5-4. However, at 355K (180°F) the aging rate of SHRP AAA-1 Fraction decreased with increasing rubber content, Figure 5-24. This was completely opposite of the effect of rubber content on the aging rate of the other asphalts studied. At 367K (200°F), the effect of rubber on the aging rate of SHRP AAA-1 Fraction had reversed itself and was the same as the other asphalts, with the aging rate increasing with increasing rubber content, Figure 5-25. However, note in Figure 5-25 that the aging rate in the first three days of aging at 367K (200°F) agrees with the aging rate at 355K (180°F) in that the rubber actually lowers the rate of carbonyl formation. However, by days 5 and 6 the carbonyl area has exploded for the asphalt-rubber blends, with the higher the rubber content the higher the carbonyl area. In fact, this explosion in carbonyl area caused CA_0 of the 10% and 15% blends to be negative, Figure 5-25. This was the only time during this entire study that a negative CA_0 was obtained. While the R values for measuring the error in the linear fit seem reasonable, these facts may suggest that at temperatures as low as 367K (200°F) when using 20 atm pure oxygen, the rate of carbonyl formation for some asphalt-rubber binders does not become constant after an initial more rapid rate region. Perhaps the asphalt base and how it interacts with the rubber during the aging process determines whether the aging rate is constant.

In the past, researchers have investigated the possibility that the reaction mechanism for the oxidation of asphalt may be different at elevated temperatures, compared to road temperatures. Van Oort (1956) reported that at temperatures above 373.2K (212°F), the reaction mechanism must involve dehydrogenation because water is produced when asphalt is oxidized. Furthermore, above this temperature, carbon dioxide may also be produced. Carbon dioxide and water do not form at lower temperatures, indicating a different reaction mechanism. More recently, Choquet and Verhasselt (1994) reported that at aging temperatures above 373.2K (212°F), the reaction mechanism may change for asphalts. If the oxidation mechanism of pure asphalt changes at approximately 373.2K (212°F), then it is logical to believe that the mechanism of heterogeneous asphalt-rubber binder would also change at elevated temperatures. This is especially true when using high-pressure

Figure 5-24: Aging rate plot for SHRP AAA-1 Fraction blends aged at 355K.

Figure 5-25: Aging rate plot for SHRP AAA-1 Fraction blends aged at 367K.

oxygen because the double bonds of the rubber are very susceptible to attack by oxygen (Rosen, 1993). From the SHRP AAA-1 Fraction results, it would appear that the reaction mechanism is different for some asphalt-rubber binders at temperatures at or above 367K (200°F) when using 20 atm oxygen.

The hardening rate of the SHRP AAA-1 Fraction blends aged at 367K (200°F) increased with the addition of rubber, Figure 5-26, completely opposite of the effect of rubber content on the hardening rate of the SHRP AAA-1 Fraction blends aged at 355K (180°F), Table 5-4. The results at 367K (200°F) were also different from the results of all the other asphalts studied. However, please note in Figure 5-26 that the degree of hardening in the first three days of aging at 367K (200°F) agrees with the results for the hardening rate at 355K (180°F) in that the rubber actually lowers the hardening rate. By days 5 and 6 the viscosity has increased greatly for the asphalt-rubber blends. This is similar to what happened to the aging rate at 367K (200°F). Furthermore, in Figure 5-26 the asphalt data are the only data that lie on a straight line. Apparently, the hardening rate for some asphalt-rubber binders does not become constant after an initial more rapid rate region at temperatures as low as 367K (200°F) when using 20 atm pure oxygen. This strongly supports the theory that the oxidation mechanism for some asphalt-rubber binders is changing with increasing temperatures around 367K (200°F) when using 20 atm pure oxygen.

The hardening susceptibility of SHRP AAA-1 Fraction blends aged at 367K (200°F) had a lot of scatter in the data, especially with the highly-aged samples, Figure 5-27. In the carbonyl area region of 0.8 to 2.0, the hardening susceptibility results are very similar to the other asphalts studied in that the rubber lowers the hardening susceptibility. However, above carbonyl area values of 3.0 the linear relationship between $\ln \eta^*$ and CA breaks down for the asphalt-rubber blends. The SHRP AAA-1 Fraction data are the only data that are lying on the straight line.

The breakdown of the linear relationship between the variables of the aging rate, hardening rate, and hardening susceptibility equations in the highly-aged region indicates that at these aging conditions, 367K (200°F) and 20 atm oxygen, there is a point during aging at which the aging mechanism of certain asphalt-rubber binders changes. This change in mechanism may be occurring at the point where the rubber is totally consumed.

Figure 5-26: Hardening rate plot for SHRP AAA-1 Fraction blends aged at 367K.

Figure 5-27: HS plot for SHRP AAA-1 Fraction blends aged at 367K.

Phase 3 and Phase 4 Results

To eliminate the effect of pressure, 1 atm air was used to oxidize the asphalt and asphalt-rubber blends in Phases 3 and 4. The temperature control was improved by totally immersing the sealed POV in a triethylene glycol bath. In Phase 3 the samples were aged in the POV at 372K (210°F). In Phase 4 the samples were aged in the POV at 353, 358, and 363 K (176, 185, and 194°F). Additionally, in Phase 3 and Phase 4 an environmental room (ENVRM) was used to age asphalt-rubber samples at 333K (140°F). The CA, η^* , and δ values for the Phase 3 and 4 blends that were POV-aged are presented in Appendix C in Tables C-4 and C-6, respectively. The CA, η^* , and δ values for the Phase 3 and 4 blends that were ENVRM-aged are presented in Appendix C in Tables C-5 and C-7, respectively. There was appreciable difference in the aging characteristics of the asphalts and the asphalt-rubbers studied in Phase 4. For both the asphalts and asphalt-rubbers, the rate of carbonyl formation became constant after an initial more rapid rate region. This is shown in Figures 5-28 and 5-29 for Exxon AC-5 and the 10% TG-40, Exxon AC-5 blend, respectively. The aging rates for the Phase 4 blends are given in Table 5-6. Furthermore, the intercept of the aging

Figure 5-28: Aging rate plot for Exxon AC-5.

Figure 5-29: Aging rate plot for 10/90, TG -40/Exxon AC-5 blend.

Figure 5-30: Activation energy plot for Exxon AC-5, Phase 4 blends.

Table 5-6: Hardening Rates (HR), Aging Rates (AR), and Hardening Susceptibilities (HS) for the Phase 4 Blends

Sears Blend	Aging Temperature	Hardening Rate (1/day)	Aging Rate (CA/day)	Hardening Susceptibility (1/CA)	
Exxon AC-5	333K (140°F)	5.136e-3	1.318e-3	3.583	2.870
	353K (176°F)	4.332e-2	1.157e-2	3.597	
	358K (185°F)	6.120e-2	1.930e-2	2.909	
	363K (194°F)	1.018e-1	3.176e-2	3.194	
10% TG -40 Exxon AC-5 1550 rpm, 6 hour 464K (375°F) N ₂	333K (140°F)	4.199e-3	1.678e-3	1.583	
	353K (176°F)	1.889e-2	1.341e-2	1.422	
	358K (185°F)	2.571e-2	2.203e-2	1.156	
	363K (194°F)	6.099e-2	2.998e-2	1.980	
20% TG -40 Exxon AC-5 1550 rpm, 6 hour 464K (375°F) N ₂	333K (140°F)	2.444e-3	2.143e-3	7.916e-1	
	353K (176°F)	1.461e-2	1.404e-2	9.919e-1	
	358K (185°F)	2.254e-2	2.289e-2	1.023	
	363K (194°F)	4.950e-2	3.174e-2	1.506	
Exxon AC-10	333K (140°F)	6.229e-3	1.799e-3	3.562	3.038
	353K (176°F)	3.918e-2	1.490e-2	2.637	
	358K (185°F)	6.318e-2	2.034e-2	3.023	
	363K (194°F)	1.074e-1	3.289e-2	3.484	
10% TG -40 Exxon AC-10 1550 rpm, 6 hour 464K (375°F) N ₂	333K (140°F)	4.090e-3	1.501e-3	1.653	
	353K (176°F)	2.334e-2	1.403e-2	1.583	
	358K (185°F)	3.697e-2	2.240e-2	1.630	
	363K (194°F)	6.886e-2	3.296e-2	2.049	
20% TG -40 Exxon AC-10 1550 rpm, 6 hour 464K (375°F) N ₂	333K (140°F)	2.086e-3	1.840e-3	1.003	
	353K (176°F)	1.549e-2	1.354e-2	1.117	
	358K (185°F)	2.357e-2	2.210e-2	1.098	
	363K (194°F)	4.812e-2	3.094e-2	1.523	

Table 5-6: Hardening Rates (HR), Aging Rates (AR), and Hardening Susceptibilities (HS) for the Phase 4 Blends (Continued)

Sears Blend	Aging Temperature	Hardening Rate (1/day)	Aging Rate (CA/day)	Hardening Susceptibility (1/CA)	
Fina Demex Resin	333K (140°F)	3.965e-3	1.882e-3	1.871	2.254
	353K (176°F)	2.650e-2	1.499e-2	1.773	
	358K (185°F)	3.587e-2	1.831e-2	2.021	
	363K (194°F)	6.263e-2	2.722e-2	2.267	
10% TG -40 Fina Demex Resin 1550 rpm, 6 hours 464K (375°F), N ₂	333K (140°F)	3.470e-3	1.870e-3	1.463	
	353K (176°F)	1.660e-2	1.585e-2	1.230	
	358K (185°F)	2.246e-2	2.493e-2	9.074e-1	
	363K (194°F)	6.028e-2	3.775e-2	1.661	
20% TG -40 Fina Demex Resin 1550 rpm, 6 hours 464K (375°F), N ₂	333K (140°F)	1.794e-3	2.073e-3	4.997e-1	
	353K (176°F)	1.034e-2	1.458e-2	6.843e-1	
	358K (185°F)	1.707e-2	2.117e-2	7.989e-1	
	363K (194°F)	4.037e-2	3.513e-2	1.142	
Fina AC-10	333K (140°F)	8.613e-3	2.008e-3	4.140	4.488
	353K (176°F)	7.281e-2	2.114e-2	3.403	
	358K (185°F)	9.171e-2	2.005e-2	4.284	
	363K (194°F)	1.555e-1	3.387e-2	4.525	
10% TG -40 Fina AC-10 1550 rpm, 6 hours 464K (375°F), N ₂	333K (140°F)	7.438e-3	1.822e-3	2.009	
	353K (176°F)	4.109e-2	1.312e-2	3.034	
	358K (185°F)	5.564e-2	2.461e-2	2.263	
	363K (194°F)	8.193e-2	3.106e-2	2.629	
20% TG -40 Fina AC-10 1550 rpm, 6 hours 464K (375°F), N ₂	333K (140°F)	5.677e-3	1.910e-3	2.284	
	353K (176°F)	2.244e-2	1.294e-2	1.614	
	358K (185°F)	2.994e-2	2.884e-2	1.005	
	363K (194°F)	7.113e-2	3.991e-2	1.765	

Table 5-7: Intercepts of the Hardening Rate (HR), Aging Rate (AR), and Hardening Susceptibility (HS) Equations for the Phase 4 Blends

Sears Blend	Aging Temperature	Intercept of HR eq., (η^*) _o (poise)	Intercept of AR eq., CA _o	Intercept of HS eq., m (poise)	
Exxon AC-5	333K (140°F)	1,623	0.6631	159.8	282.9
	353K (176°F)	1,396	0.6143	157.3	
	358K (185°F)	1,288	0.6389	219.2	
	363K (194°F)	1,519	0.6266	206.4	
10% TG -40 Exxon AC-5 1550 rpm, 6 hours 464K (375°F) N ₂	333K (140°F)	3,822	0.7532	1,346	
	353K (176°F)	4,505	0.7842	1,467	
	358K (185°F)	3,553	0.7248	1,545	
	363K (194°F)	2,030	0.7666	462.2	
20% TG -40 Exxon AC-5 1550 rpm, 6 hours 464K (375°F) N ₂	333K (140°F)	9,669	0.7663	5,655	
	353K (176°F)	9,591	0.8603	4,188	
	358K (185°F)	7,582	0.7053	3,588	
	363K (194°F)	5,202	0.8449	1,515	
Exxon AC-10	333K (140°F)	2,592	0.6080	291.5	408.6
	353K (176°F)	2,478	0.5998	508.8	
	358K (185°F)	2,415	0.6456	353.4	
	363K (194°F)	2,818	0.6451	254.4	
10% TG -40 Exxon AC-10 1550 rpm, 6 hours 464K (375°F) N ₂	333K (140°F)	7,369	0.8038	2,282	
	353K (176°F)	7,592	0.7902	2,245	
	358K (185°F)	5,410	0.6984	1,753	
	363K (194°F)	3,614	0.6772	929.9	
20% TG -40 Exxon AC-10 1550 rpm, 6 hours 464K (375°F) N ₂	333K (140°F)	16,570	0.8331	7,408	
	353K (176°F)	16,280	0.8738	6,214	
	358K (185°F)	12,660	0.7745	5,293	
	363K (194°F)	8,727	0.8473	2,456	

Table 5-7: Intercepts of the Hardening Rate (HR), Aging Rate (AR), and Hardening Susceptibility (HS) Equations for the Phase 4 Blends (Continued)

Sears Blend	Aging Temperature	Intercept of HR eq., (η^*) _o (poise)	Intercept of AR eq., CA _o	Intercept of HS eq., m (poise)	
Fina Demex Resin	333K (140°F)	1,020	0.6705	302.7	221.2
	353K (176°F)	960.5	0.5822	341.7	
	358K (185°F)	894.7	0.6187	251.1	
	363K (194°F)	1,007	0.6394	240.0	
10% TG -40 Fina Demex Resin 1550 rpm, 6 hours 464K (375°F) N ₂	333K (140°F)	1,870	0.7357	688.3	
	353K (176°F)	1,969	0.7084	726.6	
	358K (185°F)	1,705	0.6838	911.4	
	363K (194°F)	872.9	0.7045	248.9	
20% TG -40 Fina Demex Resin 1550 rpm, 6 hours 464K (375°F) N ₂	333K (140°F)	3,820	0.7745	2,785	
	353K (176°F)	4,280	0.8453	2,432	
	358K (185°F)	3,263	0.6828	1,898	
	363K (194°F)	2,120	0.8191	837.3	
Fina AC-10	333K (140°F)	5,797	0.8083	215.4	147.1
	353K (176°F)	3,784	0.6270	455.8	
	358K (185°F)	4,446	0.7975	161.1	
	363K (194°F)	6,859	0.8260	169.2	
10% TG -40 Fina AC-10 1550 rpm, 6 hours 464K (375°F) N ₂	333K (140°F)	13,150	0.9281	2,843	
	353K (176°F)	14,430	1.017	690.3	
	358K (185°F)	9,856	0.8499	1,439	
	363K (194°F)	9,325	0.7142	1,435	
20% TG -40 Fina AC-10 1550 rpm, 6 hours 464K (375°F) N ₂	333K (140°F)	26,420	0.9815	3,182	
	353K (176°F)	34,620	1.114	5,985	
	358K (185°F)	26,250	0.8418	11,530	
	363K (194°F)	14,150	0.9481	2,695	

equation, CA_0 , shown in Table 5-7 was independent of aging temperature, or within the scatter of the data. Liu et al. (1996) similarly determined the temperature independence of CA_0 .

To determine the effect of rubber on the aging rate of an asphalt, semilog plots of r_{CA} versus T^{-1} were constructed. The relationship between r_{CA} versus T^{-1} , Equation 5-2, determines the activation energy. Figure 5-30 shows the results for Exxon AC-5 and blends. Note that the fit of the data in Figure 5-30 for Exxon AC-5 is exceptional. The fit of the data for the other asphalts was not as good, although by no means bad. Figure 5-30 shows that the effect of the rubber was to increase the aging rate of Exxon AC-5 at low-temperatures. The ENVRM aging rates at 333K (140°F) of the Phase 4 asphalts and asphalt-rubbers are given in Table 5-8. Overall, the effect of the rubber on the other asphalts studied was not definitive. The ENVRM aging rates at 333K (140°F) of Exxon AC-10 and Fina Demex Resin were between the ENVRM aging rates of the 10% and 20% rubber blends. The ENVRM aging rate of Fina AC-10 at 333K (140°F) was higher than the ENVRM aging rates of the 10% and 20% asphalt-rubber blends. The ENVRM aging rates for the 4 asphalts and 8 asphalt-rubbers of Phase 4 were all between the narrow range of 1.3×10^{-3} to 2.1×10^{-3} . The rubber had the largest effect on the Exxon AC-5, with the ENVRM aging rate increasing with the addition of rubber. For the other asphalts, the effect of the rubber was within the scatter of the data. Nonetheless, it can be said that the rubber did not drastically increase or drastically decrease the ENVRM aging rate.

The ENVRM aging rates at 333K (140°F) for the Phase 3 asphalts and asphalt-rubbers are tabulated in Table 5-9. The ENVRM aging rates at 333K (140°F) of the Exxon AC-5 blends are represented graphically in Figure 5-31. The Phase 3 results agree with the Phase 4 results in that the rubber increased the ENVRM aging rate of Exxon AC-5. For Exxon AC-10, results from both Phase 3 and Phase 4 indicate that the ENVRM aging rate of Exxon AC-10 was lowered by rubber concentrations of less than 10%. The Phase 3 and Phase 4 results of Fina AC-10 disagree, with the ENVRM aging rate of Fina AC-10 being lowered by the rubber in Phase 4 and raised by the rubber in 3 of 4 cases in Phase 3. Apparently, the effect of the rubber on the ENVRM aging rate of Fina AC-10 is within the noise of the data. As in Phase 4, the ENVRM aging rates in Phase 3 had a narrow range, from 1.3×10^{-3} to 2.4×10^{-3} . Once again, the rubber did not drastically increase or decrease the ENVRM aging rate of the asphalts.

Table 5-8: Aging Rate Data for Phase 4 Asphalts and Asphalt-Rubbers

Sears Blend (1550 rpm 6 hours 464K (375°F), N ₂)	POV Rate Eq. (POVRE) (From POV Aging Rates) (CA/day)	Extrapolated Aging Rate from POVRE at 333K (CA/day) × 10 ³	ENVRM Aging Rate at 333K (CA/day) × 10 ³	POV and ENV Rate Eq. (POVENVRE) (CA/day)	Extrapolated Aging Rates from POVENVRE at 333K (CA/day) × 10 ³
Exxon AC-5	AR=9.753+13* e ^(-12,950/T)	1.281	1.318	AR=6.828+13* e ^(-12,820/T)	1.325
10% TG -40 Exxon AC-5	AR=6.945+10* e ^(-10,330/T)	2.374	1.678	AR=5.033+12* e ^(-11,860/T)	1.742
20% TG -40 Exxon AC-5	AR=1.080+11* e ^(-10,470/T)	2.425	2.143	AR=4.909+11* e ^(-11,010/T)	2.179
Exxon AC-10	AR=4.315+10* e ^(-10,140/T)	2.609	1.799	AR=3.488+12* e ^(-11,720/T)	1.838
10% TG -40 Exxon AC-10	AR=4.241+11* e ^(-10,960/T)	2.188	1.501	AR=4.543+13* e ^(-12,630/T)	1.559
20% TG -40 Exxon AC-10	AR=1.539+11* e ^(-10,610/T)	2.270	1.840	AR=2.173+12* e ^(-11,560/T)	1.851
Fina AC-10	AR=4.728+5* e ^(-6,010/T)	6.919	2.008	AR=1.676+12* e ^(-11,420/T)	2.173
10% TG -40 Fina AC-10	AR=5.822+11* e ^(-11,080/T)	2.095	1.822	AR=3.841+12* e ^(-11,750/T)	1.850
20% TG -40 Fina AC-10	AR=8.715+15* e ^(-14,470/T)	1.199	1.910	AR=2.793+13* e ^(-12,410/T)	1.855
Fina Demex Resin	AR=3.588+7* e ^(-7,639/T)	3.950	1.882	AR=3.092+11* e ^(-10,890/T)	1.968
10% TG -40 Fina Demex Resin	AR=7.771+11* e ^(-11,130/T)	2.407	1.870	AR=1.626+13* e ^(-12,220/T)	1.910
20% TG -40 Fina Demex Resin	AR=1.028+12* e ^(-11,270/T)	2.091	2.073	AR=1.176+12* e ^(-11,320/T)	2.059

Figure 5-31: Aging rate plot for Exxon AC-5, Phase 3 blends.

Figure 5-32: Hardening rate plot for Exxon AC-10, Phase 4 blends.

Table 5-9: Aging Rates and Hardening Rates at 333K for Phase 3 Asphalts and Asphalt-Rubbers

Sears Blend (500 rpm, 12 hours 464K (375°F), N ₂)	Intercept of the HR Eq., (η^*) _o (poise)	ENVRM Hardening Rate at 333K (1/day) $\times 10^3$	Intercept of the AR Eq., Ca _o $\times 10$	ENVRM Aging Rate at 333K (CA/day) $\times 10^3$
Exxon AC-5	1,623	5.136	6.631	1.318
5% TG -40 - Exxon AC-5	4,085	5.435	7.029	1.830
10% TG -40 - Exxon AC-5	4,462	4.983	7.194	2.063
5% RS -40 - Exxon AC-5	2,325	4.656	6.979	1.546
10% RS -40 - Exxon AC-5	4,414	4.809	7.025	2.118
Exxon AC-10	2,592	6.229	6.080	1.799
5% TG -40 - Exxon AC-10	13,380	6.098	8.722	1.305
10% TG -40 - Exxon AC-10	14,190	5.492	9.510	1.594
5% RS -40 - Exxon AC-10	12,270	5.626	8.470	1.656
10% RS -40 - Exxon AC-10	13,730	4.947	9.832	1.400
Fina AC-10	5,797	8.613	8.083	2.008
5% TG -40 - Fina AC-10	10,740	7.639	8.703	1.959
10% TG -40 - Fina AC-10	14,940	6.446	8.971	2.288
5% RS -40 - Fina AC-10	10,560	7.372	8.168	2.411
10% RS -40 - Fina AC-10	12,260	6.177	8.601	2.407

Table 5-8 also lists the POV rate equations (POVRE) obtained from performing regression analysis on r_{CA} versus T^{-1} in Equation 5-2. This regression analysis included only the aging rates, r_{CA} , obtained from POV data. Using the POV rate equation, it is possible to extrapolate to the aging rate of a binder at 333K (140°F). These extrapolated values are given in the third column of Table 5-8. The extrapolated values for the asphalt-rubbers are as close, if not closer, to the ENVRM asphalt-rubber values as the extrapolated values for the asphalts are to the ENVRM asphalt values, although extrapolated predictions are rather poor. In the fifth column of Table 5-8 are the POV and ENV rate

equations (POENVRE) that were obtained by performing regression analysis on r_{CA} versus T^{-1} in Equation 5-2. This regression analysis included using the aging rate, r_{CA} , obtained from both POV and ENV data. The POENVRE equations were given as a comparison to the POVRE equations. In all cases the POENVRE extrapolations were reasonably close to the ENV aging rates. These results suggest that 1 atm air, high-temperature aging (below 363K (194°F)) can be used to extrapolate the aging rate at road temperature for either an asphalt or an asphalt-rubber binder, but that this extrapolation may not be highly accurate.

Definitive results on the effect of rubber on the hardening rate of an asphalt were obtained in Phase 3 and Phase 4. The hardening rates of the Phase 4 blends for the POV and ENVRM temperatures are listed in Table 5-6. As would be expected, the hardening rate increased with aging temperature. Like the results at 20 atm, the results of aging at 1 atm indicated that the intercept of the asphalt-rubber hardening rate equation, $(\eta^*)_0$, generally decreased with increasing aging temperature, Table 5-7. The $(\eta^*)_0$ of the asphalts aged at 1 atm were independent of aging temperature, Table 5-7.

Table 5-10 lists the hardening rates for the Phase 4 samples aged in the ENVRM at 333K (140°F). For the four asphalts studied, the addition of rubber decreased the hardening rate, with the hardening rate decreasing more at the 20% rubber level than the 10% rubber level. This is shown in Figure 5-32 for Exxon AC-10 and blends. Similar results were obtained for the Phase 3 asphalt-rubbers, Table 5-9, as shown in Figure 5-33 for Fina AC-10 and blends. Thus for the asphalts studied, the addition of the rubber was beneficial to the hardening properties of an asphalt at road temperatures.

Because roadway hardening is the property of interest, obtaining the hardening rate at several elevated temperatures and extrapolating to obtain the hardening rate at road temperature by using Equation 5-2 would seem like the logical thing to do. For asphalts, this concept works well. Figure 5-34 shows the plot of HR versus T^{-1} for Exxon AC-5. Similar results were obtained for the other asphalts studied. Table 5-10 lists the POV rate equations for the asphalts. The POV rate equations were obtained by performing regression analysis on hardening rate, HR , versus T^{-1} . This regression analysis included only the hardening rates obtained from the POV data. Using the POV rate equation, it is possible to extrapolate the hardening rate of the asphalts at 333K (140°F),

Table 5-10. The extrapolated values from the POV rate equation were reasonably close to the ENVRM values. For asphalts, the hardening susceptibility is independent of aging temperature and this allows the relationship between $\ln HR$ and T' in Equation 5-9 to plot linearly. The hardening susceptibility for Fina AC-10 is the slope of the $\ln \eta^*$ versus CA plot represented by Figure 5-35. In Figure 5-35, both ENVRM- and POV-aged samples are plotted, and all of the data lie on one distinct line regardless of aging temperature. Similar results were obtained for the other asphalts studied.

Table 5-10. Hardening Rate Data for Phase 4 Asphalts and Asphalt-Rubbers

Sears Blend (1550 rpm, 6 hours 464K (375°F), N ₂)	POV Rate Eq. (POVRE) (From POV Hardening Rates) (1/day)	Extrapolated Hardening Rate from POVRE at 333K (1/day) $\times 10^3$	ENVRM Hardening Rate at 333K (1/day) $\times 10^3$
Exxon AC-5	$HR=6.927+12^* e^{(-11,570/T)}$	5.726	5.136
10% TG -40 - Exxon AC-5			4.199
20% TG -40 - Exxon AC-5			2.444
Exxon AC-10	$HR=3.070+14^* e^{(-12,930/T)}$	4.281	6.299
10% TG -40 - Exxon AC-10			4.090
20% TG -40 - Exxon AC-10			2.086
Fina AC-10	$HR=6.094+10^* e^{(-9,713/T)}$	13.275	8.613
10% TG -40 - Fina AC-10			7.438
20% TG -40 - Fina AC-10			5.677
Fina Demex Resin	$HR=8.906+11^* e^{(-11,010/T)}$	3.954	3.965
10% TG -40 - Fina Demex Resin			3.470
20% TG -40 - Fina Demex Resin			1.794

Figure 5-33: Hardening rate plot for Fina AC-10, Phase 3 blends.

Figure 5-34: Activation energy plot (hardening rate) for Exxon AC-5.

Figure 5-35: Hardening susceptibility plot for Fina AC-10.

Figure 5-36: HS plot for 20/80, TG -40B/Fina AC-10, Phase 4 blend.

The 1 atm air results agreed with the 20 atm oxygen results in that the hardening susceptibility for asphalt-rubber was found to be dependent on the aging temperature. Figure 5-36 shows this for the 20% TG -40, Fina AC-10 blend. For each aging temperature, the data appear to lie on a distinct line. Similar results were obtained for the other asphalt-rubber blends studied. Because the hardening susceptibility of asphalt-rubber is dependent on the aging temperature, at the aging temperatures we have employed, a plot of $\ln HR$ versus T^{-1} is not linear. This is shown in Figure 5-37 for the 10% and 20% TG -40, Fina Demex Resin blends. This pattern, with the 363K (194°F) point being well above the trend line, was seen in 7 of the 8 asphalt-rubber blends studied. The break with linearity most likely indicates that the reaction mechanism changes at or around 363K (194°F). The presence of the rubber causes the reaction mechanism to change and also apparently causes the activation energy of the blend to be higher in the hotter temperature region. This is represented in Figure 5-37 by the slope definitely being steeper in the 358-363K (185-194°F) temperature region.

The non-linearity of the $\ln HR$ versus T^{-1} plot makes it impossible to use high-temperature aging to obtain a viscosity-based activation energy, E_{vis} , using Equation 5-9. Without E_{vis} , it is impossible to use Equation 5-9 to extrapolate the hardening rate at road temperature. On the other hand, the linearity of the plots below 353K (176°F) indicate that it may be feasible to use high-temperature aging below 353K (176°F) to obtain E_{vis} .

Examination of the molecular weight distribution of the aged samples supported the theory that there is a change in reaction mechanism at or around 363K (194°F). Figures 5-38 and 5-39 represent Exxon AC-10 blends from Phase 3 that were aged at 372K (210°F) or 333K (140°F). The molecular weight distributions in Figures 5-38 and 5-39 were recorded with an intrinsic viscosity (IV) detector. The previous GPC chromatograms of this chapter had been obtained using a refractive index detector. The samples in each figure were chosen because they had approximately the same viscosity. It is theorized that if the reaction mechanism is the same at the different temperatures, then samples of the same viscosity will also have the same molecular weight distribution. The molecular weight distribution of the samples in both Figure 5-38 and Figure 5-39 are not the same. In both cases, the molecular weight distribution in the 20 to 23 minute retention time region is higher for the samples aged at 372K (210°F). This would indicate that at the elevated POV temperature, the reaction mechanism between the rubber and asphalt is different from the reaction mechanism at 333K

Figure 5-37: Activation energy plot (HR) for Fina AC-10, Phase 4 blends.

Figure 5-38: GPC (IV) data for 5/95, TG -40B/Exxon AC-10, Phase 3 blend.

Figure 5-39: GPC (IV) data for 10/90, TG -40B/Exxon AC-10, Phase 3 blend.

(140°F). It appears that at 372K (210°F), the rubber molecules are attacked and broken down to form bigger molecules than the molecules produced by the reaction at 333K (140°F). Apparently, these bigger molecules do not raise the viscosity as much as the molecules produced at 333K (140°F) because the GPC chromatograms indicate that for approximately the same viscosity there are more of the bigger molecules present.

GPC analyses were also performed on other aged asphalts and asphalt-rubbers. These analyses were performed using both the intrinsic viscosity detector and the refractive index detector. The difference in how these detectors measure molecular weight distribution can be seen by comparing Figures 5-40 and 5-41 and Figures 5-42 and 5-43. Figures 5-40 and 5-41 represent Fina AC-10 asphalt samples that have been aged for varying lengths of time at 372K (210°F). Figures 5-42 and 5-43 represent 10% TG -40, Fina AC-10 asphalt-rubber samples that have also been aged for varying lengths of time at 372K (210°F).

The figures show that the RI detector has better resolution than the IV detector. However, the figures also show that the IV detector accentuates the high-molecular weight retention time region much better than the RI detector. This makes the IV detector ideal for analyzing the changes asphalt-rubber samples undergo during both curing and oxidizing.

The results in Figure 5-43 represent what happens to asphalt-rubber binder during aging at elevated POV temperatures. Figure 5-44 represents the same asphalt-rubber blend that was represented in Figure 5-43. However, in Figure 5-44 the blend has been aged at 333K (140°F). Comparing Figures 5-43 and 5-44 shows that the difference between the aging process at elevated and road temperatures, as measured by molecular weight distribution, is not all that drastic. Interestingly, the rubber and asphalt interact even at road conditions, although at a much slower rate. The rubber and asphalt interaction is represented in these figures by the 21 to 25 minute retention time region being filled in with aging time.

Just as the rubber and the asphalt interaction was asphalt dependent at high-temperature and high-pressure, it was also asphalt dependent at 333K (140°F) and 1 atm air. This can be seen by comparing Figure 5-44 with Figure 5-45. All of the aging variables and curing variables are the same except that Fina AC-10 is the base asphalt for the blend represented in Figure 5-44 and Exxon AC-5 is the base asphalt for the blend represented in Figure 5-45. Similarly, the rubber and asphalt

Figure 5-40: GPC (RI) data for Fina AC-10 aged at 372K.

Figure 5-41: GPC (IV) data for Fina AC-10 aged at 372K.

Figure 5-42: GPC (RI) data for 10/90, TG -40B/Fina AC-10 blend aged at 372K.

Figure 5-43: GPC (IV) data for 10/90, TG -40B/Fina AC-10 blend aged at 372K.

Figure 5-44: GPC (IV) data for 10/90, TG -40B/Fina AC-10 blend aged at 333K.

Figure 5-45: GPC (IV) data for 10/90, TG -40B/Exxon AC-5 blend aged at 333K.

interaction was dependent on the rubber concentration, Figures 5-46 and 5-47, and on the rubber source, Figures 5-43 and 5-47.

Figure 5-48 shows the effect of aging on a Sun 125 asphalt-rubber blend. This blend was not part of the Phase 3 or Phase 4 study, but was from a preliminary study. This blend was cured with the Sears mixer at 500 rpm under N_2 at 450K (350°F) for 1 hour. Sun 125 is a commercially available recycling agent which has an advertised composition of 0.10% asphaltenes, 13.50% polar aromatics, 70.90% naphthene aromatics, and 15.50% saturates. Its viscosity is approximately 2.0 poise at 333K (140°F). Such a low viscosity indicates a lack of heavy polar aromatics. The Sun Blend was oxidized at 366K (200°F) at 1 atm air. Figure 5-48 shows that there was little or no interaction between the rubber and Sun 125 during oxidation. This supports the earlier statement that heavy polar aromatics and asphaltenes must be present for the asphalt to devulcanize and depolymerize the rubber during oxidation.

Aging Index Results for Phase 3 and Phase 4

The aging index results calculated from the highest POV-temperature data strongly agreed with the aging index results calculated from the 333K (140°F) data. The aging index results at both elevated temperatures and 333K (140°F) were calculated using the following method. Hardening rate plots, $\ln \eta^*$ versus time, were constructed for both Phase 3 and Phase 4 blend data at 333K (140°F) and the highest POV-temperature. The highest POV-temperature was 372K (210°F) for the Phase 3 blends and 363K (194°F) for the Phase 4 blends. Regression analysis was performed on the plotted data and an equation of the form of Equation 5-10 was obtained:

$$\eta^* = (\eta^*)_0 \exp(HR t) \quad (5-10)$$

where $(\eta^*)_0$ is the intercept, HR is the hardening rate, and t is the time. The variables, HR and $(\eta^*)_0$, were obtained from the regression analysis and are given for the Phase 3 and Phase 4 blends in Table 5-11 and Table 5-12, respectively. The 333K (140°F) aging time was chosen to be 200 days, a time at which sufficient oxidation had occurred and one giving asphalt-rubber viscosities in the range of the viscosities of the POV-aged asphalt-rubber blends. For each asphalt and asphalt-rubber,

Figure 5-46: GPC (IV) data for 5/95, RS -40/Fina AC-10 blend aged at 372K.

Figure 5-47: GPC (IV) data for 10/90, RS -40/Fina AC-10 blend aged at 372K.

Figure 5-48: GPC (RI) data for 10/90, TG -40/Sun 125 blend aged at 367K.

Table 5-11: Aging Index for the Phase 3 Blends, Regressed η^*
 Calculated Using 8 Days at 372K and Using 200 Days at 333K

Sears Blend	Aging Temp	Intercept, $(\eta^*)_0$ (poise)	Hardenin g Rate (1/day)	Regres sed η^* (poise)	Tank η^* (poise)	Aging Index
Exxon AC-5	333K (140°F)	1,623	5.136e-3	4,533	636.3	7.12
	372K (210°F)	956.5	1.599e-1	3,437	636.6	5.40
5% TG -40 Exxon AC-5 500 rpm, 12 hours 464K (375°F) N ₂	333K (140°F)	4,085	5.435e-3	12,144	1,597	7.59
	372K (210°F)	2,826	1.579e-1	9,995	1,597	6.26
10% TG-40 Exxon AC-5 500 rpm, 12 hours 464K (375°F), N ₂	333K (140°F)	4,462	4.938e-3	11,980	1,734	6.91
	372K (210°F)	2,903	1.343e-1	8,535	1,734	4.92
5% RS -40 Exxon AC-5 500 rpm, 12 hours 464K (375°F), N ₂	333K (140°F)	2,325	4.656e-3	5,900	1,073	5.50
	372K (210°F)	1,545	1.428e-1	4,842	1,073	4.51
10% RS -40 Exxon AC-5 500 rpm, 12 hours 464K (375°F), N ₂	333K (140°F)	4,414	4.809e-3	11,549	1,557	7.42
	372K (210°F)	3,097	1.159e-1	7,827	1,557	5.03

Table 5-11: Aging Index for the Phase 3 Blends, Regressed η^*
 Calculated Using 8 Days at 372K and Using 200 Days at 333K (Continued)

Sears Blend	Aging Temp	Intercept, $(\eta^*)_0$ (poise)	Hardening Rate (1/day)	Regressed η^* (poise)	Tank η^* (poise)	Aging Index
Exxon AC-10	333K (140°F)	2,592	6.229e-3	9,009	952	9.46
	372K (210°F)	1,492	1.844e-1	6,523	952	6.85
5% TG -40 Exxon AC-10 500 rpm, 12 hours 464K (375°F), N ₂	333K (140°F)	13,380	6.098e-3	45,302	5,922	7.65
	372K (210°F)	18,730	1.260e-1	51,322	5,922	8.67
10% TG -40 Exxon AC-10 500 rpm, 12 hours 464K (375°F), N ₂	333K (140°F)	14,190	5.492e-3	42,561	5,306	8.02
	372K (210°F)	14,650	1.433e-1	46,101	5,306	8.69
5% RS -40 Exxon AC-10 500 rpm, 12 hours 464K (375°F), N ₂	333K (140°F)	12,270	5.626e-3	37,802	5,109	7.40
	372K (210°F)	11,170	1.580e-1	39,537	5,109	7.74
10% RS -40 Exxon AC-10 500 rpm, 12 hours 464K (375°F), N ₂	333K (140°F)	13,730	4.947e-3	36,928	4,895	7.54
	372K (210°F)	12,840	1.273e-1	35,551	4,895	7.26

Table 5-11: Aging Index for the Phase 3 Blends, Regressed η^*
 Calculated Using 8 Days at 372K and Using 200 Days at 333K (Continued)

Sears Blend	Aging Temp	Intercept, $(\eta^*)_0$ (poise)	Hardening Rate (1/day)	Regressed η^* (poise)	Tank η^* (poise)	Aging Index
Fina AC-10	333K (140°F)	5,797	8.613e-3	32,458	944	34.38
	372K (210°F)	2,421	2.728e-1	21,468	944	22.74
5% TG -40 Fina AC-10 500 rpm, 12 hours 464K (375°F), N ₂	333K (140°F)	10,740	7.639e-3	49,490	2,225	22.24
	372K (210°F)	7,881	2.400e-1	53,756	2,225	24.16
10% TG -40 Fina AC-10 500 rpm, 12 hours 464K (375°F), N ₂	333K (140°F)	14,940	6.446e-3	54,230	3,913	13.86
	372K (210°F)	9,283	2.007e-3	46,237	3,913	11.82
5% RS -40 Fina AC-10 500 rpm, 12 hours 464K (375°F), N ₂	333K (140°F)	10,560	7.372e-3	46,130	1,773	26.02
	372K (210°F)	6,734	2.416e-1	46,524	1,773	26.24
10% RS -40 Fina AC-10 500 rpm, 12 hours 464K (375°F), N ₂	333K (140°F)	12,260	6.177e-3	42,171	2,437	17.30
	372K (210°F)	7,588	1.981e-1	37,017	2,437	15.19

Table 5-12: Aging Index for the Phase 4 Blends, Regressed η^*
 Calculated Using 24 Days at 363K and Using 200 Days at 333K

Sears Blend	Aging Temp	Intercept, $(\eta^*)_0$ (poise)	Hardening Rate (1/day)	Regressed η^* (poise)	Tank η^* (poise)	Aging Index
Exxon AC-5	333K (140°F)	1,623	5.136e-3	4,533	636	7.13
	363K (194°F)	1,519	1.018e-1	17,483	636	27.49
10% TG -40 Exxon AC-5 1550 rpm, 6 hours 464K (375°F), N ₂	333K (140°F)	3,822	4.199e-3	8,851	1,498	5.91
	363K (194°F)	2,030	6.099e-2	8,774	1,498	5.86
20% TG -40 Exxon AC-5 1550 rpm, 6 hours 464K (375°F), N ₂	333K (140°F)	9,669	2.444e-3	15,764	4,661	3.38
	363K (194°F)	5,202	4.950e-2	17,065	4,661	3.66
Exxon AC-10	333K (140°F)	2,592	6.229e-3	9,009	952	9.46
	363K (194°F)	2,818	1.074e-1	37,100	952	38.97
10% TG -40 Exxon AC-10 1550 rpm, 6 hours 464K (375°F), N ₂	333K (140°F)	7,369	4.090e-3	16,698	2,554	6.54
	363K (194°F)	3,614	6.886e-2	18,868	2,554	7.39
20% TG -40 Exxon AC-10 1550 rpm, 6 hours 464K (375°F), N ₂	333K (140°F)	16,600	2.086e-3	25,148	8,107	3.10
	363K (194°F)	8,727	4.812e-2	27,696	8,107	3.42

Table 5-12: Aging Index for the Phase 4 Blends, Regressed η^*
 Calculated Using 24 Days at 363K and Using 200 Days at 333K (Continued)

Sears Blend	Aging Temp	Intercept, $(\eta^*)_0$ (poise)	Hardening Rate (1/day)	Regressed η^* (poise)	Tank η^* (poise)	Aging Index
Fina Demex Resin	333K (140°F)	1,020	3.965e-3	2,254	239	9.43
	363K (194°F)	1,007	6.263e-2	4,527	239	18.94
10% TG -40 Fina Demex Resin 1550 rpm, 6 hours 464K (375°F), N ₂	333K (140°F)	1,870	3.470e-3	3,743	1,385	2.70
	363K (194°F)	872.9	6.028e-1	3,709	1,385	2.68
20% TG -40 Fina Demex Resin 1550 rpm, 6 hours 464K (375°F), N ₂	333K (140°F)	3,820	1.794e-3	5,469	2,368	2.31
	363K (194°F)	2,120	4.037e-2	5,586	2,368	2.36
Fina AC-10	333K (140°F)	5,797	8.613e-3	32,458	944	34.38
	363K (194°F)	6,859	1.555e-1	286,449	944	303.4
10% TG -40 Fina AC-10 1550 rpm, 6 hours 464K (375°F), N ₂	333K (140°F)	13,150	7.438e-3	58,208	2,820	20.64
	363K (194°F)	9,325	8.193e-2	66,621	2,820	23.62
20% TG -40 Fina AC-10 1550 rpm, 6 hours 464K (375°F), N ₂	333K (140°F)	26,420	5.677e-3	82,230	7,856	10.47
	363K (194°F)	14,150	7.113e-2	78,010	7,856	9.93

the appropriate HR and $(\eta^*)_0$ for the 333K (140°F) data, and a time of 200 days was used in Equation 5-10 to calculate a regressed viscosity. The regressed viscosity values at 333K (140°F) are given in Tables 5-11 and 5-12. Next, for each asphalt and asphalt-rubber, the regressed viscosity was divided by the tank viscosity to obtain a 333K (140°F) aging index, Tables 5-11 and 5-12. To obtain a comparison aging index at the highest POV-temperature, an aging time was chosen which gave asphalt-rubber aging index values that were very similar to the 333K (140°F) aging index values. For the Phase 3 blends, the aging time was chosen to be 8 days at 372K (210°F), and for Phase 4 blends, the aging time was chosen to be 24 days at 363K (194°F). These times and the appropriate HR and $(\eta^*)_0$ for the highest POV-temperature data were used in Equation 5-10 to calculate a regressed viscosity. As before, the regressed complex viscosity was divided by the tank complex viscosity to obtain an aging index. Both the regressed viscosity and the high-temperature aging index values are given in Tables 5-11 and 5-12.

Surprisingly, the high-temperature viscosity-based aging index is quite adept at ranking the viscosity performance at road temperatures. Figures 5-49 and 5-50 graphically compare the aging index results of the high-temperature and 333K (140°F) data. Figure 5-49 represents the Phase 3 blends and Figure 5-50 represents the Phase 4 blends. In both Figure 5-49 and Figure 5-50, the points representing the asphalt-rubber blends have a linear trend. Admittedly, there is an S-shaped region in Figure 5-49, but all these points represent Exxon AC-5 and Exxon AC-10 blends. The chemical composition of the Exxon AC-5 and Exxon AC-10 asphalt is quite similar and may explain the inability of the aging index test to definitively rank the Exxon blends. Furthermore, the difference in rubber concentration, 5%, used in Phase 3 was not very large. In Phase 4 a larger rubber concentration difference, 10%, was employed and the aging index at 363K (194°F) perfectly ranked the asphalt-rubber blends according to the 333K (140°F) aging index rank of the blends, Figure 5-50. For the Phase 4 results, the higher the percent rubber, the lower the aging index. Similarly, Shih et al. (1996) determined that the viscosity aging index decreased with increasing rubber content.

Please note that in both Figure 5-49 and 5-50, the asphalts do not lie on the linear trend line of the asphalt-rubber blends. Furthermore, the Phase 3 asphalt points are slightly below the linear line and the Phase 4 asphalt points are way above the trend line, with 3 of the 4 points being off the plot. The inability of the aging index test to simultaneously rank both asphalts and asphalt-rubbers supports

Figure 5-49: Aging index plot for Phase 3 blends.

Figure 5-50: Aging index plot for Phase 4 blends.

the theory that there is a change in the asphalt-rubber oxidation mechanism between 333K (140°F) and approximately 363K (194°F) that does not occur in the asphalt oxidation mechanism between these two temperatures.

Phase 5 Results

To thoroughly study the effect of curing on the oxidization properties of asphalt-rubber, an aging study was conducted on the high-shear blends that were produced in the Silverson study and discussed in Chapter 4, Table 4-3. This study also included Neste-Wright LTR10, a commercially available asphalt-rubber that is supposedly Exxon AC-10 base -but is suspected to be perhaps an AC-5 for comparison purposes. The Phase 5 samples were aged in the POV at 353, 358, and 363K (176, 185, and 194°F) with 1 atm of air. The CA , η^* , and δ values for the Phase 5 blends are presented in Table C-8 of Appendix C.

The aging rates of the Phase 5 asphalts and asphalt-rubbers are given in Table 5-13. Figure 5-51 is the aging rate plot for the Exxon AC-10 blend with the most common curing conditions: 10% TG -10, 4000 rpm, 533K (500°F), and is representative of the aging rate plots of the other Silverson asphalt-rubber binders. The aging rates increased with aging temperature in all cases except the Exxon AC-10 blend of 20% TG -10, 4000 rpm, 533K (500°F), Table 5-13. For this blend, FTIR analysis was performed twice and the average values plotted and regressed to obtain the aging rates. No explanation is given for this anomaly except that the amount of rubber present in 20% rubber samples makes them hard to analyze. Like the Phase 2 and 4 results, the intercept of the aging equation, CA_0 , for an asphalt-rubber was found to be independent of the aging temperature within the scatter of the data, Table 5-14. Plots of $\ln r_{CA}$ versus T^{-1} were constructed and regression analysis was performed as in Equation 5-5 for the POV aged Phase 5 Silverson blends. Figure 5-52 is a $\ln r_{CA}$ versus T^{-1} plot of some of the Exxon blends. The results of the regression analysis are given in the second column of Table 5-15. The equations in these tables were used to extrapolate to the aging rate at road conditions, 333K (140°F), with the extrapolated rates given in the third column of Table 5-15. The Silverson blends have not been fully aged at 333K (140°F). However, the aging rates at 333K (140°F) of the base asphalts were available from Phase 4 of this study, and are listed in the fourth column of Table 5-15. Additionally, the aging rate of the Supercritical (SC) Asphalt is

Figure 5-51: Aging rate plot for 2/13/96, Phase 5 blend.

Figure 5-52: Activation energy plot for Exxon AC-10, Phase 5 blends and LTR10.

Table 5-13: Hardening Rates (HR), Aging Rates (AR), and Hardening Susceptibilities (HS) for the Phase 5 Blends

Silverson Blends (Cured Under N ₂ for 6.5 hours)	Aging Temperature	Hardenin g Rate (1/day) × 10 ²	Aging Rate (CA/day) × 10 ²	Hardening Susceptibility (1/CA)	
10% TG -10 Exxon AC-10 4000 rpm - 505K (450°F)	353K (176°F)	3.189	1.401	2.280	
	358K (185°F)	3.804	2.301	1.654	
	363K (194°F)	8.070	3.395	2.266	
10% TG -10 Exxon AC-10 4000 rpm - 533K (500°F)	353K (176°F)	3.453	1.399	2.462	
	358K (185°F)	4.271	2.229	1.898	
	363K (194°F)	9.073	3.130	2.953	
10% TG -10 Exxon AC-10 8000 rpm - 533K (500°F)	353K (176°F)	4.243	1.665	2.489	
	358K (185°F)	4.576	2.692	1.699	
	363K (194°F)	9.737	3.464	2.802	
10% TG -40 Exxon AC-10 4000 rpm - 533K (500°F)	353K (176°F)	4.115	1.761	2.328	
	358K (185°F)	4.505	2.546	1.757	
	363K (194°F)	8.333	3.571	2.332	
10% TG -10 Exxon / Sun AC-5 4000 rpm - 533K (500°F)	353K (176°F)	3.064	1.509	2.006	
	358K (185°F)	4.211	2.460	1.703	
	363K (194°F)	8.761	3.721	2.324	
20% TG -10 Exxon AC-10 4000 rpm - 533K (500°F)	353K (176°F)	3.110	1.434	2.168	
	358K (185°F)	3.948	2.788	1.331	
	363K (194°F)	7.252	2.637	2.708	
Neste-Wright, Liquefied Tire Rubber 10 (LTR10),	353K (176°F)	3.856	1.439	2.685	
	358K (185°F)	6.044	2.063	2.926	
	363K (194°F)	7.992	2.807	2.863	
Supercritical (SC) Asphalt	333K (140°F)	0.5552	0.1558	2.855	2.305
	353K (176°F)	3.481	1.338	2.582	
	358K (185°F)	5.811	2.111	2.640	
	363K (194°F)	7.727	3.328	2.103	

Table 5-13: Hardening Rates (HR), Aging Rates (AR), and Hardening Susceptibilities (HS) for the Phase 5 Blends (Continued)

Silverson Blends (Cured Under N ₂ for 6.5 hours)	Aging Temperature	Hardening Rate (1/day) ×10 ²	Aging Rate (CA/day) ×10 ²	Hardening Susceptibility (1/CA)
10% TG -10 Fina Demex Resin 4000 rpm - 505K (450°F)	353K (176°F)	1.368	1.402	0.9626
	358K (185°F)	0.9909	1.960	0.5133
	363K (194°F)	2.132	3.338	0.6117
10% TG -10 Fina Demex Resin 4000 rpm - 533K (500°F)	353K (176°F)	1.487	1.509	0.9904
	358K (185°F)	1.893	1.860	1.017
	363K (194°F)	3.772	3.201	1.163
10% TG -10 Fina Demex Resin 8000 rpm - 533K (500°F)	353K (176°F)	2.036	1.697	1.191
	358K (185°F)	2.873	2.541	1.075
	363K (194°F)	4.954	3.836	1.309
10% TG -40 Fina Demex Resin 4000 rpm - 533K (500°F)	353K (176°F)	1.932	1.495	1.246
	358K (185°F)	2.318	2.043	1.132
	363K (194°F)	4.127	3.256	1.223
10% TG -10 Fina AC-5 4000 rpm - 533K (500°F)	353K (176°F)	3.019	1.972	1.536
	358K (185°F)	4.084	2.900	1.402
	363K (194°F)	7.881	4.203	1.858
20% TG -10 Fina Demex Resin 4000 rpm - 533K (500°F)	353K (176°F)	1.664	1.409	1.514
	358K (185°F)	2.538	2.394	1.066
	363K (194°F)	3.266	2.831	1.158
10% TG -10 SC Asphalt 4000 rpm - 505K (450°F)	353K (176°F)	1.247	1.279	0.9742
	358K (185°F)	3.463	2.276	1.515
	363K (194°F)	2.489	3.258	0.7585
10% TG -10 SC Asphalt 4000 rpm - 533K (500°F)	353K (176°F)	2.507	1.492	1.664
	358K (185°F)	3.991	2.456	1.622
	363K (194°F)	4.083	3.821	1.070

Table 5-14: Intercepts of the Hardening Rate (HR), Aging Rate (AR), and Hardening Susceptibility(HS) Equations for the Phase 5 Blends

Silverson Blends (Cured Under N ₂ for 6.5 hours)	Aging Temperature	Intercept of HR eq., (η^*) ₀ (poise)	Intercept of AR eq., CA ₀ ×10	Intercept of HS eq., m (poise)
10% TG -10 Exxon AC-10 4000 rpm - 505K (450°F)	353K (176°F)	4,360	6.996	883.4
	358K (185°F)	5,322	7.062	1,655
	363K (194°F)	4,290	7.092	913.1
10% TG -10 Exxon AC-10 4000 rpm - 533K (500°F)	353K (176°F)	3,628	7.132	628.3
	358K (185°F)	4,577	7.549	1,100
	363K (194°F)	3,865	7.757	382.7
10% TG -10 Exxon AC-10 8000 rpm - 533K (500°F)	353K (176°F)	3,098	6.718	594.6
	358K (185°F)	4,730	7.331	1,362
	363K (194°F)	3,585	7.970	386.2
10% TG -40 Exxon AC-10 4000 rpm - 533K (500°F)	353K (176°F)	2,713	6.282	630.9
	358K (185°F)	4,055	7.044	1,184
	363K (194°F)	3,789	6.766	781.8
10% TG -10 Exxon / Sun AC-5 4000 rpm - 533K (500°F)	353K (176°F)	2,300	7.176	549.7
	358K (185°F)	3,094	7.685	843.0
	363K (194°F)	2,357	7.073	463.9
20% TG -10 Exxon AC-10 4000 rpm - 533K (500°F)	353K (176°F)	5,033	8.189	853.4
	358K (185°F)	5,682	8.082	2,024
	363K (194°F)	5,417	9.387	433.9
Neste-Wright, Liquefied Tire Rubber 10 (LTR10)	353K (176°F)	1,549	8.263	168.2
	358K (185°F)	1,151	8.037	109.9
	363K (194°F)	902.8	8.397	80.92
Supercritical (SC) Asphalt	333K (140°F)	2,102	6.700	344.8
	353K (176°F)	2,159	6.344	423.9
	358K (185°F)	1,709	5.604	405.2
	363K (194°F)	1,579	5.068	704.9

556.8

Table 5-14: Intercepts of the Hardening Rate (HR), Aging Rate (AR), and Hardening Susceptibility(HS) Equations for the Phase 5 Blends (Continued)

Silverson Blends (Cured Under N ₂ for 6.5 hours)	Aging Temperature	Intercept of HR eq., (η^*) _o (poise)	Intercept of AR eq., CA _o ×10	Intercept of HS eq., m (poise)
10% TG -10 Fina Demex Resin 4000 rpm - 505K (450°F)	353K (176°F)	918.1	6.313	503.7
	358K (185°F)	1,231	6.567	876.5
	363K (194°F)	1,231	5.713	880.9
10% TG -10 Fina Demex Resin 4000 rpm - 533K (500°F)	353K (176°F)	754.2	6.219	406.7
	358K (185°F)	804.6	7.078	390.9
	363K (194°F)	722.7	6.211	353.7
10% TG -10 Fina Demex Resin 8000 rpm - 533K (500°F)	353K (176°F)	658.1	6.389	308.6
	358K (185°F)	729.9	6.250	382.1
	363K (194°F)	742.7	6.107	330.3
10% TG -40 Fina Demex Resin 4000 rpm - 533K (500°F)	353K (176°F)	598.0	6.268	278.0
	358K (185°F)	713.4	6.667	335.9
	363K (194°F)	699.5	5.804	351.9
10% TG -10 Fina AC-5 4000 rpm - 533K (500°F)	353K (176°F)	1,551	6.710	552.0
	358K (185°F)	1,956	6.779	759.2
	363K (194°F)	1,691	6.422	518.6
20% TG -10 Fina Demex Resin 4000 rpm - 533K (500°F)	353K (176°F)	1,125	8.018	308.3
	358K (185°F)	992.8	7.990	422.3
	363K (194°F)	1,295	8.511	482.3
10% TG -10 SC Asphalt 4000 rpm - 505K (450°F)	353K (176°F)	4,352	7.343	2,129
	358K (185°F)	3,067	6.973	1,069
	363K (194°F)	5,524	7.142	3,223
10% TG -10 SC Asphalt 4000 rpm - 533K (500°F)	353K (176°F)	2,925	7.287	874.9
	358K (185°F)	2,536	7.366	768.8
	363K (194°F)	4,368	7.262	2,077

Table 5-15: Aging Rate Data for the Phase 5 Blends

Curing Date	Silverson Blends (Cured Under N ₂ for 6.5 hours)	POV Rate Eq. (POVRE) (From POV Aging Rates) (CA/day)	Extrapolated Aging Rate from POVRE at 333 K (CA/day) x 10 ³	Actual Aging Rate at 333K (CA/day) x 10 ³
	Exxon AC-10	$AR=4.315+10 \cdot e^{(-10,140/T)}$	2.609	1.799
2/5/96	10% TG -10 - Exxon AC-10 4000 rpm, 505K (450°F)	$AR=1.317+12 \cdot e^{(-11,360/T)}$	2.045	
2/13/96	10% TG -10 - Exxon AC-10 4000 rpm, 533K (500°F)	$AR=7.292+10 \cdot e^{(-10,330/T)}$	2.493	
2/23/96	10% TG -10 - Exxon AC-10 8000 rpm, 533K (500°F)	$AR=6.414+9 \cdot e^{(-9,408/T)}$	3.490	
2/24/96	10% TG -40 - Exxon AC-10 4000 rpm, 533K (500°F)	$AR=2.504+9 \cdot e^{(-9,068/T)}$	3.781	
2/27/96	10% TG -10-Exxon / Sun AC-5 4000 rpm, 533K (500°F)	$AR=2.643+12 \cdot e^{(-11,580/T)}$	2.120	
2/29/96	20% TG -10 - Exxon AC-10 4000 rpm, 533K (500°F)	$AR=7.365+7 \cdot e^{(-7,855/T)}$	4.240	
	Neste-Wright, LTR10	$AR=5.038+8 \cdot e^{(-8,572/T)}$	3.371	
	Supercritical (SC)Asphalt	$AR=3.130+12 \cdot e^{(-11,690/T)}$	1.805	1.558
3/18/96	10% TG -10 - SC Asphalt 4000 rpm, 505K (450°F)	$AR=7.644+12 \cdot e^{(-12,000/T)}$	1.738	

Table 5-15: Aging Rate Data for the Phase 5 Blends (Continued)

Curing Date	Silverson Blends (Cured Under N ₂ for 6.5 hours)	POV Rate Eq. (POVRE) (From POV Aging Rates) (CA/day)	Extrapolated Aging Rate from POVRE at 333K (CA/day) x 10 ³	Actual Aging Rate at 333K (CA/day) × 10 ³
3/19/96	10% TG -10 - SCAsphalt 4000 rpm, 533K (500°F)	$AR=1.027+13*e^{(-12,060/T)}$	1.951	
	Fina Demex Resin	$AR=3.588+7*e^{(-7,639/T)}$	3.950	1.882
3/3/96	10% TG -10 - Fina Demex Resin 4000 rpm, 505K (450°F)	$AR=6.276+11*e^{(-11,110/T)}$	2.064	
3/7/96	10% TG -10 - Fina Demex Resin 4000 rpm, 533K (500°F)	$AR=9.755+9*e^{(-9,624/T)}$	2.776	
3/8/96	10% TG -10 - Fina Demex Resin 8000 rpm, 533K (500°F)	$AR=1.229+11*e^{(-10,460/T)}$	2.844	
3/9/96	10% TG -40 - Fina Demex Resin 4000 rpm, 533K (500°F)	$AR=2.672+10*e^{(-9,973/T)}$	2.667	
3/10/96	10% TG -10 - Fina AC-5 4000 rpm, 533K (500°F)	$AR=1.700+10*e^{(-9,705/T)}$	3.793	
3/13/96	20% TG -10 - Fina Demex Resin 4000 rpm, 533K (500°F)	$AR=1.601+9*e^{(-8,969/T)}$	3.254	

listed because it was also aged at 333K (140°F). The CA, η^* , and δ values of the Supercritical Asphalt aged at 333K (140°F) are presented in Table C-9 of Appendix C.

The extrapolated values for the Silverson blends were always higher than the ENVRM aging rate of the base asphalt, Table 5-15. The general trend of the data is that the higher the extent of curing, the higher the extrapolated aging rate. For the Exxon AC-10 blends, identified by their relation to the most common curing conditions, the rank would be 505K (450°F), most common, and 8000 rpm, for the lowest to the highest extent of curing. The extrapolated aging rate increased accordingly from 2.05×10^{-3} for the blend at 505K (450°F) (2/5/96), to 2.49×10^{-3} for the blend of most common conditions (2/13/96), and to 3.49×10^{-3} for the blend at 8000 rpm, (2/23/96). The extrapolated aging rates of the Fina Demex Resin and Supercritical blends also increased with the extent of curing in the same manner.

The LTR10 asphalt-rubber had an extrapolated aging rate of 3.37×10^{-3} , very close but slightly lower than the aging rate of 3.49×10^{-3} for the Exxon AC-10 blend at 8000 rpm. If the above analysis is correct, then the LTR10 asphalt-rubber should have a slightly higher extrapolated aging rate than the 2/23/96 blend, Table 4-1, because results from the previous chapter showed that the extent of curing of the LTR10 blend was slightly greater than the 2/23/96 blend. Apparently, the difference between the extent of curing of these two blends is within the scatter of the data.

Comparing the blends of 2/13/96 and 2/24/96 gives the effect of mesh size on the aging rate of the Exxon AC-10 blends. The blend of 2/24/96 has an extrapolated aging rate of 3.781, more than 50% higher than the extrapolated aging rate of the blend of 2/13/96. The large increase in aging rate is explained by the extent of curing. The smaller rubber particles of blend 2/24/96 apparently interact more with the asphalt during curing than the larger particles of blend 2/13/96, thus allowing for a higher extent of curing. The results for the Fina Demex Resin blends disagreed with the Exxon results. For the Fina Demex Resin blends, the -40 mesh blend of 3/9/96 had a slightly lower aging rate than the -10 mesh blend of 3/7/96. This is most likely explained by the fact that during the curing process, the lighter Fina Demex Resin can diffuse into a larger -10 mesh equally as well as it can diffuse into a smaller -40 mesh particle. Thus for the lighter Fina Demex Resin, the particle size is not the limiting factor relative to the extent of curing. That is, the extent of curing of the blend of 3/7/96 and the blend of 3/9/96 are probably almost the same and thus, they have similar aging rates.

The effect of asphalt composition for the Exxon AC-10 blends is shown by comparing the blends of 2/13/96 and 2/27/96, Table 5-15. From Chapter 4, it is known that the Sun 125, a light molecular weight recycling agent present in blend 2/27/96, probably allowed the extent of curing to be greater for the blend of 2/27/96 than the blend of 2/13/96 (Tables 4-1 and 4-3). Interestingly, the aging rate of the blend of 2/27/96 was lower than the aging rate of the blend of 2/13/96. This indicates that the Sun 125 more than made up for increasing the extent of curing by lowering the aging rate of the base asphalt to a greater degree. Recycling agents such as Sun 125 have been documented to improve the hardening characteristics of asphalts (Chaffin et al., 1995). The effect of the Sun 125 would indicate that the oxidizing characteristics of an asphalt-rubber binder are more dependent on the base asphalt than the extent of curing, at least with high-cure binders produced with the Silverson Mixer.

The aging rate of the Fina AC-5 based blend of 3/10/96 was higher than the aging rate of the comparable Fina Demex Resin blend of 3/7/96, Table 5-15. The Fina AC-5 was produced by adding the higher molecular weight Fina AC-10 to the Fina Demex Resin. The heavier Fina AC-10 most likely did not allow the extent of curing of the blend of 3/10/96 to be as great as the extent of curing of the blend of 3/7/96. However, the heavier Fina AC-10 more than made up for lowering the extent of curing by worsening the aging characteristics of the base asphalt to a larger degree. Thus once again, the modification of the base asphalt was more important than the extent of curing relative to the aging rate of an asphalt-rubber binder.

The effect of mesh size on the Exxon AC-10 blends was to increase the extrapolated aging rate, Table 5-15. The results for the 20% TG -10, Exxon AC-10 blend of 2/29/96 are suspect since the aging rate at 358K (185°F) was lower than the aging rate at 363K (194°F), Table 5-13. Nonetheless, the regression analysis predicted that the aging rate at 333K (140°F) of Exxon AC-10, 1.80×10^{-3} , would be increased by adding rubber, with the extrapolated aging rates at 333K (140°F) for the 10% blend of 2/13/96 and the 20% blend of 2/29/96 being 2.49×10^{-3} to 4.24×10^{-3} , respectively. Interestingly enough, the incremental increase is 0.694 and 0.878. Apparently, increasing the rubber concentration is approximately proportional to increasing the aging rate. Similar results were obtained for the Fina Demex Resin blends, Table 5-15.

The hardening rates for the Exxon AC-10 Silverson blends and the LTR10 asphalt-rubber

increased with increasing aging temperature, Table 5-13. The hardening rates of 5 out of the 6 Fina Demex Resin Silverson blends increased with aging temperature, Table 5-13. The one exception was the blend of 3/3/96. Figure 5-53 is the hardening rate plot for the blend of 2/13/96; 10% TG -10, Exxon AC-10, 4000 rpm, 533K (500°F), and is representative of the hardening rate plots of the other Exxon AC-10 and Fina Demex Resin Silverson blends. Note, that as in Phase 4, the hardening rate, the slope on the plot increases from 358K (185°F) to 363K (194°F). Figure 5-54 is the $\ln HR$ versus T^{-1} plot of the 2/13/96 blend. The 363K (194°F) data point lies well above the 353-358K (176-185°F) trendline in Figure 5-54. Similar behavior was present in all but one of the Exxon AC-10 and Fina Demex Resin Silverson blends. As before, these results indicate that the reaction mechanism for asphalt-rubber apparently changes above 353K (176°F). Interestingly, the $\ln HR$ versus T^{-1} plot of the LTR10 blend, the highest cured blend, was the most linear, Figure 5-55.

The intercept of the hardening rate equation, $(\eta^*)_0$, for the Silverson blends was independent of the aging temperature, within the scatter of the data, Table 5-14. This contradicts the Phase 2 and Phase 4 findings which were that the $(\eta^*)_0$ of asphalt-rubber was dependent on aging temperature. For asphalts, the $(\eta^*)_0$ of the asphalts studied was found to be independent of aging temperature in Phases 2, 4, and 5. Apparently, the higher the extent of curing, the closer an asphalt-rubber comes to behaving like an asphalt, and the lesser the results of earlier rubber aging studies are applicable.

The hardening rates of the Supercritical (SC) Asphalt behaved differently than the other Silverson blends. The hardening rate of the blend of 3/18/96; 10%TG -10 SC asphalt, 4000 rpm, 505K (450°F), was higher at 358K (185°F) than at 363K (190°F), Table 5-13. To verify these results, the viscosities of the 3/18/96 samples were run twice. Both sets of viscosities agreed and the average values were plotted in Figure 5-56 and used to obtain the hardening rates. The blend of 3/19/96 at 533K (500°F) showed similar behavior. In fact, the $\ln HR$ versus T^{-1} plots for the 3/18/96 and 3/19/96 blend show that the 363K (194°F) data point lies well below the 353-358K (176-185°F) trendline. Figure 5-57 shows this for the blend of 3/18/96.

Because the results of Phase 3 and Phase 4 indicated that a high-temperature aging index can properly rank the asphalt-rubbers with respect to their road temperature aging index, an aging index was calculated for the Silverson blends and LTR10. To calculate the Silverson and LTR10 aging index, the highest POV-temperature, 363K (194°F), data were utilized. Regression analysis was

Figure 5-53: Hardening rate plot for 2/13/96, Phase 5 blend.

Figure 5-54: Activation energy plot (HR) for 2/13/96, Phase 5 blend.

Figure 5-55: Activation energy plot (HR) for LTR10.

Figure 5-56: Hardening rate plot for 3/18/96, Phase 5 blend.

Figure 5-57: Activation energy plot (HR) for 3/18/96, Phase 5 blend.

performed on the plotted data and Equation 5-10 was employed. The constants for the Silverson blends and LTR10 are given in Table 5-13 and Table 5-14. To be consistent with the aging index of the Phase 4 results, the aging time was chosen to be 24 days at 363K (194°F). For each Phase 5 blend, the appropriate HR and $(\eta^*)_0$ for the 363K (194°F) data and a time of 24 days were used in Equation 5-6 to calculate a regressed viscosity. Next, for each Phase 5 blend, the regressed viscosity was divided by the tank viscosity to obtain an aging index, Table 5-16. Note in Table 5-16 that some of the Phase 4 aging index numbers have been listed for comparison purposes.

The results in Table 5-16 are quite informative. Generally, the higher the extent of curing the higher the aging index. For example, ranking the Exxon AC-10 blends relative to extent of curing gives; 2/5/96, 2/13/96, and 2/23/96. The aging index numbers were 16.83, 24.12, and 29.09, respectively. Similarly, the Fina Demex Resin blends and the Supercritical Asphalt blends were ranked by the extent of curing with respect to the aging index. The extent of curing of the 10% TG -40 blends cured with the Sears mixer was lower than the Silverson blends and thus, both the

Exxon and Fina Demex Resin, Sears blends had lower aging indexes than the Silverson blends, Table 5-16. These results agree with the extrapolated aging rate results which indicated the higher the extent of curing, the higher the aging rate. On the other hand, LTR10 had an aging index of 13.42, a value lower than any of the Exxon AC-10 Silverson blends. The aging index value of LTR10 should be higher than any of the aging index values of the Exxon AC-10 Silverson blends because it has been cured to a greater degree than any of the Exxon AC-10 Silverson blends.

The effect of rubber on the Exxon AC-10 blends was to lower the aging index, both for the Silverson blends and the Sears blends, Table 5-16. The aging index of 10% TG -10WT, Exxon AC-10 blend of 2/13/96, 24.12, was higher than the 20% TG -10WT, Exxon AC-10 blend of 2/29/96, 17.09. Similarly, the aging index of the 10% TG -40B, Exxon AC-10 Sears blend, 7.39, is higher than the 20% TG -40B, Exxon AC-10 Sears blends, 3.42. The effect of the rubber on the Fina Demex Resin blends was to slightly lower the aging index for the Sears blends, but slightly raise the aging index for the Silverson blends, Table 5-16. The change in aging index for both the Sears and Silverson blends was minimal; therefore, the effect of the rubber on the Fina Demex Resin blends may have been insignificant.

Asphalt composition was a very important variable in determining the aging index of a binder. The 2/27/96 Exxon / Sun blend has a higher extent of curing than the 2/13/96 Exxon AC-10 most common conditions blend because of the presence of the Sun 125, but the benefit of the Sun 125 to the hardening characteristics of the asphalt more than offset this, with the overall aging index of blend 2/27/96 being improved, Table 5-16. For the Fina Demex Resin Blends, the Fina AC-5 blend of 3/10/96 had worse hardening characteristics than the comparable Fina Demex Resin blend of 3/7/96. The Fina AC-5 was produced by combining Fina Demex Resin and the heavier Fina AC-10. The Fina AC-10 was beneficial to the aging index because it inhibited the extent of curing, but its poor hardening characteristics more than offset this, with the overall aging index being higher for the blend of 3/10/96. These results and the extrapolated aging rate results agreed in that the modification of the base asphalt was more important than the extent of curing on the oxidative aging rate and hardening characteristics of an asphalt-rubber blend.

The results were inconclusive with respect to mesh size. For the Exxon AC-10 Silverson blends, the -40 mesh blend of 2/24/96 had an aging index slightly below the aging index of the

Table 5-16: Aging Index for the Phase 5 Blends,
Regressed η^* Calculated Using 24 Days at 363K

Asphalt	Weight Percent Rubber	Mesh Size	Mixer and Speed (rpm)	Curing Temperature	Aging Index at 363K (194°F)
Exxon AC-10	Neat				38.97
Exxon AC-10	10	-40	<i>Sears, 1550</i>	464K (375°F)	7.39
Exxon AC-10	20	-40	<i>Sears, 1550</i>	464K (375°F)	3.42
Exxon AC-10	10	-10	Silverson 4000	505K (450°F)	16.83
Exxon AC-10	10	-10	Silverson 4000	533K (500°F)	24.12
Exxon AC-10	10	-10	Silverson 8000	533K (500°F)	29.08
Exxon AC-10	10	-40	Silverson 4000	533K (500°F)	23.10
Exxon AC-10	20	-10	Silverson 4000	533K (500°F)	21.30
Exxon / Sun AC-5	10	-10	Silverson 4000	533K (500°F)	17.09
Neste-Wright, LTR10	Neat				13.42
Fina Demex Resin	Neat				18.94
Fina Demex Resin	10	-40	<i>Sears, 1550</i>	464K (375°F)	2.68
Fina Demex Resin	20	-40	<i>Sears, 1550</i>	464K (375°F)	2.36
Fina Demex Resin	10	-10	Silverson 4000	505K (450°F)	14.82
Fina Demex Resin	10	-10	Silverson 4000	533K (500°F)	25.63
Fina Demex Resin	10	-10	Silverson 8000	533K (500°F)	33.80
Fina Demex Resin	10	-40	Silverson 4000	533K (500°F)	31.11
Fina Demex Resin	20	-10	Silverson 4000	533K (500°F)	30.76
Fina AC-5	10	-10	Silverson 4000	533K (500°F)	26.13
Supercritical Asphalt	Neat				14.24
SC Asphalt	10	-10	4000	505K (450°F)	6.24
SC Asphalt	10	-10	4000	533K (500°F)	8.47

comparable -10 mesh blend of 2/13/96, Table 5-16. The effect of mesh size was completely opposite for the Fina Demex Resin Silverson blends, with the -40 mesh blend of 3/9/96 having an aging index much higher than the aging index of the comparable -10 mesh blend of 3/7/96. Furthermore, these results were completely opposite of the extrapolated aging rate results, where decreasing mesh size increased the aging rate of the Exxon AC-10 blends and had little effect on the Fina Demex Resin blends.

The Supercritical Asphalt blends had hardening susceptibilities that were dependent on the aging temperature, Table 5-13. This is shown in Figure 5-58 for the blend of 3/18/96 and 505K (450°F). The hardening susceptibility not only changes with temperature, but at each temperature, the data points lie on a distinct line. This is definitely different from the behavior of the base asphalt, Supercritical Asphalt, which is shown in Figure 5-59. Figure 5-59 even includes both the 333K (140°F) data and the high-temperature POV data. The behavior exhibited in Figure 5-58, although not necessarily as severe, was seen in all of the other Silverson blends and the LTR10 blend, Tables 5-13 and Table 5-14.

GPC analyses confirmed that the extent of curing is a very important aging variable. Figures 5-60 and 5-61 represent the change in molecular weight distribution with aging at 358K (185°F) for the Exxon AC-10 blends of 2/5/96 and 2/13/96, respectively. The only difference between the curing conditions of these two blends was the curing temperature, 505K (450°F) for the 2/5/96 blend and 533K (500°F) for the 2/13/96 blend. From the previous chapter, it is known that the extent of curing of the 2/5/96 blend was much less than the 2/13/96 blend. In Figure 5-60, it appears that the devulcanized rubber peak, represented by the peak in the 20 to 22 minute retention time region, was being depolymerized during oxidation, with the mass being transferred into the 22 to 25 minute retention time region. Apparently, the devulcanized rubber acts as a "sacrificial lamb" and protects the asphalt part of the binder from oxidation. This helps explain the extrapolated aging rate and aging index results which indicated that the higher the extent of curing, the worse the oxidative aging and hardening characteristics of a binder. The results for the Fina Demex Resin blends, Figures 5-62 and 5-63, and the Supercritical Asphalt blends, Figures 5-64 and 5-65, exhibited similar behavior. Quite interestingly, the mass of evidence from all the aging data indicates that there is definitely a trade off between tank properties and aging properties.

Figure 5-58: Hardening susceptibility plot for 3/18/96, Phase 5 blend.

Figure 5-59: Hardening susceptibility plot for SC Asphalt.

Figure 5-60: GPC (IV) data for 2/5/96, Phase 5 blend aged at 358K.

Figure 5-61: GPC (IV) data for 2/13/96, Phase 5 blend aged at 358K.

Figure 5-62: GPC (IV) data for 3/3/96, Phase 5 blend aged at 358K.

Figure 5-63: GPC (IV) data for 3/7/96, Phase 5 blend aged at 358K.

Figure 5-64: GPC (IV) data for 3/18/96, Phase 5 blend aged at 358K.

Figure 5-65: GPC (IV) data for 3/19/96, Phase 5 blend aged at 358K.

Comparing Figures 5-60, 5-62, and 5-64, blends cured at 505K (450°F), and Figures 5-61, 5-63, and 5-65, blends cured at 533K (500°F) shows the effect of asphalt composition on the aging properties of asphalt-rubber binder. The rank according to asphalt and rubber interaction was Exxon AC-10, SC Asphalt, and Fina Demex Resin. This is the same order as the rank to the amount of asphaltenes and heavy polar aromatics present in each asphalt. As in Phase 3 and 4, the heavy polar aromatics and asphaltenes increased the asphalt and rubber interaction during the aging process.

The material represented by the data in Figure 5-66 was aged at 363K (194°F), in Figure 5-61 at 358K (185°F). Comparing Figures 5-61 and 5-66 shows the effect of aging temperature on the molecular weight distribution of asphalt-rubber. The attributes of the two curves are the same except at the higher temperature the material in the 20 to 25 minute retention time region is seemingly forming at a faster rate.

Figures 5-60, 5-61, 5-67, 5-68, and 5-69 show the molecular weight distribution for the 10% Exxon AC-10 Silverson blends under the same aging conditions. The blend that stands out for being different is the blend of 2/5/96, the blend cured at 505K (450°F) and thus, with the lowest extent of curing, Figure 5-60. The other molecular weight distributions were almost indistinguishable except that the growth in the 20 to 25 minute retention time region of the Exxon / Sun blend, Figure 5-69, is slower than the other blends. This agrees with the aging results in that the presence of the Sun recycling agent slows the aging process.

IMPLICATIONS OF THESE RESULTS

The results of this chapter are of great importance in developing an accurate asphalt-rubber test. Furthermore, these results provide fundamental evidence that the curing history of a binder is very important in determining the oxidative aging and hardening characteristics of an asphalt-rubber binder.

The Phase 1 results indicated that asphalt-rubber does not cure when in a high-temperature and nitrogen environment without mixing. This conclusion at least allows the further study of asphalt-rubber aging without having to worry about separating the curing mechanism from the oxidation mechanism when evaluating the results.

To have a highly accelerated aging test, high-pressure oxygen must be used. The Phase 2

Figure 5-66: GPC (IV) data for 2/13/96, Phase 5 blend aged at 363K.

Figure 5-67: GPC (IV) data for 2/23/96, Phase 5 blend aged at 358K.

Figure 5-68: GPC (IV) data for 2/24/96, Phase 5 blend aged at 358K.

Figure 5-69: GPC (IV) data for 2/27/96, Phase 5 blend aged at 358K.

results, obtained by aging asphalt-rubber binder in a 20 atm pure oxygen environment, indicated that some asphalt-rubber binders exhibit nonlinear behavior with respect to the aging rate, hardening rate, and hardening susceptibility equations. This nonlinear behavior is believed to be caused by a change in reaction mechanism at temperatures around or above 367K (200°F) when using 20 atm pure oxygen. Although high-pressure aging is feasible for some asphalt-rubber binders, the possibility of a change in reaction mechanism for any asphalt-rubber all but eliminates the use of high-pressure aging at elevated POV-temperatures. On the other hand, high-pressure oxygen aging at lower temperatures may be feasible. However, it is doubtful that high-pressure oxygen aging can accurately simulate 1 atm air aging, because the dissolved and undissolved rubber particles are highly susceptible to attack by oxygen, especially high-pressure oxygen.

The Phase 3 and Phase 4 results indicated that for asphalt-rubber binder, the aging rates obtained at elevated temperatures with 1 atm air can be used to reasonably extrapolate the aging rate at road temperatures. This, however, is of little practical value since the hardening susceptibility of an asphalt-rubber binder was determined to be dependent on the aging temperature. That is, in order to use the extrapolated aging rate to predict viscosity hardening, the real variable of interest, a hardening susceptibility curve would have to be constructed from 333K (140°F) data. Thus, with data available at 333K (140°F) to obtain the hardening rate, there is no need to obtain the high-temperature data to extrapolate to the aging rate at 333K (140°F), and with this and the hardening susceptibility, to extrapolate to the hardening rate at 333K (140°F).

Phase 3 and Phase 4 results also indicated that using the hardening rates obtained at elevated temperatures with 1 atm air to extrapolate to the hardening rate at road temperature is not feasible. The results indicated a change in reaction mechanism for asphalt-rubber around or above 353K (176°F). It may be feasible to obtain hardening rates to extrapolate to road temperature by aging in the 333K (140°F) to 353K (176°F) temperature range.

The most promising way of using high-temperature aging with 1 atm air to predict the roadway performance of asphalt-rubber was the aging index. Logically, this method should not work because we know that each asphalt and asphalt-rubber has both a unique aging rate activation energy and a unique hardening rate activation energy. That is, the rankings for the aging rates or hardening rates, at an elevated-temperature, may be reversed at road temperature. Nonetheless, the aging index

rank obtained by high-temperature aging strongly agreed with the aging index rank obtained by 333K (140°F) aging. The concept of an aging index is similar to the idea of the SHRP PAV test. However, the big difference between the testing method proposed here and the SHRP PAV testing method is that the SHRP PAV uses high-pressure air. As mentioned previously, the results of this work indicate that high-pressure aging of asphalt-rubber binder may not be feasible. Additionally, the aging index of this work was calculated by using numerous sampling times and regression analyses to obtain an equation to predict the viscosity at a specified aging time. The SHRP aging index is calculated using only one sampling time. Using numerous sampling times and regression analyses to obtain an equation to predict the viscosity is advantageous in that one bad point will not necessarily ruin the results.

Phase 5 results indicated that aging and hardening properties of an asphalt-rubber binder are very dependent on the curing history of the binder. Interestingly, a high extent of curing will give a binder good tank properties, but will also give a binder poor aging and hardening properties. Furthermore, the Phase 5 results also indicated a change in reaction mechanism in or above the temperature of 353K (176°F). The Phase 5 results also verified that the hardening susceptibility of asphalt-rubber binder is dependent on the aging temperature.

CHAPTER 6

RHEOLOGY OF CRMA BINDERS

This Chapter deals with the application of the theory of linear viscoelasticity to understand CRMA binder rheology. Master curves for the CRMA binders are generated using the time-temperature superposition principle (Ferry, 1985). Specifically, the effects of aging, rubber concentration, and curing conditions on binder rheology are considered. Rheological behavior of CRMA binders is compared to the prediction of the Maxwell element. Approximation equations are used to calculate the relaxation spectra from the storage and loss moduli. The phase behavior of the binder is studied by observing changes in Cole-Cole diagrams. The subsequent sections of this Chapter describe the materials and test method of dynamic shear analysis. Results obtained from the master curve data are also discussed. These results give valuable rheological information that needs to be known prior to successful application of CRMA technology in pavement construction.

MATERIALS

Six different asphalts (different crude sources) were obtained from Exxon, Fina, and Diamond Shamrock with initial viscosities of 500-1000 poise at 333K (140°F). These asphalts were modified by adding ground tire rubber obtained from Rouse Rubber Company, Vicksburg, Mississippi. Rouse rubber is ambiently ground and has porous surfaced particles. Two different rubber particle sizes (diameter) were used: -80 mesh (250 μm) and -10 mesh (750 μm). The smaller rubber particles have a higher surface area per unit volume which leads to a greater degree of reactivity with the asphalt.

The process used for making CRMA binders involves curing the rubber in the asphalt. This process consists of mixing asphalt and rubber in different concentrations at elevated temperatures for extended periods of time in an inert atmosphere (N_2 environment). The parameters that affect the curing process are the time, temperature, and shear intensity of mixing (mixing rate). Three different curing conditions were used in this work: (a) 1 hour at 448K (350°F), 500 rpm (low curing condition), (b) 6 hours at 463K (375°F), 1550 rpm (intermediate curing condition), and (c) 3 hours at 533K (500°F), 8000 rpm (high curing condition). It is important to note that curing conditions (a)

and (b) are performed on a low shear impeller (LSI) mixer, while condition (c) is obtained using a high shear disintegrating (HSD) mixer. The difference between the two mixers is that the HSD mixer has a more localized mixing tendency than the LSI mixer. The degree of curing determines the amount of rubber that dissolves in the mixture. Due to the type of mixing, curing condition (c) is the most severe and produces a more homogeneous binder relative to curing conditions (a) and (b). Approximately 2000 grams of asphalt and rubber were cured at a time in a mixer. Different curing conditions, as mentioned above, were used to make CRMA binders with 6%, 12%, and 18% rubber by weight. A total of 21 CRMA binders were produced in the laboratory using the different curing conditions. Description of the mixing apparatus is given in good detail by Billiter (1996). Table 6-1 describes the asphalts, rubber concentration, and curing conditions used in this work to produce CRMA binders.

Table 6-1: Materials and Curing Conditions For Making the CRMA Binders

Asphalt Type	Rubber Type and Size	Rubber Concentration	Curing Conditions and Mixer Type
Fina AC-10 Fina AC-5 Exxon AC-10 Exxon AC-5 Fina Resin Diamond Shamrock Resin	RS-80	18%	1 hour at 448K, 500 rpm (LSI)
Fina AC-10 Fina AC-5 Exxon AC-10 Exxon AC-5 Fina Resin Diamond Shamrock Resin	RS-80	18%	6 hours at 463K, 1550 rpm (LSI)
Exxon AC-10 Fina Resin	RS-80	6%, 12%	6 hours at 463K, 1550 rpm (LSI)
Exxon AC-10	RS-10	6%, 12%, 18%	3 hours at 533K, 8000 rpm (HSD)
Exxon AC-10	---	0%	---
Neste Wright	---	10%	Commercial

DYNAMIC SHEAR MEASUREMENTS

Dynamic shear analysis involves the application of stress to a material and observing the resultant strain on the sample or measuring the stress on the material to keep it under constant strain. Knowing the stress and strain, the modulus can then be calculated as the ratio of the stress and strain. The inverse of the modulus (ratio of strain and stress) is called the compliance. For dynamic analysis, it is often easier to represent properties in complex terms (refer Chapter 7, Equation 7-4). We can then define the complex shear modulus in terms of the complex stress and complex strain as:

$$G^*(\omega) = \frac{\sigma^*(\omega)}{\epsilon^*(\omega)} = G'(\omega) + j G''(\omega) \quad (6-1)$$

where $G^*(\omega)$ is the complex shear modulus, $\sigma^*(\omega)$ is the complex stress, $\epsilon^*(\omega)$ is the complex strain, $G'(\omega)$ is the storage modulus, $G''(\omega)$ is the loss modulus, and j is the imaginary number. The storage modulus represents the potential energy stored by the material during deformation, while the loss modulus represents the energy dissipated as heat during deformation. The phase angle, $\delta(\omega)$, is the angle between the applied stress and the resultant strain or vice versa. Thus, for an elastic material, $G''=0$; $\delta=0^\circ$; while for a viscous material, $G'=0$; $\delta=90^\circ$. For a viscoelastic material, both G' and G'' are non-zero, and the phase angle is between 0° and 90° . The rheology of the CRMA binder is described in the following sections in terms of $G^*(\omega)$, $G'(\omega)$, $G''(\omega)$, and $\delta(\omega)$.

The CRMA binders were aged at 333K (140°F) for a specified period of time. Samples were removed from the controlled environment periodically and their dynamic viscoelastic properties measured on a Carrimed CSL 500 dynamic shear rheometer using a parallel plate geometry. Frequency sweeps from 0.1 to 100 s⁻¹ were performed at temperatures ranging from 273-313K (32-104°F) with 15 mm diameter plates and from 333K-363K (140-194°F) with 25 mm diameter plates. A gap size of 1500 μm between the plates was used to account for the rubber particle size. This gap size was determined in our laboratory to ensure that rheological properties are independent of the "gap effect". The data at different temperatures were shifted to 273K (32°F) using the principle of time-temperature superposition. Experiments were run under a controlled strain mode with the strain values ranging from 0.5-200%, assuring that behavior of the sample was always in the

linear viscoelastic region. The Carrired rheometer is described in detail by Lin (1995) and Chaffin (1996).

RESULTS AND DISCUSSION

Figures 6-1 and 6-2 show a typical master curve for a CRMA binder referenced to 273K (32°F) by time-temperature superposition. The master curve (Figure 6-1) indicates the time dependence of the binder, while the accompanying shift factor-temperature plot (Figure 6-2) highlights the temperature dependence of the binder. The complex shear modulus, $G^*(\omega)$ and the phase angle, $\delta(\omega)$ are plotted against frequency, ω . As seen from Figure 6-1, the complex modulus increases with increasing frequency (decreasing temperature). At low frequencies, $G^*(\omega)$ increases roughly linearly with frequency until it reaches a value of approximately 10^8 dyne/cm² at high frequencies. On the other hand, the phase angle decreases from 90° toward 0° with increasing frequency. This shows that a CRMA binder displays viscous behavior at low frequencies and elastic behavior at high frequencies. The intermediate frequency region indicates a transition zone where the behavior changes from elastic at high frequencies to viscous at low frequencies.

Thus CRMA binder rheology can be characterized using three parameters:

- (a) glassy modulus, G_g^* is the value that G^* approaches at high frequencies. This parameter is material-independent and was found to have a constant value of about 10^8 dyne/cm² for all binders studied in this work. This is the region of dominant elastic behavior. This value represents the rigidity of the C-C bonds, of which the CRMA molecules are made (Bahia and Anderson, 1995).
- (b) steady-state or Newtonian viscosity, η_0^* is the limit of the dynamic viscosity (G^*/ω) as the phase angle approaches 90°. η_0^* is the slope of the master curve at low frequencies and is material specific. Typical values of η_0^* in this work varied from about 10^9 - 10^{11} poise. This is the region of dominant viscous behavior.
- (c) cross-over frequency, ω_c is a binder specific frequency at which $\tan \delta$ is 1. At this point, the storage and loss moduli are equal, indicating equal contributions of both elastic and viscous behavior. The cross-over frequency can be thought of as a hardness parameter that indicates the general consistency of the binder. Values for ω_c for the binders in this work varied from 10^{-3} to 70 s⁻¹.

Figure 6-1: Typical Master Curve for a CRMA Binder

Figure 6-2: Temperature Dependence of Shift Factors for a CRMA Binder

This is the region where the binder undergoes delayed elastic deformation which characterizes its viscoelastic behavior.

Christensen and Anderson (1992) studied the rheology of unmodified asphalts using dynamic mechanical analysis. They concluded that master curves for unmodified asphalts can be characterized using the same parameters as described above. The overall behavior of the master curves, in the case of unmodified and rubber modified asphalts, is very similar except that the high frequency value of G^* , in the case of unmodified asphalts (10^{10} dyne/cm²), is higher than that of rubber modified asphalts (10^8 dyne/cm²). Correspondingly, rubber modified asphalts show a higher η_o^* (10^9 - 10^{11} poise) than unmodified asphalts (10^7 - 10^8 poise). These results show that rubber improves the viscous response at low frequencies (high temperatures) and reduces the elastic response at high frequencies (low temperatures). The reduction in the elastic response of the modified binder at low temperatures is consistent with bending beam measurements made by Billiter (1997), where rubber modified binder displayed a lower stiffness than an unmodified binder.

Figure 6-2 shows the temperature dependence of the shift factors determined from the construction of the master curve. This can be characterized by two equations which is valid for asphalts below and above a certain defining temperature, T_d (Christensen and Anderson, 1992) which can be considered to be analogous to the glass transition temperature, T_g , defined for viscoelastic and polymeric materials. This is explained in the next paragraph. The concept of T_g is actually not valid for asphalts and CRMA binders because, unlike polymeric materials, asphalt structure lacks the presence of chains or networks. This will be shown through the master curves later on in this work.

Figure 6-3 shows the logarithm of the shift factor plotted versus reciprocal absolute temperature. It can be seen that the data, for all practical purposes, shows a constant slope, from which the activation energy can be calculated. The $a(T)$ - T relationship ($R^2=0.996$) in this work was found to be given by:

$$\log a(T) = \frac{2.303 E_a}{R} \left[\frac{1}{T} - \frac{1}{T_d} \right] \quad (6-2)$$

where E_a is the activation energy, T is the temperature, and T_d is called the defining temperature. The

Figure 6-3: Determination of the Activation Energy from a(T)-T Relation

activation energy (from the slope) in this case was calculated to be 26.04 kJ/mole, while the defining temperature (from the intercept) was determined to be -271.4K (-1.6°C). Thus values of the defining temperature are in the range of the glass transition temperature defined for polymers. The results of SUPERPAVE™ have shown that unmodified asphalts obey Equation (6-2) below a certain defining temperature, T_d , while above this temperature, the WLF equation (Equation (6-3)) can be used to describe the $a(T)$ - T relationship as follows:

$$\log a(T) = \frac{-C_1(T - T_d)}{-C_2 + (T - T_d)} \quad (6-3)$$

where C_1 and C_2 are empirically determined constants (Ferry, 1985). E_a and T_d are functions of the asphalt type, rubber type, rubber size, rubber concentration, and curing conditions and can be determined from the $a(T)$ - T relationship obtained through construction of master curves for each binder.

To verify the validity of the time-temperature superposition principle, Figures 6-4 and 6-5

Figure 6-4: Isothermal Variation of G' Vs. ω

Figure 6-5: Isothermal Variation of G'' Vs. ω

show the isothermal variations of G' and G'' versus frequency respectively. These Figures show that the isothermal data can be superimposed at any reference temperature using horizontal shift factors only. Thus, no vertical shifting is required to construct the CRMA master curves. These data show that time-temperature superposition principle can be applied successfully to CRMA binders.

The following sections of this chapter focus on the effect of aging, rubber concentration, and curing conditions on CRMA binder rheology. Discussion on the relaxation spectra is also included.

Effect of Aging

Figure 6-6 shows the effect of aging on G' and G'' master curves. Note that at low frequencies, values of G' are lower than values of G'' which indicates dominant viscous behavior at lower frequencies. At higher frequencies, both moduli approach their corresponding glassy values with the limiting value of G' being greater than that of G'' . It is important to note that the difference in values of the moduli at high frequencies is smaller than the difference in their values at low frequencies. In the intermediate frequency region, values of G' and G'' are comparable indicating that both contribute equally to response of the binder.

Aging causes an increase in the values of G' and G'' for the binders. As mentioned earlier, aging causes an increase in binder viscosity (G^*/ω) which can be seen in the form of an increase in G^* with frequency. The master curve for an unaged binder stands out by itself compared to the aged binder master curves. There is a dramatic initial jump in the master curves at the first aging time of 84 days compared to the unaged master curve; further aging, however, causes a smaller change in the moduli. Thus, we can say that aging definitely improves the elastic, viscoelastic, and viscous properties of the binder over the entire frequency range. This change in properties due to aging reduces as the binders are aged for an extended period of time.

Summarizing the above discussion, a typical master curve for a CRMA binder can be divided into three regions of viscoelasticity:

- (a) At low temperatures or high frequencies (short times), the glassy complex modulus of about 10^8 dyne/cm² is approached, δ moves toward 0° indicating near elastic behavior. G' is greater than G'' confirming elastic response of the binder. The glassy modulus is material-independent and was found to be a constant for all the binders in this work.

Figure 6-6: Effect of Aging on the Master Curves

- (b) At high temperatures or low frequencies (long times), viscous or Newtonian behavior is approached with δ approaching 90° so that the storage modulus is lower than the loss modulus, indicating dominant viscous behavior. The Newtonian viscosity is material-dependent with values in the range 10^9 - 10^{11} poise.
- (c) As the frequency decreases, the moduli (G' and G'') decrease indicating a transition from glassy behavior to viscous behavior, while δ increases. This is the region where the binder undergoes delayed elastic deformation which characterizes viscoelastic behavior. When a viscoelastic material is deformed, there is an elastic and a time-dependent viscous deformation. This viscous deformation is further divided into a viscous and a delayed elastic component. On removal of the load, viscous flow stops and cannot be recovered, while the delayed elastic deformation recovers slowly at a decreasing rate. It is this delayed elastic deformation that distinguishes a viscoelastic material from an elastic or a viscous material (Darby, 1976). It is in the intermediate frequency (temperature) region that the CRMA binder displays viscoelastic behavior.

Effect of Rubber Concentration

Figure 6-7 shows the effect of the rubber concentration on CRMA binder rheology. As can be seen from the Figure, rubber definitely improves the elastic and viscous response of the binder over the entire range of frequencies, as is evident by the increase in G' and G'' . At low frequencies, rubber increases G' and G'' which leads to improved elastic and viscous properties over the control. The increase in G' is much more than that in G'' confirming the fact that rubber imparts additional elasticity to the asphalt. Because the rutting (permanent deformation) potential of a binder is a sensitive function of binder elasticity (elasticity is directly proportional to recoverable deformation) (Estakhri et al, 1993), rubber modified binders will offer greater resistance to rutting (permanent deformation). Note that as the frequency increases, a cross-over point exists where the master curve of CRMA binder intersects the master curve of the control and the trends reverse at higher frequencies. As the frequency further increases, rubber decreases G' and G'' which results in a less elastic and viscous material compared to the control. This causes a reduction in the stiffness of the

Figure 6-7: Effect of Rubber Concentration on the Master Curves

binder at low temperatures which directly affects the low temperature cracking resistance of the binder. However, this decrease in the moduli at higher frequency is much smaller compared to their increase at lower frequency. These results at low temperatures agree qualitatively with the results of the bending beam rheometer obtained in our laboratory (Billiter, 1997) where the rubber was found to reduce the stiffness of the modified binder over an unmodified binder at low temperatures. It is advantageous to have a binder with a lower stiffness at low temperatures so that it can sustain a higher strain due to thermal stresses without failure. In other words, rubber improves the performance of the binder over the entire range of frequencies and temperatures studied in this work, and hence the modified binder should have a greater resistance to the specific distresses like cracking and rutting.

Effect of Curing

Figure 6-8 shows the effect of the different curing conditions on the rheology of the binder. At low frequencies the addition of rubber increases G' and G'' with a greater increase in G' compared to G'' , once again confirming the fact that rubber imparts additional elasticity to the binder. Note that at low frequencies, the effect of curing conditions on the rheology is very small as can be seen from almost-overlapping master curves for the three different curing conditions. As the frequency increases, once again a cross-over point exists when the master curves for CRMA binders intersects the master curve for the control and the trends reverse. At high frequencies, rubber causes a decrease in the moduli, making the binder less stiff. At these frequencies, the master curves also overlap to a fair extent for the different curing conditions. The effect of curing condition is seen primarily at intermediate frequencies where a reduction in the values of G' and G'' is observed for the 8000 rpm curing condition, compared to the other two curing conditions. This decrease in the moduli implies a reduction in the viscosity of the highly cured binder compared to a low cured binder, which happens due to the dissolution of the rubber particles. In other words, increased homogeneity of the modified binder due to a severe curing process causes a decrease in the viscosity at intermediate frequencies. It appears that curing conditions (temperature, time, and shear intensity of mixing) affects the rheology of the binder only at intermediate frequencies.

Figure 6-8: Effect of Curing on the Master Curves

In order to successfully use CRMA binder for pavement construction, it would be greatly beneficial if the binder were as homogeneous as possible for easy handling. In order to study the state of the rubber in the CRMA binder after curing, Cole-Cole diagrams (η' vs. η'') (Lenk, 1978; Graebing et al, 1993) of CRMA binders subjected to different curing conditions were obtained. Figures 6-9 through 6-11 show the diagrams for unaged CRMA binders made at low, intermediate, and high curing conditions respectively. Figure 6-9 shows two peaks, the smaller one signifying the relaxation of the dispersed phase (undissolved rubber particles) and the larger peak indicating the relaxation of the asphalt matrix. The smaller peak qualitatively describes the amount of rubber particles that have not dissolved due to the curing process. As the intensity of curing is increased (Figure 6-10), more rubber particles dissolve in the asphalt, reducing the size of the small peak. On further curing (Figure 6-11), all the rubber particles dissolve in the asphalt resulting in the elimination of the small peak. Thus, the presence of one peak in Figure 6-11 indicates a homogeneous system of asphalt and rubber. This confirms that severe curing of the rubber in the asphalt results in complete

Figure 6-9: Cole-Cole Diagram For a Low Cured Binder

Figure 6-10: Cole-Cole Diagram for an Intermediate Cured Binder

Figure 6-11 Cole-Cole Diagram for a High Cured Binder

dissolution of rubber particles, making the resulting CRMA binder homogeneous. SEC analyses were performed on these binders to further verify dissolution of rubber particles. The description and operating procedure of the SEC used in this work is described well by Chaffin (1996). Results showed that as the intensity of curing condition was increased, it resulted in a larger rubber peak, which implies that more rubber particles are dissolving in the asphalt matrix. These results are also documented by Billiter (1997).

We know from the analysis of the master curves that aging affects the physical properties of the binder such as viscosity, ductility, etc. These changes in physical properties are also accompanied by corresponding changes in its chemical properties. The oxidation of asphalt molecules results in the addition of carbonyl groups ($C=O$). Excellent correlations have been obtained between carbonyl groups, measured using a Fourier Transform Infrared Spectrometer (FTIR) and oxygen content measured on an elemental analyzer (Lunsford, 1994). On the other hand, chemical effects of oxygen on rubber are not yet fully understood. It has been shown (Billiter, 1996) that oxygen reacts with

rubber and breaks down the rubber particles, resulting in dissolution of rubber particles in asphalt. Oxygen also has the effect of reducing the viscosity of CRMA binder due to particle breakdown, which explains the small effect that aging for extended periods has on the master curves (Figure 6-6).

To further investigate the effect of aging (oxygen) on CRMA binder, specifically rubber, Figures 6-12 and 6-13 show the Cole-Cole diagrams for a CRMA binder at two different aging times: unaged and aged for nine months. As shown before, Figure 6-12 shows two peaks, the smaller one indicating the presence of undissolved rubber particles and the larger peak indicating the presence of the matrix (asphalt). However as the binder is aged, the Cole-Cole diagram (Figure 6-13) shows only one peak signifying the presence of only one phase, confirming that oxygen has the effect of dissolving the rubber particles in the matrix. In order to further confirm that this is indeed the case, the Cole-Cole diagram (Figure 6-14) for the control (asphalt with no added rubber) shows just one peak indicating the absence of a dispersed phase. Thus, aging a CRMA binder over a period of time results in a more homogeneous binder.

Figure 6-12: Cole-Cole Diagram For an Unaged CRMA Binder

Figure 6-13: Cole-Cole Diagram For a CRMA Binder Aged For Nine Months

Figure 6-14: Cole-Cole Diagram for Control (0% Rubber)

Qualitative comparisons between master curves of Newtonian, polymeric, and CRMA binders were made to get a better perspective of CRMA binder rheology. Newtonian liquids, by definition, show a plateau in G' at high frequencies, while G'' increases linearly with the frequency, the slope of which is the Newtonian viscosity. On the other hand, the polymeric master curves show two plateaus in G' . These plateaus have been studied in detail in the literature (Rosen, 1993; Graebbling et al, 1993). The master curve for polymers can be divided into five regions: glassy/elastic region at high frequencies with a modulus of about 10^8 dyne/cm², leathery region at intermediate frequencies, the rubbery region (modulus of about 10^6 dyne/cm²) indicated by the presence of a plateau which represents the uncoiling of chains, the rubbery flow region where there is a significant elastic and viscous component, and the viscous flow region at the lowest frequencies (Rosen, 1993). In contrast, a binder master curve can be divided into three regions: the glassy region at higher frequencies with a glassy modulus of about 10^8 dyne/cm², transition/viscoelastic region at intermediate frequencies, and the viscous region at lower frequencies. The master curves for a CRMA binder do not show the presence of plateaus, which indicates the absence of chains or networks in the binder structure. This means that any molecular associations in the CRMA structure are relatively few in number or small in size. This is the reason that a glass transition temperature is not defined for a binder; instead CRMA binders are characterized in terms of just a transition or defining temperature. Note that the binder master curves display almost linear behavior at low frequencies, which is similar to Newtonian behavior, until they reach their glassy limits.

Comparison with Maxwell Element

Several mechanical models have been postulated in the literature to predict and understand viscoelastic behavior of materials. One such model was devised by James Clerk Maxwell who realized that a linear viscous element (dashpot) could be combined with a linear elastic element (spring) in series to describe the deformation of asphalts. This model was chosen because it estimates the response of a viscoelastic material during stress relaxation (controlled strain). For the Maxwell element, the storage and loss moduli are given by the following equations (Rosen, 1993):

$$G' = \frac{G(\omega\tau)^2}{1 + (\omega\tau)^2}$$

$$G'' = \frac{G(\omega\tau)}{1 + (\omega\tau)^2}$$
(6-4)

where ω is the angular frequency, G is the relaxation modulus given by the limiting value of the G' - ω master curve at high frequencies, and τ is the relaxation time given by

$$\tau = \frac{\eta}{G}$$
(6-5)

where η is the viscosity given by the slope of G'' vs. ω master curve at low frequencies. The relaxation times are calculated using experimental values of the viscosity and the relaxation modulus from the master curve data.

Figures 6-15 and 6-16 compare the master curve of the binder with the estimated response of a Maxwell element. At low frequencies, both the spring and the dashpot respond to the deformation as is evident from the linear increase in G' and G'' with frequency. At high frequencies, high resistance limits the response to the spring, resulting in a plateau for G' and a decrease in G'' . This decrease in G'' implies a reduction in the energy dissipated. As seen from the Figures, the Maxwell element does a poor job of quantitatively fitting dynamic data for the binder. However, it does illustrate the frequency dependence of dynamic properties and that the theory of viscoelasticity can indeed be applied to understand the CRMA binder rheology.

Figure 6-15: Comparison of CRMA Binder Response to Prediction of Maxwell Element (G' Vs. ω)

Figure 6-16: Comparison of CRMA Binder Response to Prediction of Maxwell Element (G'' Vs. ω)

Determination of the Relaxation Spectrum

The frequency dependence of the storage and loss moduli for a single Maxwell element is described by Equations 6-4 and 6-5. However, for a viscoelastic material, the stress-strain curves cannot be described by these simple expressions. A more complex combination of elements is required. The relaxation modulus, $G(t)$, is then the sum of the responses of the individual Maxwell elements:

$$G(t) = \sum_{i=1}^n G_i \exp\left(-\frac{t}{\tau_i}\right) \quad (6-6)$$

where n is the number of Maxwell elements, τ_i denotes the relaxation times of the individual elements as given by Equation 6-5, and t is the time.

Increasing the number of elements of the Maxwell element (see Figure 7-3 in Chapter 7) infinitely in parallel results in a continuous spectrum called the relaxation spectrum, $H(t)$ (Ferry, 1985), where t denote the relaxation times. This relaxation spectrum is a measure of the contribution to rigidity associated with the relaxation times and represents the distribution function of relaxation times on a logarithmic time scale. In other words, the relaxation spectrum deals directly with the stress relaxation mechanisms in the material as a function of time (frequency). Mathematically, H can be defined in terms of the relaxation modulus, $G(t)$, and can be given as:

$$G(t) = G_e + \int_{-\infty}^{\infty} H \exp\left(-\frac{t}{\tau}\right) d\ln \tau \quad (6-7)$$

where G_e is a constant that is used to allow for a discrete contribution to the spectrum with $\tau = \infty$ for viscoelastic solids; for viscoelastic liquids (Maxwell element), $G_e = 0$. There are several approximation methods that are available in the literature to calculate this spectra from the knowledge of the storage and loss moduli (Ferry, 1985). These equations (method of Williams and Ferry) can be written as:

$$\frac{H(\tau)}{A} = G' \frac{d \log G''}{d \log \omega} \quad (6-8)$$

and

$$\frac{H(\tau)}{B} = G'' \left[1 - \left| \frac{d \log G''}{d \log \omega} \right| \right] \quad (6-9)$$

where $\tau=1/\omega$ and A, B are constants which are functions of m , slope of the double logarithmic plot of G' or G'' and frequency, ω . In terms of the stress and strain, the relaxation spectrum is given as (Lenk, 1978):

$$H(\tau) = - \frac{1}{\frac{d\epsilon}{d\tau}} \frac{1}{\tau} \frac{d\sigma(\tau)}{d \ln t} \quad (6-10)$$

where τ , the relaxation time, ϵ is the strain, and σ is the stress.

Figures 6-17 and 6-18 show the relaxation spectra calculated from the knowledge of the storage and loss moduli as a function of frequency, respectively. The accuracy of this calculation is confirmed through Figure 6-19, which shows a good overlay of the two spectra calculated from the storage and loss moduli. The shapes of the relaxation spectra are similar to those of G'' plotted versus the loading time. The characteristic zones of the viscoelastic nature of CRMA from $H(\tau)$ can be identified as follows: glassy zone at small times, the transition zone where $H(\tau)$ drops steeply, and the "pseudo-terminal" region at long times where $H(\tau)$ approaches 0. It is called the "pseudo-terminal" region because in a true terminal region (in the case of polymers), G' and G'' are proportional to ω^2 and ω respectively (Ferry, 1985), which was not found to be true in the case of CRMA binders.

Note that in the glassy zone at low times (high frequency), $H(\tau)$ approaches a value of 8 on a logarithmic scale, which confirms the limiting value of 10^8 dyne/cm² approached by $G^*(\omega)$ at high frequencies as described earlier. The glassy zone at short times indicates that there is very little stress

Figure 6-17: Relaxation Spectrum of CRMA Binder
From Storage Modulus

Figure 6-18: Relaxation Spectrum of CRMA Binder
From Loss Modulus

Figure 6-19: Comparison of Relaxation Spectrum Calculated from Storage and Loss Modulus

relaxation over a few decades of logarithmic times. In this time scale, if the material were perfectly elastic, then $H(\tau)$ would vanish completely; however, it remains finite, indicating that some relaxation does take place at short times. At intermediate times in the transition zone, the stress gradually falls, while at long times, $H(\tau)$ completely vanishes due to complete relaxation of the stress. In terms of the Maxwell model, this corresponds to a complete relaxation of all the springs. The relaxation spectrum is thus a useful qualitative tool to understand the distribution of relaxation mechanisms in different regions of the time scale. Knowledge of the master curves and relaxation spectra can then be used to calculate other viscoelastic functions and viscoelastic constants using various interrelations as described in Ferry (1985).

SUMMARY

The dynamic complex shear modulus of a CRMA binder is a sensitive function of both frequency and temperature. It increases with increasing frequency and decreasing temperature. On the other hand, the phase angle increases with decreasing frequency and increasing temperature. Modification of the asphalt with rubber improves both the high and low temperature properties of the resulting CRMA binder, as reflected by changes in G' and G'' . Rubber imparts additional elasticity to the asphalt at high temperatures which improves its rutting resistance. At low temperatures, rubber reduces the stiffness of the resulting CRMA binder which decreases its thermal cracking potential.

The rheological properties of CRMA binder are affected by the curing process more at intermediate frequencies (temperatures). A more severe curing process (high temperature, high shear intensity of mixing) causes more rubber particles to dissolve, making the binder homogeneous, eventually leading to a reduction in its viscosity.

Aging affects the physical properties of the CRMA binder such as viscosity, ductility, etc adversely. At the same time, oxygen reacts chemically with the asphalt to form $C=O$ groups. The chemical effect of oxygen on rubber is to break down the particle size and reduce the viscosity of the CRMA binder. The break down of the particle size causes the rubber to dissolve in the asphalt matrix which eventually leads to a homogeneous binder. These changes in the phase behavior of the CRMA binder due to curing and aging have been shown through changes in the respective Cole-Cole diagrams.

The rheology of CRMA binder differs qualitatively from either Newtonian or polymeric rheology in certain regions of frequencies (temperatures). Unlike other polymeric or viscoelastic materials, CRMA binder does not show the presence of plateaus which indicate an absence of chain entanglements in the molecular structure. CRMA binder master curves can be divided into three regions of viscoelasticity: glassy region at high frequencies, transition/viscoelastic region at intermediate frequencies, and viscous region at low frequencies.

The storage and loss moduli information as a function of frequency has been used to calculate the relaxation spectra of the materials. These spectra confirm the three viscoelastic zones of behavior: glassy zone at short times, transition zone at intermediate times, and a "pseudo-terminal"

zone at long times. Viscoelastic information as part of this work can be used to obtain other viscoelastic functions of interest under different deformations using either exact or approximate interrelations (Ferry, 1985). Overall it has been shown that addition of rubber to the asphalt produces a rheologically superior binder, which will result in enhanced pavement performance through better resistance to pavement failure mechanisms.

This chapter describes the rheological behavior of the CRMA binder by itself. In addition to the CRMA binder rheology, it is imperative to understand the rheology of the binder and aggregate as a system (mix). This is important to develop rheological relationships between the binder and mix. The next two chapters deal with the characterization of the rheology (viscoelasticity) of the mix. Three different test methods, transient and dynamic, are used for this purpose. These test methods, along with a discussion of the results obtained from them, are also described. The results of these tests, if incorporated, brings us a step closer towards successful application of CRMA technology in the field.

CHAPTER 7

MIX RHEOLOGY - TRANSIENT PROPERTIES

This Chapter presents the rheological characteristics of CRMA laboratory mixes based on creep and recovery and direct tension tests. These tests were chosen primarily because of their simplicity, cost-effectiveness, and speed of testing. The test data can be used to characterize the rutting and failure (fracture) properties of the mixes respectively.

Specifically, the effects of rubber concentration, curing conditions, air voids, and base asphalt on the performance of the mix under the test conditions are considered. Master curves for the mix are determined from the creep and recovery test data. These master curves are compared with the master curves for the corresponding CRMA binder determined from dynamic shear analysis. Results indicate that CRMA mixes display a higher rutting and cracking resistance compared to asphalt mixes. Note that these tests have been performed on laboratory mixes and not on field cores. It is shown that the creep and recovery test and the direct tension test provide a satisfactory laboratory basis to evaluate CRMA mixes.

MATERIALS AND MIX DESIGN

As described in Chapter 6, different asphalts with initial viscosities ranging from 500-1000 poise at 333K (140°F) were obtained from Exxon, Fina, and Diamond Shamrock. These asphalts were modified by curing with ground tire rubber obtained from Rouse Rubber Company, Vicksburg, Mississippi. Two different particle sizes were used: -80 mesh (250 μ) and -10 mesh (750 μ). The curing process consists of mixing asphalt and rubber in different concentrations at elevated temperatures for extended periods of time in an inert atmosphere (N_2 environment). The parameters that affect the curing process are the time, temperature, and shear intensity of curing. Three different curing conditions were used in this work: (a) 1 hour at 448K (350°F), 500 rpm (low curing condition), (b) 6 hours at 463K (375°F), 1550 rpm (intermediate curing condition), and (c) 3 hours at 533K (500°F), 8000 rpm (high curing condition). The degree of curing dictates the amount of rubber that dissolves in the mixture. Thus curing condition (c) produces the most homogeneous

binder relative to conditions (a) and (b). Approximately 2000 grams of asphalt and rubber were cured in a mixer at a time. Different curing conditions, as mentioned above, were used to make CRMA binders with 6%, 12%, and 18% rubber by weight. A total of 21 CRMA binders (Table 6-1) were produced to determine the effect of rubber concentration, curing conditions, and base asphalt on mix rheology. The rheology of these CRMA binders has been described in detail in Chapter 6.

These CRMA binders were then used in compacted mixes in the laboratory. TxDOT's method (Tex-232-F) was used to design these mixes. This method is a volumetric design procedure normally used for coarse matrix, high rubber content mixes. The aggregates used for mix design are crushed limestone and field sand. The design criteria for this mix design are listed below:

- (a) target air voids = 4-6%
- (b) optimum laboratory molded density = 97%
- (c) minimum volume of the binder = 6%
- (d) percent aggregate passing #200 sieve = 6%

The mix design for the control mix (0% rubber) was the same as that used for the CRMA mixes to minimize the variables. A detailed description of the design process for the laboratory mixes is given by Estakhri et al (1993).

Two samples were fabricated per CRMA binder and subjected to creep and recovery and direct tension tests to determine their rheological properties. These tests were run on the mixes to identify important mix properties that affect their performance. The subsequent sections of this paper briefly describe the tests run on the mixes along with a discussion of rheological properties obtained from them. Important results obtained from these tests that affect the mix performance are also discussed.

TEST METHODS

Creep and Recovery Test

Before going into details of the rheological tests used in this work, it is important to give a brief background about transient and dynamic rheological properties. There are two distinct types of rheological experiments that are generally performed to understand material properties: transient

(function of time) and periodic or dynamic (function of frequency). For a transient experiment, knowledge of the stress and strain defines the extensional creep compliance, $D(t)$, as:

$$D(t) = \frac{\epsilon(t)}{\sigma(t)} \quad (7-1)$$

where ϵ is the strain, σ is the stress, and t is the loading time. The creep compliance is the inverse of the creep modulus, which can be determined experimentally using the creep and recovery test. The stiffness modulus, $S(t)$, used for SUPERPAVETM low temperature specification is defined on the basis of the extensional creep compliance as:

$$S(t) = \frac{1}{D(t)} \quad (7-2)$$

However, in order to provide information at short loading times and to supplement the above transient experiments, the stress or strain may be varied periodically, usually with a sinusoidal alternation at a frequency ω . For linear viscoelastic behavior, the strain also alternates sinusoidally, but will be out of phase with the stress (phase angle, δ). These concepts can be mathematically represented as:

$$\begin{aligned} \sigma &= \sigma^0 \sin \omega t \\ \epsilon &= \epsilon^0 \sin(\omega t + \delta) \end{aligned} \quad (7-3)$$

It is mathematically more convenient to use complex notation to represent the above dynamic stresses and strains as follows:

$$\begin{aligned} \sigma^* &= \sigma^0 \exp(i \omega t) \\ \epsilon^* &= \epsilon^0 \exp[i(\omega t + \delta)] \end{aligned} \quad (7-4)$$

where σ^0 is the maximum stress amplitude, ϵ^0 is the maximum strain amplitude, and δ is the phase

angle between stress and strain. In general, a periodic (dynamic) experiment at frequency ω is qualitatively similar to a transient experiment at time $t=1/\omega$ (Ferry, 1985). Dynamic properties of the mix are discussed in detail in Chapter 8. In this Chapter, we focus on transient properties of the mix.

An unconfined uniaxial compressive creep test was used in this work to characterize the rutting potential of mixes. A schematic of the specimen geometry and its configuration is shown in Figure 7-1. The applied load (stress vs. time) and the observed deformation (strain vs. time) are also shown. The stress path used in this work was a static load in which a constant load in compression was applied to the sample for one hour (creep) with a small ramp time. Uniaxial vertical deformation of the sample as a function of time was observed from which creep strain and modulus was calculated. To evaluate the effect of aggregate on the performance of the mix, the resilience offered by the aggregate in response to the load should be considered. A simple and direct way to do this is to perform a recovery test for one hour immediately following the creep test in which the load is removed and the sample is allowed to recover its deformation for one hour. The recovery part of the test gives an indication of the elastic or healing power of the mix subject to a constant stress.

A testing temperature of 313K (104°F) was selected because of its common use in creep testing especially by AAMAS (Asphalt-Aggregate Mixture Analysis System), and also because rutting or permanent deformation is more likely at high temperatures. This temperature is also a good approximation for a nominal high pavement layer temperature (Little and Youssef, 1992). A stress level of about 5 psi was used to ensure minimum damage to the sample and also to stay within the linear viscoelastic region for obvious reasons (Estakhri et al, 1993). As a result, the permanent strain on the sample was kept under 1% at all times. These conditions do not simulate field conditions accurately; however they do a reasonably good job of achieving our objectives of characterizing CRMA mixes in the laboratory.

Direct Tension Test

To effectively design materials against failure, a reliable method of determining failure strength and toughness is required. One such test that is commonly used is the direct tension test which is a practical method of characterizing failure properties. Therefore, the results of this test can be related

Figure 7-1: Creep and Recovery Test, Specimen Configuration and Response

to resistance of the mix to fatigue and thermal cracking.

The test used in this work is a static constant strain rate test to failure carried out at 298K (77°F). The sample is subjected to a constant rate of elongation (0.254 cm/min) and the stress and strain are monitored as a function of loading time until failure is reached. A schematic of this test configuration is shown in Figure 7-2. The observed stress and strain, as a function of time until failure, are also shown.

THEORY

Creep and Recovery Test

Direct experimental measurements from this test are basically the stress and strain as a function of loading time. Using the theory of viscoelasticity, the stress-strain behavior of the samples can be used to obtain other valuable rheological information.

Knowing the strain as a function of time at constant stress, it is possible to obtain the creep modulus as:

$$E_c(t) = \frac{\sigma_0}{\epsilon(t)} \quad (7-5)$$

where $\epsilon(t)$ is the strain on the sample, t is the loading time in seconds, σ_0 is the constant stress applied during creep (1 hour), and $E_c(t)$ is the creep modulus.

Knowing the creep modulus, the creep compliance, $J(t)$, can be calculated as:

$$J(t) = \frac{1}{E_c(t)} = \frac{\epsilon(t)}{\sigma_0} \quad (7-6)$$

For a viscoelastic material (solid or liquid), the creep compliance can be separated into two parts as:

$$J(t) = J_e^0 + J_v(t) \quad (7-7)$$

where J_e^0 is the equilibrium compliance for a solid or steady-state compliance for a liquid (elastic

Figure 7-2: Direct Tension Test, Specimen Configuration and Response

component), and $J_v(t)$ represents the viscous component of the compliance which is a function of the loading time, t (Ferry, 1985). Equation (7-7) is based on the creep and recovery behavior of a viscoelastic liquid. The creep of a viscoelastic material is the sum of a deformation approaching a constant value $J_e^0 \sigma_0$ plus a viscous flow contribution $\sigma_0 t / \eta_0$ where t is the loading time during creep period. The former quantity is a measure of the elastic deformation (recovered) during steady flow while the latter denotes the viscous component (unrecovered) of the deformation. The total creep strain of the sample can be expressed in terms of the steady-state compliance and steady-state Newtonian viscosity as:

$$\varepsilon(t) = \sigma_0 \left(J_e^0 + \frac{t}{\eta_0} \right) \quad (7-8)$$

where the first term represents the recovered deformation and the second term represents the unrecovered deformation. Thus under constant stress (creep), the rate of strain approaches a limiting value, and a steady-state flow is eventually attained which is governed by the Newtonian viscosity η_0 . The Newtonian viscosity directly affects the strain that is not recovered by the sample at the end of recovery period.

As will be seen later in this Chapter, the strain of a mix in a creep and recovery test does not reach the state of true equilibrium; hence unlike the case of a viscoelastic solid, there is no equilibrium compliance which corresponds to the absence of a cross-linked network in the molecular structure. The model of a viscoelastic liquid is valid in this case due to the experimental observation of the fact that the strain rate approaches a constant during creep. If the mix were a viscoelastic solid, then the strain would reach a constant magnitude characterized by an equilibrium compliance instead of a steady-state compliance. The strain recovery is complete for a viscoelastic solid and incomplete for a viscoelastic liquid (Figure 7-1).

In terms of mechanical models, the model of a viscoelastic liquid is analogous to a generalized Maxwell model (Figure 7-3) with finite viscosities (Darby, 1976; Ferry, 1985; Rosen, 1993). In terms of this model, in the steady state region, the springs are stretched to equilibrium extensions, which represents the stored elastic energy that is recoverable after stress removal. This elastic energy directly controls the strain that is recovered by the sample during the recovery period.

Figure 7-3: Generalized Maxwell Model of a Viscoelastic Liquid

The steady-state compliance can be visualized as the sum of the deformations of the springs divided by the stress coupled with a dashpot (viscosity) in series to make it a viscoelastic liquid. From Equation (7-8), the rate of strain ($d\epsilon/dt$) is equal to σ_0/η_0 , which represents the linear extension of the dashpot with time. Thus, the Maxwell fluid will continue to deform as long as the stress is applied. The calculation and importance of these parameters is discussed in the subsequent sections. Relaxation mechanisms for the Maxwell element have been discussed in detail in Chapter 6.

Knowing the strains as a function of loading time, it is possible to define a steady-state region (between 1000 s and 3600 s in this case) and obtain the slope of the creep curve (m-value) in this region as:

$$m = \frac{\log(\epsilon_{3600}) - \log(\epsilon_{1000})}{\log 3600 - \log 1000} = \left[\frac{d \log \epsilon}{d \log t} \right]_{SS} \quad (7-9)$$

where the numbers represent loading time in seconds and *SS* stands for steady state. This m-value is analogous to the m-value obtained from the bending beam rheometer measurements as defined in the Superpave specifications and essentially represents the creep rate of the specimen.

The total permanent strain, (ϵ_p) which characterizes the resiliency of the material, is then obtained as the difference between the strains at the end of the creep and recovery periods (ϵ_C and ϵ_R respectively) as:

$$\epsilon_p = \epsilon_C - \epsilon_R \quad (7-10)$$

Another parameter that is often used to characterize the material is called % strain recovery or simply % recovery which can be obtained as:

% Recovery

$$\% Recovery = \frac{\epsilon_C - \epsilon_R}{\epsilon_C} \times 100 \quad (7-11)$$

In general for low rutting levels, the permanent strain of the sample (ϵ_p) and the m-value should be as low as possible, while the modulus ($E_c(t)$) should be as high as possible. Rutting criteria based

on these properties are available in the literature (Little and Youssef, 1992). However, these criteria (AAMAS rutting charts) are not really applicable to the results of this work because of the difference in mix design procedures and different loading levels (lower loading levels in this case).

Direct Tension Test

From experimental measurements of stress and strain as a function of time until failure, it is possible to obtain the failure stress, σ_f (strength) and failure strain, ϵ_f (strain at strength). Knowing the failure stress and failure strains, it is then possible to calculate the secant modulus of the sample, E_s , as:

$$E_s = \frac{\sigma_f}{\epsilon_f} \quad (7-12)$$

To get a better perspective of the failure phenomenon, it is important to understand the failure mechanism of a viscoelastic material in terms of energy. When a viscoelastic material is subjected to a tensile stress, energy is stored as potential energy until failure. Upon reaching failure, this stored energy is used in two ways: energy dissipated as heat and energy required to create two surfaces (surface energy or work of cohesion). The total dissipated energy to failure (failure energy or toughness) can then be determined by integrating the area under the stress-strain curve as:

$$E_f = \int \sigma d\epsilon = 2\gamma + E_h \quad (7-13)$$

where γ is the surface energy of the binder, determined, e.g., from the Wilhemy plate apparatus (2γ =work of cohesion), and E_h is the energy that is dissipated as heat at failure. The surface energy is multiplied by 2 to include both surfaces that are created upon failure. The second term in Equation (7-13) represents the energy that is dissipated due to geometrical and material effects of the specimen. Equation (7-13) assumes that the direct tension test on the mix primarily yields failure properties of the binder rather than the aggregate. The direct tension test on the mix is a three-dimensional test, unlike the direct tension test on the binder (Superpave specification), which is more a one-dimensional test. The three-dimensional effect of the test complicate the analysis and interpretation of results.

The validity of this assumption is checked later in this Chapter. The remainder of the chapter discusses the results obtained from these two tests in terms of mix rheology.

RESULTS AND DISCUSSION

Creep and Recovery Test

The results of the creep and recovery test are discussed in terms of the following parameters obtained from creep and recovery measurements:

- (1) Creep modulus at the end of 3600 s, E_c ,
- (2) m-value (m),
- (3) permanent strain (ϵ_p) or % strain recovery.

In terms of these parameters for a mix to have good performance characteristics, it should have a high creep modulus, low m-value, and low permanent strain (high % strain recovery). A high creep modulus of the sample implies that it exhibits a smaller strain for a constant applied stress (Equation 7-5). On the other hand, a low m-value indicates a small rate of strain (Equation 7-9). Variables of interest in evaluating the performance of these mixes include:

- (1) Rubber concentration,
- (2) Air voids,
- (3) Curing conditions,
- (4) Base asphalt.

Figure 7-4 shows a typical creep and recovery curve (creep and recovery strain vs. loading time) obtained for a mix from creep and recovery measurements. This curve can be divided into two regions: the primary stage, where the rate of deformation increases rapidly, and the secondary (steady-state) region where the rate of deformation approaches a constant. There is no tertiary or failure region in this case, because the load levels were kept low enough to keep the permanent strain under 1%. The absence of the tertiary or failure region validates the assumption of linear viscoelasticity of the mix under these loading conditions.

Figure 7-4: Typical Creep and Recovery Test, Strain Vs. Time,
Calculation of J_e^0 and η_0

As discussed in the earlier section, this creep and recovery curve can be explained on the assumption that the mix is a viscoelastic liquid. Equating the recovered strain to $\sigma_0 J_e^0$ and the unrecovered strain to $\sigma_0 t / \eta_0$ at the end of the creep test (3600 s), it is possible to calculate J_e^0 and η_0 . Typical values of J_e^0 and η_0 calculated from the experimental creep and recovery curves are given in Table 7-1. No specific dependence was observed of the steady-state compliance and viscosity on the material variables such as rubber concentration, air voids, etc. These results show that under the conditions of this test, the viscous or unrecoverable strain is more important compared to the elastic or recoverable strain when one considers the rutting potential, which agrees with the results reported by Estakhri et al (1993).

The steady-state compliance is plotted against the Newtonian viscosity for all the CRMA mixes in Figure 7-5. As seen from the Figure, J_e^0 was found to decrease as η_0 increases. A fairly good correlation ($R^2=0.80$) is obtained between the two considering significant differences in the mix variables involved. Regression of these parameters showed that they are related by a power law

equation of the form:

$$\eta_0 = a (J_e^0)^b \quad (7-14)$$

where $a > 0$, and $b < 0$ were determined in this work to be 1.51×10^{10} and -0.15 respectively.

Table 7-1: Steady-State Compliance and Newtonian Viscosities of Typical CRMA Mixes
Calculated from Creep and Recovery Experimental Data

CRMA Description	Steady-State Compliance (J_e^0) cm^2/dyne	Steady-State Newtonian Viscosity (η_0) dyne s/cm^2
Exxon AC-10, 0% Rubber (Control)	178.0×10^{-11}	3.1×10^{11}
Neste Wright	38.1×10^{-11}	3.3×10^{11}
DS Resin, RS-80, 18%, Low Cure	173.0×10^{-11}	2.5×10^{11}
DS Resin, RS-80, 18%, Intermediate Cure	114.0×10^{-11}	3.3×10^{11}
Exxon AC-10, RS-10, 6%, High Cure	5.5×10^{-11}	5.0×10^{11}
Exxon AC-10, RS-10, 12%, High Cure	160.0×10^{-11}	5.1×10^{11}
Exxon AC-10, RS-10, 18%, High Cure	89.7×10^{-11}	2.3×10^{11}

Figure 7-5: Relation Between Creep Parameters, η_0 Vs. J_e^0

The parameters, J_e^0 and η_0 , can be used to calculate other rheological parameters like creep compliance, $J(t)$, and complex modulus, $G^*(\omega)$, given by:

$$J(t) = J_e^0 + \frac{t}{\eta_0} \approx \left| \frac{1}{G^*(\omega)} \right| \quad \left(t \rightarrow \frac{1}{\omega} \right) \quad (7-15)$$

where t represents the loading time in seconds and ω is the angular frequency in rad/s. Assuming the model of a viscoelastic liquid, Equation (7-15) can then be used to generate master curves of the mix in terms of either $J(t)$ or $G^*(\omega)$. These master curves of the mix can be used to obtain valuable rheological information over a range of loading time (frequency) and temperatures. Figure 7-6 shows typical master curves ($G^*(\omega)$ vs. ω) for the mixes obtained from the creep and recovery measurements. As seen from the Figure, $G^*(\omega)$ increases linearly with frequency at low frequencies. The slope of $G^*(\omega)$ vs. ω at low frequencies represents the Newtonian steady-state viscosity, η_0 , which is comparable for all the mixes ($\sim 10^{11}$ poise), as indicated by the parallel and overlapping lines

Figure 7-6: Master Curves of Mixes Determined From Creep and Recovery Data

at low frequencies (Table 7-1). As in the case of binder master curves (Chapter 6), the low frequency behavior characterizes the viscous component, while the high frequency behavior characterizes the elasticity of the mix. This linear behavior continues until $G^*(\omega)$ reaches a limiting value (plateau) of 10^9 dyne/cm² (corresponding $J(t)=10^{-9}$ cm²/dyne) at high frequencies. These master curves basically show that both the elastic and viscous components respond to the deformation at low frequencies, while at high frequencies, the response to the loading is elastic resulting in the plateau for $G^*(\omega)$. Similar master curve behavior was observed for all the mixes studied in this work.

Master curve for the corresponding CRMA binder is superimposed on the master curve for the mix in Figure 7-7. The master curve for the CRMA binder was obtained using the time-temperature superposition principle (Ferry, 1985) from frequency sweeps at different temperatures on a dynamic shear rheometer as discussed in Chapter 6. Figure 7-7 shows that the rheology of the mix is dictated by both the rheology of the binder and the aggregate. There is a distinct difference of almost an order of magnitude between the limiting values of $G^*(\omega)$ for the binder ($\sim 10^8$ dyne/cm²)

Figure 7-7: Comparison of Master Curves of a CRMA Binder and Its Mix (Dynamic Shear Analysis and Creep and Recovery)

and the mix ($\sim 10^9$ dyne/cm²), with the value of $G^*(\omega)$ of the binder at high frequencies being lower than that of the mix. The steady-state Newtonian viscosities of the binder ($\sim 10^9$ dyne s/cm²) and the mix ($\sim 10^{11}$ dyne s/cm²) at low frequencies indicate that there is a significant difference (two orders of magnitude) in the viscous response of the binder and mix.. These comparisons show that the rheology of the aggregate contributes significantly to the overall performance of a CRMA mix and must be considered in performance evaluation. The rheology of the binder is discussed in detail in Chapter 6.

Arbitrary criteria were selected in order to rank the binders in comparison with each other, because the mix design procedure was the same in all the cases (Estakhri et al, 1993). These criteria are not necessarily related to field performance or specifications. Three different properties were selected: permanent strain, ϵ_R , creep modulus after 3600 seconds of creep, E_c (3600), and m-value.

Based on the permanent strain obtained in our testing, it is possible to divide all the mixes into two categories:

(1) $\epsilon_p < 0.0025\%$

6% and 12%, RS-10, high cure binders

6% and 18%, RS-80, intermediate cure binders

(2) $0.0025\% < \epsilon_p < 0.01\%$

18%, RS-10, high cure binder

12%, RS-80, intermediate cure binders

Control, 0% rubber

Neste Wright

Based on the permanent strain, CRMA binders used to fabricate category 1 mixes were the best in terms of their performance under creep and recovery conditions. These binders would have a higher resistance to rutting than those of category 2. It is seen that in most cases, CRMA mixes perform better than unmodified asphalt mixes based on the permanent strain.

Another criterion that was used is the creep modulus ($E_c(3600)$) at the end of the creep period (3600 s). The range of $E_c(3600)$ obtained in this work is 2.75×10^7 to 27.5×10^7 dyne/cm² (400 to 4000 psi). The mixes were again divided into two categories:

(1) $E_c(3600) < 8.27 \times 10^7$ dyne/cm² (1200 psi)

Control, 0% rubber

Neste Wright

12%, RS-80, intermediate cure binders

18%, RS-10, high cure binder

all low cure binders except Fina AC-10

(2) $E_c(3600) > 8.27 \times 10^7$ dyne/cm² (1200 psi)

all intermediate cure binders with 18%, RS-80 except Exxon AC-5 and Fina AC-5

6% and 12%, RS-10, high cure binders

Based on creep modulus, we can see that CRMA binder used to fabricate mixes in category 2 (greater rutting resistance) will perform better under creep and recovery conditions than those of category 1 (lesser rutting resistance). Once again using the creep modulus criteria, CRMA mixes perform better

than unmodified asphalt mixes.

Another sensitive parameter that can be used to rank these mixes is the slope of the steady-state creep curve, m -value (rate of strain). It has been shown by several independent studies that the m -value has a significant effect on the rutting potential of a mix. Mixes with m -values below 0.25 showed a greater resistance to rutting (Rauhut et al, 1979; Little and Youssef, 1992). Taking this into account, the mixes could then be divided into two categories based on the m -value as follows:

(1) $m < 0.25$

Control, 0% rubber

Neste Wright

all low cure binders except Fina AC-10

all intermediate cure binders except Fina AC-10

12% and 18%, RS-10, high cure binder

(2) $m > 0.25$

Fina AC-10, RS-80, 18%, low cure and intermediate cure binders

6%, RS-10, high cure binders

Based on this information (m -value criterion), it can be concluded that all the CRMA binders except three can be used to make rut resistant mixes. m -values for all the mixes were found to vary from 0.04 to 0.40. In general, all the mixes displayed stable behavior as far as rutting is concerned based on the permanent strain, creep modulus, and m -value.

As mentioned earlier, for good performance (high resistance to rutting), the permanent strain and the m -value should be as small as possible, while the creep modulus should be as high as possible. From the above analysis, it can be seen that addition of rubber to the binder decreases ϵ_p , and increases $E_c(t)$ over that of the control asphalt (0% rubber). It can also be seen that a more homogeneous CRMA binder (high curing conditions) has a lower permanent strain and a higher creep modulus. It was found that in terms of the m -value, none of the mixes, including the control, were significantly different from each other. These results agree qualitatively with the results obtained by Estakhri et al (1993) through their investigation of CRMA binder mixes. Quantitative comparisons could not be made with their results because of significant differences in mix design procedures and stress levels used. These creep and recovery results definitely give an indication of the improvement

in properties caused by the addition of rubber to the binder, especially those properties that increase the rutting resistance. These results also give an indication of the importance of using a homogeneous CRMA binder for fabricating mixes. The effects of the individual mix variables such as rubber concentration, air voids, curing conditions, and base asphalt on the creep and recovery parameters are discussed in more detail in the following sections.

The effect of rubber concentration on the creep and recovery parameters is shown in Tables 7-2 through 7-4. Changes in the m -value, creep modulus at the end of the creep period (3600 s), and % strain recovery are shown as the concentration of rubber is increased. Based on these data, it can be seen that both the m -value and creep modulus of the mix decrease as the concentration of rubber in the binder is increased. Thus, a compromise in terms of m -value and creep modulus is required to select a concentration of rubber in the binder. A similar decrease in m -values was reported by Little and Youssef (1992) in their creep and recovery experiments with asphalt and polymer (LDPE) modified asphalts (m -value decreased as the concentration of polymer was increased).

Tables 7-5 through 7-9 show the effect of air voids on the creep and recovery parameters. In most cases, as air voids increase, the m -value increases, while $E_c(t)$ decreases. As mentioned earlier, for better performance, the m -value should be as small as possible, while the creep modulus should be as high as possible. From this we can conclude that for a mix to perform well, it should have a low % air voids which implies good compaction of the aggregate and binder. Coincidentally the results of Davison et al (1989) showed that a low void content in the field will decrease the rate of oxidation to a significant extent and this in turn reduces the deterioration in binder properties.

Tables 7-10 and 7-11 show the effect that the curing conditions of CRMA binder have on the creep and recovery parameters. It has been shown that as the intensity of curing conditions increases, the homogeneity of the CRMA binder increases due to higher dissolution of the rubber particles (Billiter, 1996; Sheth et al, 1997). The creep and recovery results show that a mix made with a more homogeneous CRMA binder will have a higher creep modulus and a lower m -value. These results basically show that a homogeneous CRMA binder should be used to fabricate laboratory mixes so that it will perform better under creep and recovery conditions.

Table 7-2: Effect of Rubber Concentration on Creep and Recovery Parameters
(Exxon AC-10 RS-10 538K 3h 8000rpm)

Rubber Concentration (%)	m-value	$E_c(3600)$ (dyne/cm ²)	% Strain Recovery
6	0.386	13.4×10^7	1
12	0.143	11.8×10^7	18
18	0.035	6.1×10^7	6

Table 7-3: Effect of Rubber Concentration on Creep and Recovery Parameters
(Fina Resin RS-80 463K 6h 1550rpm)

Rubber Concentration (%)	m-value	$E_c(3600)$ (dyne/cm ²)	% Strain Recovery
6	0.123	11.7×10^7	12
12	0.111	7.4×10^7	9

Table 7-4: Effect of Rubber Concentration on Creep and Recovery Parameters
(Exxon AC-10 RS-80 463K 6h 1550rpm)

Rubber Concentration (%)	m-value	$E_c(3600)$ (dyne/cm ²)	% Strain Recovery
6	0.139	12.3×10^7	14
12	0.161	7.6×10^7	10

Table 7-5: Effect of Air Voids on Creep and Recovery Parameters
(Exxon AC-10 RS-80 12% 463K 6h 1550 rpm)

Air Voids (%)	m-value	$E_c(3600)$ (dyne/cm ²)	% Strain Recovery
3.71	0.161	8.0×10^7	10
3.96	0.162	7.2×10^7	15

Table 7-6: Effect of Air Voids on Creep and Recovery Parameters
(Fina Resin RS-80 6% 463K 6h 1550 rpm)

Air Voids (%)	m-value	$E_c(3600)$ (dyne/cm ²)	% Strain Recovery
2.28	0.087	17.0×10^7	16
3.89	0.167	6.4×10^7	7

Table 7-7: Effect of Air Voids on Creep and Recovery Parameters
(Fina Resin RS-80 12% 463K 6h 1550 rpm)

Air Voids (%)	m-value	$E_c(3600)$ (dyne/cm ²)	% Strain Recovery
4.54	0.085	5.8×10^7	9
6.31	0.137	8.9×10^7	8

Table 7-8: Effect of Air Voids on Creep and Recovery Parameters
(Exxon AC-10 0% Rubber)

Air Voids (%)	m-value	$E_c(3600)$ (dyne/cm ²)	% Strain Recovery
4.00	0.133	6.4×10^7	12
4.77	0.112	8.5×10^7	15

Table 7-9: Effect of Air Voids on Creep and Recovery Parameters
(Neste Wright Commercial Blend)

Air Voids (%)	m-value	$E_c(3600)$ (dyne/cm ²)	% Strain Recovery
5.01	0.174	9.4×10^7	2
6.55	0.224	5.4×10^7	3

Table 7-10: Effect of Curing Conditions on Creep and Recovery Parameters
(DS Resin RS-80 18%)

Curing Conditions	m-value	$E_c(3600)$ (dyne/cm ²)	% Strain Recovery
1h, 500 rpm	0.214	6.4×10^7	11
6h, 1550 rpm	0.117	8.3×10^7	10

Table 7-11: Effect of Curing Conditions on Creep and Recovery Parameters
(Exxon AC-5 RS-80 18%)

Curing Condition	m-value	$E_c(3600)$ (dyne/cm ²)	% Strain Recovery
1h, 500 rpm	0.122	4.5×10^7	43
6h, 1550 rpm	0.234	3.3×10^7	8

The base asphalts that were used in this work are ranked in terms of increasing m-values and decreasing $E_c(3600)$ values (best to worst) as follows:

- (1) increasing m-values

Low curing conditions

Exxon AC-5 (best)
DS Resin
Fina AC-10
(worst)

Intermediate curing conditions

DS Resin
Exxon AC-10
Fina AC-5
Exxon AC-5
Fina AC-10

- (2) decreasing $E_c(3600)$

Low curing conditions

Fina AC-10 (best)
DS Resin
Exxon AC-5
(worst)

Intermediate curing conditions

Fina AC-10
Exxon AC-10
DS Resin
Fina AC-5
Exxon AC-5

From above, it can be seen that the m -value and E_c (3600) have similar trends, i.e., a mix with a low m -value generally has a lower E_c (3600). Considering the fact that a low m -value and high E_c (t) are needed for better performance, a compromise in terms of m -value and E_c (t) has to be reached when selecting an asphalt. The starting viscosity of the base asphalt (tank viscosity) is also an important consideration when selecting an asphalt. It appears that in terms of m -values, an asphalt with a lower tank viscosity is better, but in terms of E_c (t), an asphalt with a higher tank viscosity will perform better.

Direct Tension Test

Having defined the properties that can be extracted from the direct tension test on the mix, the next section discusses the important results that were obtained in this work.

The results of the direct tension test are discussed in terms of the following parameters obtained from measurements:

- (1) Failure stress or strength, σ_f ,
- (2) Failure strain or strain at strength, ϵ_f , and
- (3) Dissipated energy to failure (toughness or failure energy), E_f

In terms of these parameters for a mix to have good performance characteristics, it should have a high failure stress and high failure strain. If this is achieved, then it will have a high failure energy, because the failure energy is the integrated area under the stress-strain curve (Equation (7-13)).

Figure 7-8 shows typical stress-strain behavior until failure of a mix sample, subjected to a direct tension test. As observed in the Figure, the stress varies linearly with strain for a very short loading time, indicating linear elasticity of the material as described by Hooke's law of elasticity:

$$\sigma = Y \epsilon \quad (7-16)$$

where Y is the Young's modulus of elasticity which is given by the slope of the linear portion of the stress-strain curve. However, after a short linear behavior, the stress-strain characteristics of the mix sample are predominantly non-linear for the majority of the loading time. This means that the modulus

Figure 7-8: Typical Stress-Strain Behavior, Tested by Direct Tension

is then a function of the loading time and is given by the slope of the stress-strain curve which changes at different points along the curve. This non-linear behavior of the sample continues until it reaches failure, at which point the modulus of the mix is called the secant modulus. These results show that the deformation response of a CRMA mix is predominantly viscoelastic over most of the loading time, with a short-time initial elastic response.

Figure 7-9 shows % failure strain plotted against the secant modulus (Equation (7-12)) for all the mixes. As expected the failure strain decreases as the secant modulus increases. For all the mixes studied in this work, a universal correlation ($R^2=0.87$) was obtained between the two variables that was quite good considering the difference in materials and mix variables involved in the analysis and the inherent variability in failure properties. It was concluded that the secant modulus and % failure strain are related by a power law relationship given by:

$$y = ax^b \quad (7-17)$$

Figure 7-9: Failure Strain as a Function of Secant Modulus

where y is the % failure strain, x is the secant modulus, and $a > 0$, $b < 0$ are constants determined from regression of experimental direct tension data. In this case, the values of a and b were determined to be 8.79 and -0.37 respectively.

Table 7-12 shows the relationship between different properties from the creep and recovery and direct tension tests. Important rheological properties pertinent to this discussion include the creep modulus from creep and recovery test, and failure stress, failure strain, and toughness from the direct tension test. Figures 7-10 through 7-13 show the correlation between these properties. Considering the difference in mix variables and the testing procedures, reasonably good correlations exist between the failure stress and failure strain, Figure 7-10, and failure stress and toughness, Figure 7-11. As expected, the failure strain decreases and the toughness increases as the failure stress increases. On the other hand, the toughness was found to be approximately independent of the creep modulus, Figure 7-12, while the creep modulus was approximately independent of the failure stress,

Figure 7-13. It is anticipated by the authors that the power law may hold for mixes fabricated with different binders, aggregates, and mix design procedures, with the constants of the power law being determined from regression of experimental data.

Table 7-12: Power Law Coefficients to the Equation $y=ax^b$
(Relating Different Parameters from Creep and Recovery¹ and Direct Tension Tests²)

y-variable	x-variable	a	b	Correlation Coefficient (R ²)
Failure Strain (ϵ_f)	Failure Stress (σ_f)	20.99	-0.48	0.73
Creep Modulus	Failure Stress (σ_f)	404.33	0.30	0.60
Toughness (E_f)	Creep Modulus	0.12	0.33	0.66
Toughness (E_f)	Failure Stress (σ_f)	0.09	0.79	0.85

¹Creep & recovery test was performed at a temperature of 104°F (40°C).

²Direct tension test was performed at a temperature of 77°F (25°C).

No definite conclusions could be reached to determine the effect of the mix variables such as rubber concentration, curing conditions, air voids, and base asphalt on the results of the direct tension test. This can be explained on the basis that, although this work used the same mix design procedure for all the mixes, the compaction of the binder and aggregate in the mix plays a very important role on the mix failure properties. However, in most cases the CRMA mixes reached a higher failure stress and failure strain compared to that of the control mixes. For most mixes, failure stresses in this work ranged from 10 to 78 psi (6.89×10^5 to 5.38×10^6 dyne/cm²), while the failure strains varied from 2 to 8%. Results in terms of failure energies for different mixes are discussed later in this report.

Figure 7-10: Failure Strain as a Function of Failure Stress

Figure 7-11: Creep Modulus as a Function of Failure Stress

Figure 7-12: Toughness or Failure Energy as a Function of Creep Modulus

Figure 7-13: Toughness or Failure Energy as a Function of Failure Stress

Failure Energy Consideration

One can expect the direct tension test on the mix to yield important failure property information primarily about the binder rather than the aggregate. In order to confirm this, fracture toughness (failure energy) values calculated from direct tension test on the mixes were compared with corresponding energies calculated from direct tension tests on binders (SuperpaveTM specification) performed in our laboratory and surface energies of binders measured by the Wilhemy plate technique (Elphinstone, 1997). Considering the geometrical configuration of the specimen, the direct tension test on binders is truly a one-dimensional, uniaxial test (binder-binder interface effects), while the direct tension test on the mix is a three dimensional, triaxial test (an effect of binder-binder interface, binder-aggregate interface, and binder-aggregate compaction). Relative orders of magnitude were compared to gain a better perspective on failure properties of the mix based on the failure energy approach.

Table 7-13 shows the surface energies of various asphalts and CRMA binders, calculated from the Wilhemy Plate method, and failure energies calculated from direct tension tests on the binders and mixes. Note that these energies do not correspond to the same materials. However, it is important to note that the surface energies are very close to each other, as are the failure energies, indicating that the two parameters can be approximated as material-independent parameters. Failure energies for both the binder and the mix are much larger in magnitude compared to the surface energy of the binder. Failure energies calculated from direct tension tests include the surface energy (work of cohesion) of the binder (Equation (7-13)). From Table 7-13, it is seen that most of the stored energy during tension is dissipated as heat upon fracture and a negligible amount of energy is actually used to create two surfaces. All of this implies that the direct tension test on the mix primarily yields information similar to that obtained from the direct tension test on the binder. This also means that the direct tension test on the mix can be approximated as a one-dimensional, uniaxial, tensile test which primarily characterizes failure (tensile) properties of the binder.

Table 7-13: Surface Energies and Failure Energies (Toughness) for CRMA Binders and Mixes

Surface Energy (mJ/m ²) (Wilhemmy Plate Apparatus)	Failure Energy (mJ/m ²) (Direct Tension on Binder)	Failure Energy (mJ/m ²) (Direct Tension on Mix)
30.8	1.13 x 10 ⁶	7.89 x 10 ⁵
30.3	2.13 x 10 ⁵	1.22 x 10 ⁶
27.6	7.09 x 10 ⁵	7.94 x 10 ⁵
28.0	4.31 x 10 ⁵	6.99 x 10 ⁵
27.9	1.22 x 10 ⁶	5.63 x 10 ⁵
27.7	2.15 x 10 ⁵	5.31 x 10 ⁵
27.4	9.29 x 10 ⁵	5.69 x 10 ⁵
33.7	8.77 x 10 ⁵	7.56 x 10 ⁵
31.8	5.24 x 10 ⁴	3.25 x 10 ⁵

Figure 7-14 shows the relationship between the failure energy of the mix and the binder. These failure energies have been calculated from the data obtained from the direct tension test on the mix and binder respectively. The direct tension test method for the binder is the SUPERPAVETM specification for low temperature properties. These data are given in Table 7-13. It can be seen that there is a one-to-one correlation between two similar parameters of different materials. This implies that the failure properties of the mix are directly dependent on the failure properties of the binder.

Correlation with SuperpaveTM Parameters

An important parameter identified by the results of SHRP is $G^* \sin \delta$ which is used as a parameter to characterize fatigue cracking of the binder. The average energy dissipated as heat ($\langle \dot{E} \rangle$) within a material is given as (Rosen, 1993):

$$\langle \dot{E} \rangle = 0.5 (\epsilon^0)^2 \omega G^* \sin \delta \quad (7-18)$$

where ϵ^0 is the strain amplitude and ω is the angular frequency. $\langle \dot{E} \rangle$ is calculated as the area under the stress-strain curve of any material undergoing cyclic deformation in shear. If $G^* \sin \delta$ is a true indicator of fatigue cracking for the binder, then values of E_f obtained for the mixes from the direct

Figure 7-14: Relation Between Mix and Binder Toughness

tension test should correlate with $G^* \sin \delta$ of the corresponding binder. This is valid only if the direct tension test on the mix primarily yields tensile properties of the binder. Figure 7-15 shows the correlation between the failure energy (toughness) of the mix obtained from direct tension measurements and $G^* \sin \delta$ of the corresponding binder at 10 s^{-1} obtained from dynamic shear rheometer analysis (Chapter 6). From this Figure, it can be concluded that $G^* \sin \delta$ of the binder bears a very poor correlation with the failure energy and hence use of $G^* \sin \delta$ as a parameter for fatigue cracking could not be validated within the confines of this research work.

The rheological parameter, $G^*/\sin \delta$, was identified by SHRP to characterize the rutting potential of the binder. As stated earlier, the creep modulus of a mix at the end of the creep period, $E_c(3600)$, and the creep rate, m , characterize the rutting potential of the mix. Figures 7-16 and 7-17 show the relationship between the rutting parameters of the CRMA binder and its corresponding mix. $G^*/\sin \delta$ for the binder was determined at 10 s^{-1} and 313K using the dynamic shear rheometer in our laboratory (Chapter 6). It can be seen from the Figures that a direct relationship (power law form)

Figure 7-15: Mix Toughness as a Function of Binder $G^* \sin \delta$

Figure 7-16: Mix Creep Rate, m , as a Function of Binder $G^* / \sin \delta$

Figure 7-17: Mix Creep Modulus, $E_c(3600)$, as a Function of Binder $G^* / \sin \delta$

exists between $G^*/\sin\delta$ (binder) and m (mix) ($R^2=0.78$) and $G^*/\sin\delta$ (binder) and $E_c(3600)$ (mix) ($R^2=0.82$). This indicates that m and $E_c(3600)$ are reasonable parameters that can be used to characterize the rutting potential of the mix. These Figures show that if a binder with a high value of $G^*/\sin\delta$ is used to fabricate a mix, the resultant mix will have a high value of m and $E_c(3600)$. But as stated earlier in this work, a rut-resistant mix should have a small value of m and high $E_c(3600)$. Thus, it can be concluded that a binder which will result in a mix with optimum values of m and $E_c(3600)$ should be used in the fabrication process. Also, a mutual compromise has to be reached between m -value and $E_c(3600)$ of the mix for good performance. This confirms the fact that binder properties play an important role in characterizing the rutting potential of a mix.

Estimation of Paris Law Parameters

To acquire more insight into the crack growth process, the continuously changing stress distribution during the crack growth process can be described by linear fracture mechanics principles using Paris law (Paris and Erdogan, 1963):

$$\frac{dc}{dN} = A K^n \quad (7-19)$$

where dc/dN is the rate of crack propagation, c is the crack length, N is the number of load cycles, K is the stress intensity factor, and A and n are material parameters. These material parameters directly govern the amount of cracking in the pavement subjected to specified values of stresses. Currently, very time-consuming and laborious tests are needed to determine A and n . It would therefore be very practical to determine the values of these parameters through simple and feasible test methods.

Jacobs et al (1996) determined the material parameters through extensive dynamic experiments and found that A and n are related as:

$$\log A = a + bn \quad (7-20)$$

Lytton et al (1993) found that n is related to the m -value, slope of the steady-state portion of the creep strain vs. time plot obtained from creep and recovery tests as follows:

$$n = 0.8 \frac{m+1}{m} \quad (7-21)$$

Extensive investigation by Lytton et al (1993) determined the following equation relating A and n after field calibration:

$$\log A = 4.389 - 2.52 \log (10000 \sigma_f n) \quad (7-22)$$

where σ_f is the failure strength (failure stress) of the mix determined from direct tension tests.

Equations 7-21 and 7-22 are used in this work to determine the values of A and n from the creep and recovery and direct tension data. Values of A for the control and CRMA mixes were of the order of 10^{-10} to 10^{-12} , while n ranged from 2 to 10.

Linear regression was performed on all the mixes to verify the use of Equation 7-20. On this basis, the mixes in this work could be divided into two categories (Figure 7-18). The mixes fabricated with the control and the low cured CRMA binder obeyed the following equation relating A and n ($R^2=0.85$):

$$\log A = -9.69 - 0.18 n \quad (7-23)$$

On the other hand, the mixes fabricated with high cured CRMA binders and Neste Wright satisfied the following equation ($R^2=0.84$):

$$\log A = -10.95 - 0.17 n \quad (7-24)$$

Values of a and b reported by Jacobs et al (1996) for asphalt mixes are -2.36 and -1.14 respectively. Values of a and b for the control (0% rubber) mixes found in this work are -2.71 and -1.20 respectively, which compare quite well to the values reported by Jacobs et al (1996). Values of a and b for the other mixes found in this work differ significantly possibly due to the difference in binder used (CRMA in this case) and mix design procedures. The difference in the values may actually be related to the effect of rubber on mix performance. Taking into account the large variation in the mix variables, a unique relationship was found to exist between the Paris material constants, A and n , which may be applicable for all asphalt and CRMA binder mixes. These results show that simple laboratory tests like the creep and recovery and direct tension tests as described in this work can be used to obtain valuable information about the fracture mechanics of CRMA binder mixes.

Figure 7-18: Relation Between Paris Law Material Constants

SUMMARY

To summarize, the creep and recovery test is a valuable tool to observe the behavior of a mix under loading conditions. The results of this test can be used to obtain important rheological properties of the mix and this in turn can be used to characterize the rutting potential of the mix. The strains incurred by the sample during creep and recovery can be used to generate master curves for the mix in terms of the creep compliance, $J(t)$ and the loading time, t . The master curve information can then be used to calculate other viscoelastic properties of the mix such as $G^*(\omega)$ using the theory of linear viscoelasticity.

The rutting potential of a mix can be evaluated on the basis of the following parameters obtained from the creep and recovery test: creep modulus, $E_c(t)$, creep rate, m , permanent strain of the sample, ϵ_p , and % strain recovered by the sample at the end of the recovery period. In terms of these parameters, a mix will have low rutting potential (high rutting resistance), if it has a high $E_c(t)$,

low m , low ϵ_p , and high % recovery. Results indicate that for low rutting potential, the CRMA binder used to fabricate the mix should be as homogeneous as possible, and the compaction procedure of the mix should result in low air voids. In general, the CRMA mixes tested in this work showed stable behavior (low rutting potential) under the conditions of the test. However, these results require further validation using test conditions that more closely simulate field conditions.

The direct tension test on the mix has been used to characterize the failure characteristics of mixes. Failure stress, failure strain, and failure energies have been determined which are very useful parameters to evaluate mix performance. The failure energy of the mix, as determined from the direct tension test, compares very well in magnitude to the failure energy of the binder, as determined from the direct tension test on the binder. The energy required to break the binder-binder interface was found to be negligible compared to the failure energies. CRMA mixes reached a higher value of the stress and strain before reaching failure compared to unmodified asphalt mixes.

Power relationships were found to exist between different parameters of the creep and recovery and direct tension tests. The results of these tests have also been used to determine the material constants in the Paris Law of crack propagation. A unique relationship was found to exist between these constants which is a sensitive function of the curing conditions. Good correlations were found to exist between the rutting parameters of the mix and that of the binder as established in the SuperpaveTM specifications.

Having established that creep and recovery and direct tension tests are suitable transient tests to evaluate mix performance, the next Chapter focusses on the application of a dynamic test, the fully reversed frequency sweep test in tension and compression, to characterize the performance of mixes, specifically with reference to aging effects.

CHAPTER 8

MIX RHEOLOGY - DYNAMIC PROPERTIES

This Chapter is concerned with the laboratory evaluation of CRMA mixes through measurement of their dynamic properties. In Chapter 7, we discussed the transient characterization of these mixes using the creep and recovery and direct tension tests. Chapter 6 described the rheology of the CRMA binders used to fabricate these mixes. The fully reversed frequency sweep test in tension and compression is used in this work for dynamic characterization of CRMA mixes. This test provides a simple, fast, and economical method of characterizing the rutting potential of mixes. In particular, the effect of aging on these mixes is determined through changes in their dynamic properties. In addition, the effects of rubber concentration and curing conditions are also discussed. The compressibility of the mix is discussed in terms of the Poisson's ratio.

Dynamic results indicate that CRMA mixes are more rut resistant than unmodified asphalt mixes. The effect of aging is to deteriorate the rheological properties of the mix, which can eventually cause instability or failure. Note that these tests have been performed on laboratory mixes and not on field cores. It is also shown that the frequency sweep test provides a satisfactory laboratory procedure to evaluate the rutting potential of CRMA mixes.

MATERIALS AND MIX DESIGN

Although the materials and mix design procedure has been described in Chapter 7, these procedures and methods will be discussed again for the benefit of the reader. Different asphalts with initial viscosities ranging from 500-1000 poise at 333K (140°F) were obtained from Exxon, Fina, and Diamond Shamrock. These asphalts were modified by curing with ground tire rubber obtained from Rouse Rubber Company, Vicksburg, Mississippi. Two different particle sizes were used: -80 mesh (250 μm) and -10 mesh (750 μm). The curing process consists of mixing asphalt and rubber in different concentrations at elevated temperatures for extended periods of time in an inert atmosphere (N_2 environment). The parameters that affect the curing process are the time, temperature, and shear intensity of curing. Three different curing conditions were used in this work: (a) 1 hour at

448K (350°F), 500 rpm (low curing condition), (b) 6 hours at 463K (375°F), 1550 rpm (intermediate curing condition), and (c) 3 hours at 533K (500°F), 8000 rpm (high curing condition). The degree of curing dictates the amount of rubber that dissolves in the mixture. Thus, curing condition (c) produces the most homogeneous binder relative to conditions (a) and (b). Approximately 2000 grams of asphalt and rubber were cured in a mixer at a time. Different curing conditions, as mentioned above, were used to make CRMA binders with 6%, 12%, and 18% rubber by weight. A total of 21 CRMA binders were produced to determine the effect of aging, rubber concentration, curing conditions, and base asphalt on mix rheology. The rheology of these CRMA binders has been discussed in Chapter 6.

These CRMA binders were then used in compacted mixes in the laboratory. TxDOT's method (Tex-232-F) was used to design these mixes. This method is a volumetric design procedure normally used for coarse matrix, high rubber content mixes. The aggregates used for mix designs are crushed limestone and field sand. The design criteria for this mix design are listed below:

- (a) target air voids = 4-6%
- (b) optimum laboratory molded density = 97%
- (c) minimum volume of the binder = 6%
- (d) percent aggregate passing #200 sieve = 6%

The mix design for the control mix (0% rubber) was the same as that used for the CRMA mixes to minimize the variables. A detailed description of the design process for the laboratory mixes is given by Estakhri et al (1993).

Three samples were fabricated per CRMA binder and subjected to fully reversed frequency sweep test (tension and compression) to determine their initial dynamic rheological properties. Their initial transient properties using the creep and recovery and direct tension tests have been discussed in Chapter 7. These mixes were then aged in a controlled environment at 333K (140°F) and atmospheric pressure. These conditions were chosen because they approximately simulate field conditions. The frequency sweep test was performed periodically on the samples to determine the effect of aging. This test was run on the mixes to identify important dynamic properties of the mix that affect its performance. The subsequent sections of this Chapter briefly describe the test run on the mixes along with a discussion of rheological properties obtained from them. Important results

that affect the mix performance under dynamic loading conditions are also discussed.

TEST METHOD

To determine the initial rheological properties of the mix and subsequent changes in these properties due to aging, mix samples were subjected to frequency sweep test in tension and compression. The mix sample has a diameter of 3 inches (7.6 cm) and a height of 6 inches (15.2 cm). Epoxy endcaps are glued at both ends of the specimen so that it can be held between the fixtures of the frequency sweep test apparatus. The applied load is sinusoidal, with the frequency of the sine wave varying from 20 Hz to 0.01 Hz (125.7 s^{-1} to 0.063 s^{-1}). In general, the load levels and resulting displacements are relatively small. Six LVDT's (linear variable differential transducer) are glued to the sample 120° apart, so that the effective gage length of the sample was kept at 2 inches (5.08 cm). These LVDT's are used in such a way that three LVDT's measure the axial strain, while the other three measure the radial strain. These LVDT's are connected to a data acquisition system, which records the applied axial stress and resulting axial and radial strains. A schematic of the specimen geometry and configuration is shown in Figure 8-1.

Figure 8-1 also shows the axial stress (applied load) and strain (axial and radial strain response) of the sample subjected to the frequency sweep test. Experimental stress and strain data are fitted using Equation (8-4) which is discussed in the next section. The test is conducted in such a way that the amplitude of the load in tension is equal to the amplitude of the load in compression. This results in a greater amount of strain observed in the tensile direction than in the compressive direction. This is an indication of the fact that the response of the mix to tensile loading is controlled by the binder, while the compressive response reflects the properties of the aggregate.

Figure 8-1: Frequency Sweep Test, Specimen Configuration and Response

THEORY

Either tensile or a fully reversed (tension and compression) loading can be applied to the sample. Tensile loading sometimes results in a large amount of creep within an individual frequency which can cause permanent damage to the sample. To reduce the creep (permanent damage) during testing, fully reversed (tension and compression) sinusoidal loading is used. As mentioned earlier, the tensile portion of the test is controlled by binder properties, while the compressive portion of the test reflects the properties of the aggregate. This test was performed at room temperature.

Direct experimental measurements from this test are the stress (axial) and strain (axial and radial) of the sample as a function of frequency (1/loading time). Knowing the stress and the strain, the theory of viscoelasticity can then be used to obtain valuable rheological information required to characterize mix performance. The data analysis software developed at Texas Transportation Institute, Texas A&M University by Lytton et al. (1993) was used to calculate the creep compliance, complex compliance, Poisson's ratio, and rut depth as a function of frequency. A brief background about transient and dynamic rheological properties (stress and strain) was discussed in Chapter 7.

Considering this background, the extensional complex compliance, $D^*(\omega)$, can then be defined as:

$$D^*(\omega) = \frac{\epsilon^*(\omega)}{\sigma^*(\omega)} \quad (8-1)$$

where ω is the frequency, and the superscript denotes a complex quantity. The complex stress, $\sigma^*(\omega)$, and the complex strain, $\epsilon^*(\omega)$, are given by Equation (7-4). As with any complex number, Equation (8-1) can be written as:

$$D^*(\omega) = D'(\omega) - i D''(\omega) \quad (8-2)$$

where D' is the real or storage component of the compliance and D'' is the imaginary or loss component of the compliance (Ferry 1985). Thus D' is the ratio of the strain in phase with the stress to the stress ($\delta=0^\circ$), while D'' is the ratio of the strain 90° out of phase with the stress to the stress.

D' is the elastic component of the deformation, while D'' is the viscous component of the deformation. Thus D' is zero for a viscous fluid, while D'' is zero for an elastic solid. For a viscoelastic material, both D' and D'' are non-zero and finite. Based on the theory of viscoelasticity, the transient and dynamic compliances are related through Laplace transforms as:

$$D^* = sL[D(t)] \quad (8-3)$$

where s is the Laplace parameter in the frequency domain, L represents the Laplace transform, and $D(t)$ is the transient extensional creep compliance.

Another parameter used to describe the extensional deformation of an elastic material is the Poisson's ratio, μ , which is defined as the ratio of the axial extension to the lateral (radial) contraction. Poisson's ratio is an indicator of the compressibility of the material. For an incompressible material, the Poisson's ratio is 0.5.

Axial stress, axial strain, and radial strain are obtained as raw data which are then input to a Crockford pattern search routine which is a modified non-linear least squares minimization program (Lytton et al, 1993). This data analysis program fits the raw data to the following equation:

$$Y(t) = \beta_0 + \beta_1 t + \beta_2 \sin(\beta_3 + \beta_4 t) \quad (8-4)$$

where $Y(t)$ is the axial stress, axial strain, or radial strain, β_0 is the intercept for long term trend line, β_1 is slope of long term trend line, β_2 is amplitude of sine wave, β_3 is related to wavelength, β_4 is related to phase angle, and t is the loading time. The Crockford pattern search program is used to compute the coefficients, β_0 through β_4 for each frequency. These coefficients are then used to calculate axial and radial strain amplitudes, which in turn are used to compute storage and loss compliances and Poisson's ratio, all in tension, compression, and shear. This program assumes that the extensional creep compliance, $D(t)$, is given by a power law equation of the form:

$$\frac{\epsilon^*(\omega)}{\sigma_0} = D(t) = D_0 + D_1 t^m \quad (8-5)$$

where t is the loading time, D_0 and D_1 and m are coefficients to be determined through linear regression of the following equations:

$$\begin{aligned} D'(\omega) &= D_0 + D_1 \Gamma (1 + m) \cos\left(\frac{m \pi}{2}\right) (2 \pi \omega)^{-m} \\ D''(\omega) &= D_1 \Gamma (1 + m) \sin\left(\frac{m \pi}{2}\right) (2 \pi \omega)^{-m} \end{aligned} \quad (8-6)$$

where ω is the frequency, $D'(\omega)$ and $D''(\omega)$ the storage and loss components of the complex compliance respectively as defined by Equation (8-2). The storage and loss components of the compliance in Equation (8-2) are calculated from the knowledge of the axial and radial strain amplitudes. Knowing the compliances and the frequency of loading, it is then possible to use Equation (8-6) to determine D_0 , D_1 , and m . The power law assumption of the creep compliance (Equation (8-5)) is also assumed in the SUPERPAVETM pavement distress model for permanent deformation.

Equations (8-4) through (8-6) are valid in tension, compression, and shear. The program for analyzing the frequency sweep test includes an algorithm for predicting expected rut depth as a function of loading frequency. Input to the rut depth model includes travel speed, tire inflation pressure, tire radius, depth of asphalt layer, and number of loading times between load repetitions. The rut depth, r_d , calculated by the algorithm takes into account the rutting due to compression, r_c , and lateral shear movement, r_l . This can be represented mathematically as:

$$r_d = r_c + r_l \quad (8-7)$$

where r_c and r_d are functions of the tire inflation pressure, asphalt layer thickness, number of load repetitions, D_c^* , D_s^* , m_c , m_s , m_c , m_s , and other geometrical factors. In the preceding, the subscript 'c' denotes compression, while the subscript 's' stands for shear. Further details of these calculations can be obtained in Lytton et al (1993). Thus, important properties obtained from this test include the extensional creep compliance, extensional complex compliance, Poisson's ratio, and rut depth as a function of frequency.

The tensile, compressive, and shear compliances, calculated in this work, are important indicators of the amount of rutting that will occur in the frequency ranges. The range of frequencies used in this work represent traffic loading rates depending on the speed of the vehicle. This simulation is identified with vehicle speeds as follows:

Highway speeds: 2-20 Hz (12.57-125.67 s⁻¹)

Street and intersection speeds: 0.2-2 Hz (1.26-12.57 s⁻¹)

Parking area speeds: 0.02-0.2 Hz (0.13-1.26 s⁻¹)

The slopes of the creep compliance curves in tension, compression, and shear, m_t , m_c , and m_s , respectively control the rate of growth of the tensile, compressive, and shear components of rutting in the binder layer. On the other hand, Poisson's ratio is the best indicator of the effect of gradation and particle shape of the aggregate used for mix design. The Poisson's ratio dictates the size of the tensile stresses that develop in the binder and stiffen the binder so that rutting can be reduced. In summary, the mix should have a high compliance and an optimum Poisson's ratio in tension, compression, and shear for good resistance to rutting. Lytton et al (1993) have set the following rutting-performance related specifications:

slope of the creep compliance curve: $m_c \leq 0.6$; $m_s \leq 0.5$.

Poisson's ratio: $0.3 < \mu_t < 0.5$; $0.5 < \mu_c < 0.8$ (2 Hz < ω < 20 Hz)

These values have been specified for the frequency sweep test performed at 313K (104°F). The next section puts all this into perspective by discussing the results obtained from this test.

RESULTS AND DISCUSSION

The results of the frequency sweep test are discussed in terms of the following parameters obtained from dynamic measurements:

- (1) creep compliance, $D(t)$, in tension, compression, and shear.
- (2) complex compliance, $D^*(\omega)$, in tension, compression, and shear,
- (3) Poisson's ratio, μ , in tension, compression, and shear,
- (4) rut depth, r_d .

In terms of these parameters for a mix to have good performance characteristics, it should

have a high compliance and small rut depth. Results are discussed in terms of creep compliance, $D(t)$, since similar arguments will apply to changes in complex compliance, $D^*(\omega)$. This is because $D(t)$ and $D^*(\omega)$ are inter-convertible through Laplace transforms (Equation 8-3). Variables of interest in evaluating the performance of these mixes include:

- (1) Aging,
- (2) Rubber concentration,
- (3) Curing condition.

Effect of Aging

Figures 8-2 through 8-4 show the effect that aging has on the creep compliance (tension, compression, and shear) of the mix as determined from frequency sweep test in tension and compression. It can be clearly seen that the mix shows a big reduction in its compliance (tensile, compressive, and shear) due to aging. A similar effect was seen on the complex shear modulus, $G^*(\omega)$, of the corresponding CRMA binder measured by dynamic shear analysis. In this case an increase in $G^*(\omega)$ of the binder was observed due to aging (Chapter 6). It is suggested that this reduction in the compliance of the mix due to aging is mainly due to the deterioration in physical (rheological) properties (increase in viscosity) that the binder undergoes as a result of aging.

Atmospheric oxygen has a great affinity towards asphalt molecules which is accelerated by elevated temperature and pressure, resulting in the formation of carbonyl ($C=O$) groups. Increase in oxygen content, due to aging, has been correlated directly with the formation of carbonyl groups measured via surface analysis using the Fourier Transform Infrared Spectrometer (FTIR) (Lunsford, 1994). In addition changes in chemical composition of the asphalt due to aging has been an area of several investigations (Lin, 1995; Chaffin, 1996).

An asphalt structure is essentially made up of asphaltenes, aromatics, and saturates. Aging results in the conversion of aromatics into asphaltenes, which are the primary contributors to the viscosity of asphalt. On the other hand, the saturate content remains relatively constant during aging. Thus as the asphalt ages, the asphaltene content increases, which directly results in an increase in its viscosity. This increase in viscosity is also accompanied by a loss of ductility which can eventually lead to binder failure. In other words, aging causes a deterioration in the rheological properties of

Figure 8-2: Effect of Aging on Tensile Creep Compliance

Figure 8-3: Effect of Aging on Compressive Creep Compliance

Figure 8-4: Effect of Aging on Shear Creep Compliance

the binder due to associated chemical compositional changes.

The exact effect of aging on rubber is not yet fully understood; however it has been reported that oxygen tends to break down the rubber particles, thereby making the CRMA binder more homogeneous (Chapter 6). This dissolution of the rubber particles in the asphalt matrix may also contribute to the increasing viscosity of the binder due to aging. The effect of aging on the aggregate is not known; however it would be fair to assume that aging would have a much smaller effect on the rheological properties of the aggregate compared to that of the binder. This illustrates that binder properties are of prime importance in the overall performance of a mix, specifically with regard to aging.

Comparison of the relative order of magnitudes of compressive, tensile, and shear compliance shows that the shear compliance has the highest value followed by the tensile compliance, and then the compressive compliance. This implies that the shear strain is greater than the tensile strain, which in turn is greater than the compressive strain for the same applied stress on the sample. This is an

important observation, because each of the compliances indicate which of the materials (binder, aggregate, or mix (binder-aggregate)) play a dominant role in responding to deformation. It is our understanding that the shear compliance represents binder-aggregate interactions, the tensile compliance indicates binder-binder interactions, while the compressive compliance characterizes aggregate-aggregate interactions. Thus, we can say that binder-aggregate interactions are very important in the overall performance of the mix. This emphasizes the need for good compatibility between the binder and the aggregate for optimal mix performance. Thus compatibility between the binder and aggregate is a more important consideration relative to the independent performance of the binder and the aggregate. Coincidentally, this agrees qualitatively with the results of Elphinstone (1997) who reported that the receding work of adhesion (work required to break a binder-aggregate interface) was greater in magnitude than the receding work of cohesion (work required to break a binder-binder interface). His results imply that larger strains are incurred on the sample due to binder-aggregate interactions (shear strain) than binder-binder interactions (tensile strain).

Figures 8-5 through 8-7 show a selection of CRMA binders that are low- and intermediate-cured. Comparing the compliances of these mixes to those of the control (Exxon AC-10 and 0% rubber), we can see that the CRMA mix has a significantly different compliance than that of the control mix. It is interesting to note that addition of rubber decreases the tensile and shear compliances of the mix, while it increases the compressive compliance. This indicates that rubber while improving the binder properties (reduction in tensile compliance), also causes an improvement in aggregate properties (increase in compressive compliance). This is because the tensile compliance indicates binder-binder interactions, compressive compliance indicates aggregate-aggregate interactions, while the shear compliance reflects binder-aggregate properties. Thus, modification of the asphalt by addition of rubber causes an increase in the mix compliance, which should result in better mix performance under dynamic loading conditions. Of course this change in mix compliance is a function of the base asphalt, rubber type, rubber size, rubber concentration, and curing conditions. This change in the compliance is definitely due to binder effects, because the same mix design procedure was used in all cases. Further details on the effect of rubber on mix compliance is given in the next section.

Figure 8-5: Comparison of Control and CRMA Tensile Creep Compliance

Figure 8-6: Comparison of Control and CRMA Compressive Creep Compliance

Figure 8-7: Comparison of Control and CRMA Shear Creep Compliance

Effect of Rubber Concentration

Rubber is a desirable additive for modifying asphalt primarily because of the additional elasticity and resiliency displayed by the modified binder. To illustrate this, Figures 8-8 through 8-10 show the change in mix compliance with rubber concentration. It should be noted that the blends presented in Figures 8-8 through 8-10 represent the high-cure conditions exclusively, as opposed to the earlier low- and intermediate-cure figures. It can be clearly seen that $D(t)$ of the mix in all three modes, tension, compression, and shear, increases with an increase in rubber concentration. Since $D(t)$ is inversely proportional to $S(t)$ as given by Equation (8-2), increase in rubber concentration results in a reduction of the stiffness of the modified mix. This is very beneficial because a mix with a lower stiffness will display a higher resistance to cracking. It has also been shown that addition of rubber to the binder results in a similar reduction in the stiffness of the modified binder at high frequencies (lower temperatures), as measured by dynamic shear rheometer and bending beam rheometer (Billiter, 1996; Chapter 4). These results once again emphasize the improvement caused

Figure 8-8: Effect of Rubber Concentration on Tensile Creep Compliance

Figure 8-9: Effect of Rubber Concentration on Compressive Creep Compliance

Figure 8-10: Effect of Rubber Concentration on Shear Creep Compliance

by addition of rubber on mix performance.

There is greater increase in compressive $D(t)$ compared to tensile and shear $D(t)$ of the mix as the rubber concentration is increased. The compressive part of the compliance, as mentioned earlier, reflects aggregate properties, particularly mix resiliency. It is quite possible that rubber further improves the mix resiliency, thereby causing a greater increase in the compressive compliance relative to tensile and shear compliance. This would benefit the healing period that the mix undergoes between successive load applications in actual field conditions.

Effect of Curing

The homogeneity of the CRMA binder is a sensitive function of its curing conditions. It has been shown that as the intensity of curing is increased (time, temperature, mixing speed), rubber particles dissolve in the asphalt matrix, resulting in a homogeneous binder (Billiter, 1996; Chapter 6). This has also been confirmed by SEC measurements performed on CRMA binders. Figure 8-11 shows the effect that curing has on the creep compliance in tension, compression, and shear. As

expected, the mix compliance in all the three modes increases with the intensity of curing. These results show that binder-binder, aggregate-aggregate, and binder-aggregate interactions are strengthened as a more homogeneous CRMA binder is used. This shows that use of a homogeneous CRMA binder will result in a mix that will exhibit better performance characteristics under the conditions of this test because of the improvement in its rheological properties.

Binder-Mix Property Correlations

Rheological properties of CRMA binders used in this test have been measured on a dynamic shear rheometer (Carrimed CSL 500). Frequency sweep at various temperatures were run on these binders to determine the master curve using the time-temperature superposition principle at a

Figure 8-11: Effect of Curing on Creep Compliance

reference temperature of 273K (32°F) (Chapter 6). Mixes fabricated from these binders were subjected to frequency sweep tests at 298K (77°F) and creep and recovery tests at 313K (104°F) (Chapter 7). These tests were performed on the mixes to determine their performance under various transient and dynamic test conditions. As mentioned earlier, it is imperative to relate binder rheology to mix rheology to understand the effect of binder and aggregate properties on mix performance.

With this in mind, Figure 8-12 provides a relative magnitude comparison by superimposing master curves of both a CRMA binder and its resultant binder-aggregate mix, determined by binder dynamic shear analysis, mix frequency sweep and mix creep and recovery, as indicated. The figure shows two master curves of the binder determined from dynamic shear analysis referenced to 273K (32°F) and 298K (77°F). The creep compliance in shear is plotted versus the loading time ($t=1/\omega$). It is important to note that the master curve of the binder indicates interactions between binder molecules, while the mix master curves account for binder-binder as well as binder-aggregate interactions. It is clearly seen that mix performance is a sensitive function of both binder and aggregate properties. Perhaps future efforts can develop a model relating these varied properties to real-world mix performance.

It is interesting to note that mix master curves determined from the frequency sweep (298K [77°F]) and creep and recovery test (313K [104°F]) are placed above and below the binder master curve respectively. This is probably because the shear compliance obtained from the frequency sweep test yields information about binder-binder as well as binder-aggregate interactions. On the other hand, the creep and recovery test, being a compressive test, relates more to aggregate properties than binder properties. Another reason for this difference is the fact that the mix tests have been carried out at two different temperatures and it is well known that viscoelastic properties are very sensitive functions of temperature. Despite this difference, binder and mix rheology exhibit a similar response (master curve trend and shape) to shear deformation over a range of loading times.

The limiting values of the shear compliance reached at low loading times (high frequency; low temperature) by the binder is 2×10^{-9} cm²/dyne, while the mix has a value of 2×10^{-11} cm²/dyne from creep and recovery data and 3×10^{-6} cm²/dyne from frequency sweep data. These high frequency values characterize the elastic/glassy behavior of the material. The high frequency value of the binder corresponds to a stiffness of 1.5×10^9 dyne/cm² (150 MPa) that would be obtained from the bending

Figure 8-12: Comparison of Binder and Mix Master Curves

beam rheometer under equivalent test conditions (loading time and temperature). On the other hand, the slopes of the master curves (steady-state Newtonian viscosities) at high loading times (low frequency; high temperature) can be used to describe the viscous behavior of the materials. The binder has a steady-state viscosity of 2×10^9 poise (dyne s/cm^2), while the mix displays a steady-state viscosity of 2×10^{11} poise from creep and recovery and 3.3×10^7 poise from the frequency sweep test data. The intermediate frequency region describes the viscoelastic nature of the materials under different loading and temperature conditions.

The phase angle is an important parameter that indicates the viscoelastic response of a material to deformation. It is defined as the angle between the stress and strain and hence is 0° for an elastic material (Hooke's law) and 90° for a viscous material (Newton's law). Figure 8-13 shows a comparison of the phase angle of the binder (dynamic shear analysis) and its corresponding mix (frequency sweep test) plotted against frequency. The phase angle of the mix as a function of frequency is calculated assuming the mix to behave as a Maxwell element (viscoelastic liquid). It can

be seen that the phase angles of both the binder and mix approach 90° at low frequencies (high temperatures), which is a direct indication of viscous behavior. However, as the frequency increases, the difference in the phase angles of the binder and mix increases, with the phase angle of the binder approaching 30° and that of the mix approaching 0.003° at high frequencies (low temperatures). This value of the phase angle at high frequencies characterizes elastic behavior, which means that for all practical purposes, the mix approaches elastic behavior more closely than the binder. This once again proves that the aggregate rheology does affect mix performance in terms of its response to deformation. Hence both CRMA binder and aggregate properties must be considered for effective implementation of this technology in pavement construction.

The rate of deformation of the mix is an important parameter to be considered in evaluating mix performance. The rate of deformation obtained in this work is called the m-value, which is

Figure 8-13: Comparison of Binder and Mix Phase Angles

mathematically given by:

$$m = \frac{d\epsilon}{dt} \quad (\text{creep and recovery}) \quad (8-12)$$

and

$$m = \frac{d \log D(t)}{d \log t} \sim \frac{d \log \epsilon}{d \log t} \quad (\text{frequency sweep}) \quad (8-13)$$

Three different m-values in tension, compression, and shear are calculated from the frequency sweep analysis program, Equation (8-13), while the m-value obtained from the creep and recovery test, Equation (8-12), is valid in compression only. It would be really interesting to relate the compressive m-values obtained from the two tests. Figure 8-14 shows the comparison between the compressive m-values obtained from creep and recovery (313K) and frequency sweep tests (298K). It is important to note that both the m-values, as described by Equations (8-12) and (8-13), essentially represent the rates of deformation in the mix in compression. An important difference between the two m-values is that the frequency sweep test is a dynamic test in which a sinusoidally varying stress is applied in tension and compression, while the creep and recovery test is a transient test where a constant load is applied in compression. In addition, the tests have been carried out at different temperatures. Considering the above differences, a fairly good correlation ($R^2=0.68$) between the two parameters is obtained.

This section showed that both binder and aggregate properties have to be considered in evaluating the performance of a mix. In order to enhance the life-time of the pavements, it is imperative to develop high quality asphaltic materials (CRMA) and aggregate, specifically with regard to their rheological properties. The subsequent sections of this Chapter discuss the compressibility of the mix in terms of the Poisson's ratio and the rutting performance of the CRMA mixes in terms of the rut depth predicted by the frequency sweep software.

Mix Compressibility

A change in the Poisson's ratio of the mix with aging would indicate the change in

Figure 8-14: Correlation between m-values from Frequency Sweep (FS) and Creep and Recovery (C&R) Tests

compressibility of the material when exposed to oxygen (aging). Prior investigations in asphalt and modified asphalts have assumed the binders to be incompressible with a Poisson's ratio of 0.5. Frequency sweep tests on unaged mixes show that μ is a function of frequency (loading conditions) and possibly temperature, and yield different values of the Poisson's ratio in tension and compression. In general, the tensile Poisson's ratio decreases with frequency, while the compressive Poisson's ratio increases with frequency for a particular sample (Figure 8-15). For an unaged mix sample, it can be seen from the figure that both tensile and compressive μ is usually less than 0.5, except at high frequencies where the compressive μ approaches a maximum, while the tensile μ approaches a minimum. This shows that the assumption of incompressibility is not valid for a mix.

Once again in this case, the tensile μ characterizes the compressibility of the binder in the mix, while the compressive μ describes the compressibility of the aggregate in the mix. It is seen from the figure that for a given mix, both tensile and compressive μ 's are constant at lower frequencies (0.1-1 Hz), but at higher frequencies they begin to decrease and increase respectively with frequency. This

Figure 8-15: Variation of Poisson's Ratio as a Function of Frequency

means that compressibility of the mix is an important issue at higher vehicle speeds compared to lower speeds. In general, the Poisson's ratio was found to relate exponentially to the frequency mathematically as:

$$\mu = a \exp[b \omega] \quad (8-14)$$

where $0 < a < 1$ in tension and compression; $0 < b < 1$ in compression, and $-1 < b < 0$ in tension are material constants determined from regression of experimental data.

The Poisson's ratio is a sensitive function of aging as shown in Figure 8-16. In most cases, both the tensile and the compressive components of the Poisson's ratio decrease due to aging. As mentioned before, aging causes a reduction in the compliance of the mix and an increase in the viscosity of the binder. In both cases, the rheological properties of the materials deteriorate due to aging, which is one of the major causes of performance failure. A high value of the Poisson's ratio

implies higher strains which indirectly indicates instability of the mix. Poisson's ratio for most mixes in this work varied from 0 to 1.0; however, in some cases, ratios as high as 3.0 were obtained, particularly at higher frequencies. Thus, a reduction in the Poisson's ratio due to aging is actually a beneficial rheological consequence as far as the rutting performance of the mix is concerned. So, aging of the mix improves its rutting resistance, which will be confirmed again in the next section, which discusses the prediction of rut depth as a function of loading conditions and aging.

Figure 8-16: Effect of Aging on Poisson's Ratio

Prediction of Rut Depth

The frequency sweep analysis software includes an algorithm for predicting the expected rut depth after any specified number of load repetitions and for any loading frequencies. The following values of the different input parameters are used in this work:

tire pressure: 100 psi,
travel speed: 55 mph,
number of load repetitions: 1.5×10^6 ,
depth of asphalt layer: 4 inches,
tire radius: 12 inches.

Figure 8-17 shows the variation in rut depth of some random mixes as a function of the frequency. It is interesting to note that the rut depth predicted by the algorithm was found to be approximately independent of the frequency (loading). However, rutting is known to occur in the field due to frequent repetitions of heavy axle loads. Also, rutting gradually develops due to increasing number of load applications. It is possible that the low load levels (a single cyclic load at varying frequencies) and small number of load applications used in this work may contribute to the observation that the rut depth is independent of the frequency. It is also likely that the environment, as measured by the temperature, has a more profound effect on the rutting potential of mixes compared to the loading conditions. However, the temperature effect could not be evaluated in this work, because the test was performed at room temperature only. Overall, it was found that all the mixes used in this work were found to be rut resistant and stable.

Figure 8-18 shows the effect of aging on the rut depth predicted by the algorithm. It is seen that as the sample is aged, the rut depth decreases at a constant value of the frequency. This can be explained on the fact that aging deteriorates the rheological properties of the mix, specifically causing an increase in its viscosity. This increase in viscosity is accompanied by an increase in its modulus which in turn causes an increase in its stiffness. It is known that a mix with a higher value of the stiffness displays a greater resistance to rutting relative to a mix with a lower value of the stiffness. This result is well-supported by actual observations of rutting in the field. In other words, aging enhances the rutting resistance of the mix, which implies that rutting should be a problem of major concern for a newly-laid pavement.

Figure 8-17: Variation of Rut Depth as a Function of Frequency

Figure 8-18: Effect of Aging on Rut Depth

SUMMARY

Fully reversed frequency sweep tests in tension and compression have been successfully used to determine the dynamic rheological properties of the mix. Specifically, the effect of aging, rubber concentration, and curing conditions are considered. Experimental measurements from this test can be used to characterize the rutting performance of mixes.

Data show that extensional creep and complex compliance are important indicators of the rutting potential of mixes. Aging deteriorates the rheological properties of mixes which is consistent with the effect of aging on binder properties as described in Chapter 6. On the other hand, it was found that modification of asphalt, by the addition of rubber, will enhance the rutting potential of mixes. However, this improvement in mix performance is a strong function of the curing conditions, with a more homogeneous CRMA binder showing better performance.

Comparison of the master curves of the binder (Chapter 6) and the master curves of the mix from creep and recovery and frequency sweep tests (Chapter 7 and Chapter 8) shows that the overall performance of a mix is a sensitive function of both binder and aggregate properties. Analogous to the binder master curves, the master curve for the mix can be divided into three regions of viscoelasticity. Phase angle master curves for the mix show that the mix approaches elastic behavior more closely than the corresponding binder. The phase angles of the binder and mix compare very well at low frequencies; however they begin to deviate at higher frequencies.

Poisson ratio calculations show that the assumption of incompressibility is not valid for the mix. It was found that Poisson's ratio is a function of frequency and decreases due to aging. On the other hand, rut depth predictions by the frequency sweep software show that under the conditions of the test, the rut depth is independent of the frequency, while decreasing due to aging. Both the Poisson's ratio and rut depth results show that aging enhances the rutting resistance of the mix and is a problem of concern for newly-laid pavements.

Based on the results of the test, it seems that modification of the asphalt by rubber will enhance the overall performance of the mix, specifically its rutting properties. Overall, it has been shown that the frequency sweep test can be used as an effective tool to measure the dynamic properties of CRMA mixes, which parallels the transient properties discussed in Chapter 7.

CHAPTER 9

ADHESION TEST PROPERTIES

The strength of an asphalt-aggregate composite mix and its performance under varying loads and environmental conditions are key factors in determining pavement lifetimes. These factors strongly depend on the cohesive properties of the asphalt constituent and the adhesive properties at the asphalt-aggregate interface (Labib, 1992). A cohesive fracture is illustrated in Figure 9-1 and an adhesive one is shown in Figure 9-2. The relative strengths of these two factors help determine where the failure is more likely to occur.

The work of cohesion is the work required to create two interfaces from one phase, as illustrated in Figure 9-3:

$$\Delta G_i^c = 2 \gamma_i \quad (9-1)$$

where ΔG^c is the Gibbs free energy of cohesion, and γ_i is the surface energy of phase i . The work of adhesion is what is needed to create two interfaces from two phases in contact as in Figure 9-4:

$$\Delta G_{ij}^a = \gamma_i + \gamma_j - \gamma_{ij} \quad (9-2)$$

where ΔG_{ij}^a is the Gibbs free energy of adhesion and γ_{ij} is the interfacial surface energy of phase i and phase j .

The cohesive and adhesive bonding interactions in asphalt-aggregate systems arise mainly from two effects: (1) the Lifshitz-van der Waals interactions of electron shells of neighboring molecules and (2) the acid-base interactions between constituent molecules (Good and van Oss, 1992). The acid-base interactions are generally dominant for asphalt-aggregate composites and are particularly critical in establishing strong adhesive bonds as well as bonds that are resistant to water enhanced stripping (Labib 1992). The acid-base interaction term is further partitioned into a Lewis acid parameter and Lewis base parameter. Thus, three parameters must be determined to calculate the surface energy of the material: Lifshitz-van der Waals, Lewis acid, and Lewis base. The surface energies of the materials, the asphalt and aggregate, are used to calculate the work of cohesion and the work of adhesion. It should be noted that the Lifshitz-van der Waals force is present in all molecules, but acid-base interactions are not. In fact, the acid-base interactions are an important key in determining the compatibility of asphalts and aggregates.

Figure 9-1: Cohesive Fracture in Asphalt-Aggregate Mix

Figure 9-2: Adhesive Fracture in Asphalt-Aggregate Mix

Figure 9-3: Free Energy Change (Work) of Cohesion in Vacuum

Figure 9-4: Free Energy Change (Work) of Adhesion in Vacuum

The advantages of calculating the work of cohesion and adhesion by measuring the surface free energies of asphalts and aggregates are fourfold:

1. The mechanical work required to crack an asphalt-aggregate interface is related to the free energies of adhesion and cohesion in certain limiting cases. The theoretical work of adhesion would correspond to a fracture test measured below the brittle-ductile transition temperature.
2. Numerous crack propagation models exist; but, these models require difficult experiments to determine the parameters. It can be shown that these parameters are functions of the surface energies of the materials. By measuring the surface energies of asphalts and aggregates, these parameters can be calculated.
3. Asphalt-aggregate systems can be evaluated for the propensity to be water susceptible. Suitable asphalts may be found for the so-called "stripping aggregates."
4. Asphalts have an inherent ability to heal after cracking which is related to the surface free energies of the asphalts and aggregates.

The focus of this portion of the project was to establish a framework for predicting adhesion and cohesion in asphalt-aggregate systems. The main goals of this investigation were:

1. To develop experimental methods to measure the surface free energies of asphalts,
2. To determine if a link exists among the theoretical work of adhesion and cohesion and:
 - a. the strength of an asphalt concrete mix,
 - b. the susceptibility to water,
 - c. healing.
3. To evaluate various asphalt-aggregate mixes for strength, healing, and water susceptibility.

ADHESION TESTING

Wilhelmy Plate Method

The Wilhelmy plate method (Wilhelmy, 1863) is an established technique for measuring contact angles of liquid/solid systems and was used in this study. Glass plates are coated with asphalt to produce a smooth solid surface. The apparatus consists of three main components as shown by Figure 9-5: the Cahn C2000 balance, which supports the plate and measures the forces on the plate; the moveable platform with stepper motor to advance and recede the liquid; and a computer for data acquisition and control. The entire apparatus was operated on a vibration free table. The balance and moveable platform with stepper motor was further isolated inside a Plexiglas shield.

Figure 9-6 illustrates various plate positions and force balances. The Wilhelmy Plate Method is based on a simple force balance about a plate while immersed in a fluid:

$$F = \rho_p V_p g + p_t \sigma_L \cos \theta - V_{im} \rho_L g \quad (9-3)$$

where F is the force required to hold the plate; ρ_p is the density of the plate; V_p is the volume of the plate; g is the acceleration of gravity; p_t is the *perimeter* of the plate at the three phase interface, where solid, liquid, and gas are present; σ_L is the surface tension of the liquid; θ is the contact angle; V_{im} is the volume of the immersed plate; and ρ_L is the density of the liquid. Equation 9-3, then, is simply the sum of three force terms acting in the vertical alignment; the gravity induced weight of the plate and the surface tension interactions pull the plate downward while and the buoyancy forces of the fluid partially support the immersed mass. For a plate suspended in air, Figure 9-6a, both buoyancy and surface tension are negligible and Equation 9-3 reduces to the mass of the plate alone and becomes:

$$F = \rho_p V_p g \quad (9-4)$$

Figure 9-5: Wilhelmy Plate Apparatus

Figure 9-6: Dynamic Wilhelmy Plate Method Force Balance

Equation 9-4 is subtracted from Equation 9-3 to obtain an equation for the partially immersed plate.

$$\Delta F = p_t \sigma_L \cos \theta - V_{im} \rho_L g \quad (9-5)$$

Because the volume immersed is related linearly to the depth of the plate, a plot of force, F , versus depth yields an intercept at zero depth, Figure 9-6b. Buoyancy forces and interactions are then eliminated and the intercept provides the liquid surface tension force:

$$F_\sigma = \lim_{V_{im} \rightarrow 0} \Delta F = p_t \sigma_L \cos \theta \quad (9-6)$$

From Equation 9-6, the contact angle θ can be calculated, if σ_L is known à priori.

In Figure 9-7 below, the lower, negative sloping straight-line region corresponds to the liquid advancing onto the plate due to the lifting of the platform (Figure 9-5), while the upper straight-line region corresponds to the receding phase. For each experiment, a total of 5 cycles, each with one advancing and receding sweep, were measured. As can be seen from Figure 9-7, the reproducibility for a single plate is quite good and the limiting force at zero depth can be readily calculated.

Figure 9-7: Sample Asphalt Coated Plate AAG-1 in Glycerol

An inherent problem with the Wilhelmy plate technique is contact angle hysteresis; note the offset between advancing and receding phases in Figure 9-7. Hysteresis is the difference between the advancing contact angle and the receding contact angle:

$$H = \theta_{adv} - \theta_{rec} \quad (9-7)$$

where H is the contact angle hysteresis. This effect is caused by the heterogeneity of the solid and its failure to meet conditions of ideality. In order to eliminate hysteresis, the solid must be smooth, homogeneous, and rigid on an atomic scale. Because no real material can satisfy these criteria, contact angle hysteresis will always be present.

The peaks and valleys of rough surfaces force the contact angle to change while the fluid passes over them. A heterogeneous surface causes similar problems. While the fluid advances onto the surface, the liquid at first only contacts with or “sticks” to the high energy regions but wets the lower energy regions, as seen in Figure 9-8 (Shanahan, 1991; Nadkarni and Garoff, 1992; de Jonghe and Chatain, 1995). As the fluid is forced to contact the solid surface continuously, the fluid finally wets or “slips” in both the high and low energy regions. This repeated “stick-slip” process results in the wetting cycle to appear jagged. During the receding cycle, the liquid preferentially wets the high energy regions, and added force is required to break the high energy wetting, thus the offset in advancing versus receding in Figure 9-7. The advancing angle is therefore the maximum angle, and the retreating angle is the minimum angle. The contact angles that are actually observed depends upon the detailed shapes and configurations of the patches or strips of heterogeneity (Good, 1992).

Figure 9-8: Stick Slip Theory of Contact Angle Hysteresis

Equation 9-6, coupled with the results of an experimental run, may be employed to obtain the three parameters necessary to calculate the surface energy of the material: Lifshitz-van der Waals, Lewis acid, and Lewis base. Elphinstone (1997) presents a derivation of the equation relating these three parameters to one another, Equation 9-8:

$$\gamma_L (1 + \cos \theta) = 2\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + 2\sqrt{\gamma_S^- \gamma_L^+} + 2\sqrt{\gamma_S^+ \gamma_L^-} \quad (9-8)$$

where the subscripts *S* and *L* represent solid (asphalt) and liquid (test fluid), respectively, *LW* is the Lifshitz-van der Waals surface free energy parameter, and + and – represent the Lewis acid and base parameters, respectively. The above equation contains eight variables, the experimental contact angle θ from Equation 9-6, four surface free energies, all γ_L terms, obtained from the literature, and three surface free energies for the asphalt sample, γ_S^{LW} , γ_S^+ , and γ_S^- . By varying the liquids used, the four liquid parameters, those of subscript *L*, are also varied, and a system of independent linear equations in 9-8 may be obtained. Solving this system allows the three asphalt parameters to be obtained. Numerous fluids were examined for suitability in this study until four fluids were chosen: water, glycerol, ethylene glycol, and formamide. These fluids were selected for their relatively large surface free energy, immiscibility with asphalt, and differing acid-base parameters (see Table 9-1; Good, 1992; Good and van Oss, 1992). Advancing (obtained from θ_{adv}) and receding values for each parameter may be determined by using any three of the fluids. The remaining fluid is used to verify the results.

Table 9-1: Surface Free Energies of Various Fluids (mJ/m²)

Material	γ	γ^{LW}	γ^{AB}	γ^+	γ^-
Chloroform	27.1	27.1	0.0	3.8	0.0
Ethylene Glycol	48.0	29.0	19.0	1.9	47.0
Formamide	58.0	39.0	19.0	2.28	39.6
Glycerol	64.0	34.0	30.0	3.6	57.4
Methyl Propyl Ketone (MPK)	24.7	24.7	0.0	0.0	19.6
n-Hexane	18.4	18.4	0.0	0.0	0.0
Water	72.8	21.8	51.0	25.5	25.5

A total of 32 asphalts have been characterized using the Wilhelmy plate method and are listed in Table 9-2. Figures 9-9 and 9-10 are graphical representations of the two surface energy components: γ^{LW} is the Lifshitz-van der Waals force while γ^{AB} is the acid-base interactions. Figure 9-9 refers to advancing cycles, Figure 9-10 to receding cycles. All of the asphalts exhibit a wide range of values.

Gas Adsorption

The aggregates pose a more difficult problem experimentally than the asphalts. Because a smooth surface cannot be made from the aggregates, gas adsorption must be utilized. Figure 9-11 is the diagram of the gas adsorption apparatus utilized for this work. Contact angles cannot be measured between solids and gas, in fact the contact would be complete and $\theta = 0^\circ$ or $\cos \theta = 1.0$. Then Equation 9-9 below is similar to Equation 9-8 (Elfphingstone 1997):

$$2 \gamma_V + \pi_{eSV} = 2 \sqrt{\gamma_S^{LW} \gamma_V^{LW}} + 2 \sqrt{\gamma_S^- \gamma_V^+} + 2 \sqrt{\gamma_S^+ \gamma_V^-} \quad (9-9)$$

π_{eSV} is the equilibrium film pressure of the gas, subscript V , on the solid and is the component of Equation 9-9 that is measured experimentally. Similar to the Wilhelmy plate technique, a total of four gases are used in this experiment; three to characterize each aggregate, with the fourth being used to check the results. The gases used are hexane, water, methyl propyl ketone (MPK), and chloroform. Note from Table 9-1, the use of n-hexane allows for the direct calculation of the Lifshitz-van der Waals parameter; then chloroform and MPK may be used to obtain the Lewis acid and Lewis base data, respectively. Water would be employed as the check fluid. The surface free energies of twenty aggregate material-size combinations, shown in Table 9-3, have been characterized by Li (1997). Figure 9-12 presents the two components of the surface energy for some of these aggregates.

Pendant Drop

The pendant drop method was used to verify a selection of results obtained from the Wilhelmy Plate. A description of the apparatus may be found in Appendix A.

Table 9-2: Asphalts Characterized by the Wilhelmy Plate Method

Code	Description
AAA-1	SHRP Lloydminster 150/200 Pen Grade
AAB-1	SHRP Wyoming Sour AC-10
AAD-1	SHRP California Coastal AR 5000
AADN	AAD-1 + 6% PE, Novophalt
AAF-1	West Texas Sour AC-20
AAF3	AAF-1 Fraction 3
AAFa-1	AAF-1 Repeated
AAFTot	AAF-1 and AAFa-1 Combined
AAG-1	SHRP California Valley AR 4000
AAK-1	SHRP Boscan AC-30
AAM-1	West Texas Intermediate AC-20
EX10	Exxon AC-10
EX10a	EX10 + 5% CaO
EX5	Exxon AC-5
EX5a	EX5 with 5% Rouse -40 Mesh 7 hrs 1550 rpm
FI10	Fina AC-10
FI10a	Fina AC-10 with 10% TG-10 500°F 7hrs 1550rpm
FID	Fina Demex Resin
FIDa	FID with 10% TG-10 500F 6.5hrs 8000rpm
JA31	RTFO Aged JG31
JG31	Kuwait 80/100
JG32	Saudi 80/100 (Esso)
JG33	Venezuela 80/100 (Nynas)
JG33a	JG33 Repeated
JG33b	JG33 Bubble Aged for 240 hours
JG33c	JG33 Bubble Aged for 191 hours
JG33d	JG33 Bubble Aged for 144 hours
JG33e	JG33 Bubble Aged for 95 hours
JG33Tot	JG33 and JG33a Combined
JG34	Kuwait 45/60
JG34a	JG34 Repeated
JG34b	JG34 Repeated
JG34Tot	JG34 and JG34a Combined
JG35	Venezuela 80/100 (Esha)
NW	Neste-Wright Asphalt Rubber

Figure 9-9: Advancing Surface Free Energy of Asphalts

Figure 9-10: Receding Surface Free Energy of Asphalts

Figure 9-11: Gas Adsorption Experimental Apparatus

Table 9-3: Aggregates Characterized by Gas Adsorption

Code	Description
JG01	Meuse River Gravel, Dutch, 125-250 μm Weathered
JG02	Meuse River Gravel, Dutch, 125-250 μm Weathered
JG03	Rhine River Moraine Gravel, German 125-250 μm Weathered
JG04	Quenast Porphyry, France 125-250 μm Weathered
JG05	125-250 μm Weathered
JG05a	63-125 μm Unweathered
JG05b	125-250 μm Unweathered
JG05c	500-1000 μm Unweathered
JG11a	Meuse River Sand 500-1000 μm
JG11b	Meuse River Sand 250-500 μm
JG11c	Meuse River Sand 125-250 μm
JG11d	Meuse River Sand 125-250 μm repeated
JG11e	Meuse River Sand 63-125 μm
JG11f	Meuse River Sand <63 μm
JG11g	Meuse River Sand <63 μm crushed
JG12	Lake IJsselmeer 125-250 μm
JG13	Glansanda Crushed Granite 125-250 μm
JG21	Limestone Filler from Winterswijk
JG22	Wigras 40K from Winterswijk (Limestone dust, fly ash, and hydrate)
JG23	Wigro 60K from Winterswijk (Limestone dust and hydrate)

Figure 9-12: Surface Free Energy of Aggregates

Work of Cohesion and Adhesion

While the various surface free energies are interesting components, their importance is in the application to the material properties of cohesion and adhesion. The work of cohesion and adhesion is calculated using the free energy of adhesion required to create two interfaces from two different phases in contact in a third medium (Israelachvili, 1992):

$$\begin{aligned}
 \Delta G_{132}^a = & 2\gamma_3^{LW} + 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}} - 2\sqrt{\gamma_1^{LW}\gamma_3^{LW}} - 2\sqrt{\gamma_2^{LW}\gamma_3^{LW}} \\
 & + 4\sqrt{\gamma_3^+\gamma_3^-} - 2\sqrt{\gamma_3^+}(\sqrt{\gamma_1^-} + \sqrt{\gamma_2^-}) - 2\sqrt{\gamma_3^-}(\sqrt{\gamma_1^+} + \sqrt{\gamma_2^+}) \\
 & + 2\sqrt{\gamma_1^+\gamma_2^-} + 2\sqrt{\gamma_1^-\gamma_2^+}
 \end{aligned} \tag{9-10}$$

where subscripts 1 and 2 refer to the materials being bonded, i.e. asphalt-aggregate for adhesion or asphalt-asphalt for cohesion; and subscript 3 refers to the medium in which the data are desired, either vacuum or water, in this work. Note $\gamma_{\text{water}} > 0$ and $\gamma_{\text{vacuum}} = 0$.

DISCUSSION

Aggregates

Recalling Figures 9-9, 9-10, and 9-12, the surface free energy of the aggregates (from 150 to 400 mJ / m²) is much greater than the advancing (from 10 to 35 mJ / m²) or receding (from 30 to 50 mJ / m²) surface free energy of the asphalts. The aggregates possess various magnitudes of the Lifshitz-van der Waals and the Lewis acid-base component of the surface free energy.

The effect of the aggregate size distribution seems contradictory for the two aggregates where size variation was examined, JG05 and JG11, Table 9-3. For material JG05 (JG05a, JG05b, and JG05c), the Lifshitz-van der Waals component of the surface free energy decreases with an increase in aggregate size. This change may be insignificant compared to experimental errors. However, the change in the Lewis acid and Lewis base parameters appears to be much more important. The Lewis acid parameter increases, and the Lewis base parameter decreases as the size increases. The effect on material JG11, specifically JG11a, JG11c, JG11f, and JG11g, is the opposite; as the size is increased, the Lewis acid parameter decreases, and the Lewis base parameter increases. In both cases, the Lewis acid and Lewis base parameters change in different directions. Overall, size does appear to be a factor in the magnitude of the surface free energy, but this fact may not be important for determining the ranking of various aggregates. From the receding work of adhesion data, Figure 9-13 shows that for various aggregates with asphalt AAF-1 in vacuum, the different sizes of the same aggregate type all group together, with a small percentage of their average magnitude.

The effect of weathering is similar to the effect of size distribution. The Lewis acid and Lewis base parameters change in opposite directions, and the effects of size are consistent from the largest sample to the weathered sample. The weathered sample of JG05 is effectively the same as a larger size distribution sample of JG05. Because there was only one weathered sample tested in this project, it is not known if this is a real effect.

Figure 9-13: Receding Work of Adhesion of Various Aggregates in Vacuum

Asphalts

The magnitude of the acid-base forces and Lifshitz-van der Waals forces are different for each asphalt. The advancing surface free energies of asphalts have various levels of the overall surface free energy while the receding surface free energies of asphalts are all of the same order of magnitude with the exception of asphalt JG34, as shown in Figures 9-9 and 9-10, respectively.

The surface free energy measurements of the asphalts were verified using the pendant drop method. Although the pendant drop is not a measure of the surface free energy, the surface tension provides a good comparison for the range of the values. The pendant drop surface tension results, Table 9-4, compares favorably to the receding surface free energy measurements, Table 9-5.

Mixing various additives with asphalt has differing effects on the surface free energy. The addition of lime, CaO, to asphalt EX10, greatly decreases the overall advancing surface free energy; see EX10a, as shown in Figure 9-9. The lime treated asphalt, EX10a, has a Lifshitz-van der Waals component of the advancing surface free energy five times smaller than the untreated asphalt.

Table 9-4: Surface Tension (and sampling error) from Pendant Drop of Various Asphalts at 83.3 °C (mJ/m²) (Table 9-2, page 276)

Material	σ	$\pm s$
AAD-1	29.93	0.33
AAF-1	31.04	0.88
AAF3	33.65	0.31
AAM-1	33.09	0.57

Table 9-5: Surface Free Energies (and sampling error) from Wilhelmy Plate Receding Angles of Various Asphalts (mJ/m²) (Table 9-2, page 276)

Material	γ	$\pm s$	γ^{LW}	$\pm s$	γ^{AB}	$\pm s$	γ^+	$\pm s$	γ	$\pm s$
AAB-1	30.8	1.0	17.8	0.5	12.9	0.8	3.3	0.4	12.7	0.7
AAD-1	30.3	0.8	27.8	0.6	2.5	0.5	0.2	0.1	7.3	1.2
AAF-1	27.6	0.8	13.5	0.2	14.1	0.8	1.9	0.1	3.7	0.1
AAF3	28.0	0.4	21.3	0.2	6.7	0.4	1.1	0.1	10.0	0.2
AAFa-1	27.9	1.0	16.0	0.5	11.9	0.8	2.6	0.3	13.9	0.8
AAFTot	27.7	0.7	14.8	0.2	13.0	0.6	3.1	0.3	13.7	0.5
AAK-1	27.4	1.1	22.6	0.9	4.9	0.6	0.8	0.2	7.6	0.3
FI10	33.7	2.4	24.8	1.9	8.9	1.5	0.8	0.3	24.2	1.1
FI10a	31.8	0.9	12.3	0.2	19.5	0.8	5.9	0.4	16.1	0.7
JG34a	50.6	4.2	50.0	4.1	0.5	0.9	0.01	0.03	8.9	0.5
JG34Tot	48.5	3.8	47.4	3.6	1.0	1.1	0.02	0.04	12.4	1.1

The supercritical fraction, AAF3, of asphalt AAF-1 has a larger advancing surface free energy and a receding surface free energy that is almost the same as asphalt AAFTot (again Figures 9-9 and 9-10). AAFTot is the surface free energy calculated using all of the contact angle data for asphalts AAF-1 and AAFa-1. For the advancing surface free energy, the Lifshitz-van der Waals component increases and the acid-base component decreases for the fraction AAF3 compared to the original AAFTot. The same phenomenon occurs in the receding surface free energy although it is less pronounced.

The Novophalt asphalt, AADN, is a mixture of polyethylene with asphalt AAD-1. This mixture displays increased Lewis acid and Lewis base components of the advancing surface free energy while the Lifshitz-van der Waals portion remains virtually constant (see Figure 9-9). The advancing surface free energy is therefore larger than the original asphalt AAD-1.

The rubber modified asphalt, FI10a, has a larger advancing surface free energy than the tank asphalt FI10 while the receding surface free energy is essentially constant (Figures 9-9 and 9-10). For the advancing surface free energy, the addition of rubber increases the Lifshitz-van der Waals component and decreases the Lewis acid component. The Lifshitz-van der Waals component decreases, the Lewis acid component increases, and the Lewis base component decreases in the receding surface free energy.

Strength

The ability of an asphalt-aggregate system to withstand external tension and compression forces determines the strength of the system. This property depends both on the adhesive and cohesive properties of the mix. The effect of various aggregates upon strength may be extracted from the *receding* work of adhesion data. Figure 9-13 is a bar graph of the receding work of adhesion for various aggregates with one asphalt, AAFTot. The various aggregates all have different works of adhesion, and these values are always higher than the work of cohesion of the asphalt binders. Fracture, therefore, should occur within the asphalt for every combination.

Figure 9-14 shows a very good adhering asphalt cannot overcome a poor aggregate, but since the work of adhesion, even for the poor aggregates, is sufficiently high, selection of the aggregate is not so important (excluding water susceptibility as a consideration). Asphalts, then, are more

important than the aggregates for strength considerations. The aggregates and asphalts are ranked based upon an average work of adhesion, shown in Tables 9-6 and 9-7, respectively. The rubber modified binder produces the highest ranked asphalt, FI10a. The addition of rubber increases the adhesion properties of asphalt FI10 by about 16%. The supercritical fraction, AAF3, has lowered the average receding work of adhesion in vacuum by 9% of the original asphalt, AAFTot.

Tables 9-8 and 9-9 rank the asphalts based on the average work of cohesion for advancing and receding Wilhelmy plate cycles respectively. The addition of rubber to FI10 has greatly increased the advancing work of cohesion for FI10a, and a similar result is obtained for AADN compared to AAD-1. The use of lime in sample EX10a is detrimental, given that EX10 has by far the largest advancing work of cohesion. Sample AAF3 is also improved over its constituent material. Nonetheless, it is the receding work of cohesion that weighs more heavily in strength determination. Comparing these results graphically in Figures 9-15 and 9-16, most of the samples are bunched together, Figure 9-16, with only JG34 derivatives being vastly different. These data seem inconclusive and the smaller sample size is difficult to analyze. Here the use of rubber appears slightly detrimental.

Figure 9-14: Effect of Various Asphalts on the Receding Work of Adhesion in Vacuum

Table 9-6: Rank of Aggregates from the Receding Work of Adhesion in Vacuum (mJ/m^2) (Table 9-3, page 279)

Aggregate	Average Work
JG05	202.7
JG05b	196.3
JG05a	195.1
JG03	187.6
JG05c	184.8
JG01	184.8
JG02	177.2
JG04	175.9
JG12	171.6
JG13	169.9
JG23	169.1
JG22	162.0
JG11g	156.0
JG11f	153.5
JG11c	141.4
JG11a	135.6
JG21	135.1

Table 9-7: Rank of Asphalts from the Receding Work of Adhesion in Vacuum (mJ/m^2) (Table 9-2, page 276)

Asphalt	Average Work
FI10a	200.0
AAB-1	187.3
AAFTot	177.7
AAFa-1	174.9
JG34Tot	174.9
JG34a	174.3
FI10	172.7
AAF3	161.6
AAK-1	155.9
AAF-1	148.2
AAD-1	148.2

Table 9-8: Rank of Asphalts from the Advancing Work of Cohesion in Vacuum (mJ/m^2) (Table 9-2, page 276)

Asphalt	Average Work	Asphalt	Average Work
EX10	66.9	FI10	26.8
FID	45.6	JG33b	26.7
FI10a	44.0	AAG-1	26.0
AAF3	40.7	JG33d	25.1
JG34To	37.0	AAA-1	23.9
JG32	36.7	AAFTot	23.7
AADN	36.4	EX5a	23.6
JG33c	33.7	AAFa-1	23.3
JG31	31.4	JF34a	20.5
JG33To	29.4	AAB-1	20.3
JG33	28.8	AAF-1	19.8
JG33a	28.3	AAM-1	16.6
JG33e	28.2	EX10a	16.4
AAD-1	27.8	AAK-1	16.3

Table 9-9: Rank of Asphalts from the Receding Work of Cohesion in Vacuum (mJ/m^2) (Table 9-2, page 276)

Asphalt	Average Work
JG34a	101.2
JG34To	96.8
FI10	67.2
FI10a	63.6
AAB-1	61.5
AAD-1	60.4
AAFa-1	56.0
AAF3	55.9
AAFTot	55.7
AAK-1	55.1
AAF-1	37.6

Figure 9-15: Advancing Work of Cohesion of Various Asphalts in Vacuum

Figure 9-16: Receding Work of Cohesion of Various Asphalts in Vacuum

Water Susceptibility

Pavement failure at the asphalt-aggregate interface caused by water is termed "water stripping." If the work of cohesion is greater than the work of adhesion in the presence of water, water stripping can occur. Figure 9-17 is a bar graph of the receding work of adhesion in water for all of the aggregates with asphalt AAFTot; every combination has the potential for water stripping. Figure 9-18 compares various asphalt aggregate combinations, showing the most variability in changing the aggregate.

The works of cohesion of various asphalts in water are presented graphically in Figures 9-19 and 9-20. Note that these energies are all positive, but of varying magnitude. Figure 9-19 and 9-20 indicate that the use of rubber in samples EX5a, FI10a requires more work of cohesion, as does the supercritical fraction AAF3, but EX10a is less desirable. In the receding work plot, Figure 9-20, the lighter fractions and materials have smaller magnitudes, requiring less energy to strip, but compared to negative values for adhesion, the role of cohesion in water stripping is secondary.

Because every asphalt-aggregate system is susceptible to water stripping, adhesion is probably not the rate limiting step. Some possibilities for the limiting step are: transport of the water to the asphalt-aggregate interface, or formation of emulsions with the asphaltenes in asphalt (Fromm, 1974). Variations of the potential exist for different systems. The rankings of aggregates and asphalts according to the receding work of adhesion are tabulated in Tables 9-10 and 9-11, respectively.

Once again, the rubber modified asphalt binder produces the highest ranked asphalt, FI10a. The addition of rubber increases the adhesion properties of asphalt FI10 by about 27%. The supercritical fraction, AAF3, has lowered the average receding work of adhesion in water by 10% for the original asphalt, AAFTot.

The ranking of the aggregates due to water susceptibility is almost the exact opposite of the ranking in vacuum (see Tables 9-6 and 9-10). It is not known which phenomenon is more important. Most likely, the aggregates should be chosen based upon strength and therefore the receding work of adhesion in vacuum, because all aggregates have the potential for water stripping and variations are probably unimportant. This is an area which requires more work.

Figure 9-17: Receding Work of Adhesion of Various Aggregates in Water

Figure 9-18: Effect of Various Asphalts on Receding Work of Adhesion in Water

Figure 9-19: Advancing Work of Cohesion of Various Asphalts in Water

Figure 9-20: Receding Work of Cohesion of Various Asphalts in Water

Table 9-10: Rank of Aggregates from the Receding Work of Adhesion in Water (mJ/m^2) (Table 9-3, page 279)

Aggregate	Average Work
JG11f	-55.8
JG11g	-58.7
JG11c	-71.3
JG11a	-77.6
JG21	-100.3
JG13	-102.9
JG04	-103.7
JG02	-110.5
JG22	-111.6
JG23	-115.0
JG05	-120.6
JG01	-133.1
JG12	-135.0
JG03	-142.6
JG05c	-142.7
JG05b	-185.9
JG05a	-186.1

Table 9-11: Rank of Asphalts from the Receding Work of Adhesion in Water (mJ/m^2) (Table 9-2, page 276)

Asphalt	Average Work
FI10a	-93.0
AAB-1	-101.5
AAFTot	-108.6
AAFa-1	-111.5
AAF-1	-114.6
JG34a	-118.0
AAF4	-119.2
AAK-1	-120.5
JG34Tot	-121.5
FI10	-127.7
AAD-1	-128.0

Healing

An asphalt mix can regain some its lost strength during a rest period. This effect is known as healing. Some key factors in healing include: viscosity, the asphalt must be able to flow to repair cracks; cohesion, the thermodynamic potential must exist to repair adhesive fractures. The *advancing* work of cohesion and adhesion are possible indicators of healing.

Figure 9-21 is a bar graph of the advancing work of cohesion in vacuum, and is arranged by rank of asphalts for cohesive healing potential. The top performer is the untreated sample EX10. Notice that the lime treated sample, EX10a, is the worst performer decreasing the potential by about 75%. The addition of rubber to asphalt, FI10a, has increased the cohesive healing potential of the asphalt FI10 by 64%. Surprisingly, the supercritical fraction, AAF3, also outperforms its native asphalt, AAFTot, increasing the healing potential by 71%. The Novophalt asphalt exceeds its original binder, AAD-1, by 31%.

The advancing work of adhesion in vacuum for various asphalts and three aggregates appears in Figure 9-22. The choice of aggregates seem to be more important for adhesive healing; a good asphalt does not overcome a poor aggregate. The adhesive healing potential is tabulated in Tables 9-12 and 9-13. The rank of aggregates by adhesive healing potential is very similar to the ranking obtained by strength (compare Tables 9-6 and 9-12). The ranking of asphalt adhesive healing potential is almost the opposite of the cohesive healing potential (compare Tables 9-13 and 9-8, respectively). Because the choice of aggregates has more variability in adhesive healing, and both cohesive damage and cohesive healing are more likely to occur, the cohesive healing potential ranking, Table 9-8, should be used.

Figure 9-21: Advancing Work of Cohesion of Various Asphalts in Vacuum
Possible Healing Indicator

Figure 9-22: Advancing Work of Adhesion of Various Asphalts in Vacuum
Possible Healing Indicator

Table 9-12: Rank of Aggregates from the Advancing Work of Adhesion in Vacuum (mJ/m^2) (Table 9-3, page 279)

Aggregate	Average Work
JG05a	175.9
JG05b	175.6
JG05c	159.2
JG03	154.9
JG01	152.6
JG12	151.4
JG05	150.4
JG23	145.0
JG13	143.2
JG02	142.9
JG04	139.6
JG22	135.3
JG21	115.2
JG11a	105.6
JG11f	104.4
JG11c	103.7
JG11g	102.6

Table 9-13: Rank of Asphalts from the Advancing Work of Adhesion in Vacuum (mJ/m^2) (Table 9-2, page 276)

Asphalt	Average Work
JG33c	169.8
JG33e	164.8
JG33d	164.3
JG34a	161.8
JG33b	161.5
AAG-1	160.1
AAM-1	152.7
AAA-1	150.9
AADN	147.9
EX10a	146.9
AAF-1	145.9
AAFa-1	145.6
JG33	141.8
AAFTot	141.2

Asphalt	Average Work
AAK-1	140.4
EX10	135.8
AAB-1	132.9
FI10	131.3
JG33a	128.9
JG33Tot	128.8
FID	128.1
JG34Tot	126.9
FI10a	126.5
AAF3	120.3
JG32	116.9
JF31	113.9
EX5a	101.2
AAD-1	95.9

CONCLUSIONS

A series of experiments has been designed to measure the surface free energy of asphalts. The results from these experiments have been combined with the surface free energy measurements of Li (1997) and used to calculate the work of adhesion for asphalt-aggregate interfaces and cohesion for asphalt-asphalt interfaces. The combined surface free energies have been used in an attempt to predict macroscopic behavior for asphalt-aggregate systems (overall strength of the mix, water susceptibility, and healing). Further investigation is necessary to establish that the results reported here are actually linked to verifiable pavement performance. An attempt has been made to rank various asphalts and aggregates based upon the links of cohesion and adhesion with macroscopic behavior.

The aggregates should be ranked based upon strength (receding work of adhesion in vacuum) and healing (advancing work of adhesion in vacuum). The aggregate material is the largest contributor to the magnitude of the adhesive bonds. This is an interesting and counter intuitive conclusion. The glue, asphalt, is less important than the material which is glued. A final ranking is calculated by adding the strength and adhesive healing rank numbers, Table 9-14.

The asphalts should be ranked based upon physical properties (aging, low temperature properties, etc.), cohesive healing (advancing work of cohesion in vacuum), strength (receding work of cohesion in vacuum) and water susceptibility (receding work of adhesion in water). Because the aggregates appear to be the major contributor to bond strength, the first criterion for an asphalt should be physical properties. A low rate of aging is important to maintain the elasticity of the binder to absorb applied energy. A final ranking from this study, Table 9-15, is calculated by adding the cohesive healing, strength, and water susceptibility rank numbers.

Not enough data exist to infer the effect of various asphalt additives upon the surface free energy properties, but some possibilities are apparent. Rubber, especially EX5a and FI10a, appears to be an excellent candidate for improving the adhesive and cohesive characteristics of an asphalt. Also, the supercritical fraction does not appear to affect the adhesion and cohesion adversely. Therefore, it may be that this fraction, AAF3, proves to be the best overall asphalt because of its excellent aging properties (Chaffin, 1996).

Table 9-14: Overall Rank of Aggregates (Table 9-3, page 279)

Rank	Aggregate
1	JG05a
1	JG05b
3	JG05
3	JG03
3	JG05c
6	JG01
7	JG12
8	JG02
9	JG04
9	JG13
9	JG23
12	JG22
13	JG11f
14	JG21
14	JG11a
14	JG11g
17	JG11c

Table 9-15: Overall Rank of Asphalts (Table 9-2, page 276)

Rank	Asphalt
1	FI10a
2	AAFTot
3	AAB-1
4	AAFa-1
5	AAF3
5	JG34Tot
7	JG34a
8	FI10
9	AAF-1
10	AAD-1
11	AAK-1

There is still much work to be done. The effects of temperature on the surface free energy have not been examined. The cause of water susceptibility has not been determined. If emulsion formation is the cause, chemicals for asphaltene stabilization are commercially available; these should be investigated for their effectiveness. The effects of the various additives were inconclusive; further investigation into the adhesion properties of the modified asphalts is necessary. Field trials should also be performed to validate the predictions made.

This work is the first to apply fundamental surface science to asphalt-aggregate systems. The usefulness of this study lies in the understanding of asphalt-aggregate adhesion and in the prediction of where and when cracks form and its application is part of the much larger problem of designing and manufacturing superior asphalts to improve road lifetimes.

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ABBREVIATIONS

AASHTO	American Association of State Highway and Transportation Officials
AC	asphaltene content
AM	aromatic material
AR	asphalt rubber
ASTM	American Society for Testing and Materials
ATR	attenuated total reflectance
BBR	bending beam rheometer
CA	carbonyl area
CRM	crumb rubber modifier
CRMA	crumb-rubber modified asphalt
DOE-OIT	Department of Energy Office of Industrial Technologies
DOT	Department of Transportation
DS	Diamond Shamrock
DSR	dynamic shear rheometer
DT	Direct tension
ENV	environmental
ES	exposed surface
EX	Exxon AC-10
FDR	Fina Demex Resin
FTIR	Fourier transform infrared spectroscopy
GCI	gyratory compactibility index
GPC	gel permeation chromatography
GSI	gyratory stability index
GTM	gyratory test machine
HPLC	high performance liquid chromatography
HSD	high shear disintegrating
IJ	initial jump
IRR	internal rate of return
LSI	low shear impeller
MP	metering pump
P	pressure or pressure gauge
PAV	pressure aging vessel
POV	pressure oxygen vessel
PTFE	poly tetrafluoroethylene
RA	recycling agent
ROSE	residual oil supercritical extraction
RPM	revolutions per minute
RS	Rouse
RTFO(T)	rolling thin film oven (test)
S	separators

SA	superior asphalt
SC	supercritical
SHRP	Strategic Highways Research Program
TG	Tire Gator
THF	tetrahydrofuran
TK	tank
TxDOT	Texas Department of Transportation
WC	water cooled condenser

NOTATION

A	Paris Law material parameter or cross-sectional area
a(T)	shift factor as a function of temperature, T
CA	carbonyl area
c	crack length
D(t)	extensional creep compliance as a function of time
D'(ω)	real component of extensional complex compliance as a function of frequency, ω
D''(ω)	imaginary component of extensional complex compliance as a function of frequency, ω
D*(ω)	extensional complex compliance as a function of frequency, ω
E _a	activation energy
E _c (t)	creep modulus as a function of time
E _f	failure energy or toughness
E _h	energy dissipated as heat
E _s	secant modulus
G	relaxation modulus
G'(ω)	storage modulus as a function of frequency, ω
G''(ω)	loss modulus as a function of frequency, ω
G*(ω)	complex modulus as a function of frequency, ω
HS	hardening susceptibility
H(τ)	relaxation spectrum
J(t)	shear creep compliance as a function of time
J _e ⁰	steady-state compliance, elastic component of creep compliance
J _v (t)	viscous component of creep compliance
K	stress-intensity factor
L _e	effective gauge length
ΔL _f	elongation at failure
m	creep strain rate
N	number of loading cycles
n	Paris Law material parameter
P _f	load at failure
R	gas constant
r	rut depth
s	Laplace parameter
T	temperature
T _d	defining temperature
t	loading time
LSI	mixer type, low shear impeller
HSD	mixer type, high shear disintegrating

Greek Letters

δ	phase angle or phase lag
$\epsilon(t)$	strain as a function of time
ϵ^0	strain amplitude
ϵ_C	creep strain
ϵ_f	failure strain
ϵ_p	permanent strain
ϵ_R	recovered strain
ϵ^*	complex strain
γ	surface energy
γ^{AB}	Lewis Acid-Base component of surface energy
γ^+	Lewis Acid component of surface energy
γ^-	Lewis Base component of surface energy
γ^{LW}	Lifshitz-van der Waal's component of surface energy
μ	Poisson's ratio
η_0	steady-state Newtonian viscosity
η_0^*	low shear limiting complex viscosity
η'	real component of η^*
η''	imaginary component of η^*
η^*	complex viscosity
σ_0	constant applied stress
σ_f	failure stress
σ^*	complex stress
τ	relaxation time
ω	angular frequency

Superscripts

*	complex property
'	real component
''	imaginary component

Subscripts

0	constant parameter
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APPENDIX A

EXPERIMENTAL METHODS

BENDING BEAM RHEOMETER

Low-temperature properties of the asphalt-rubber binder, are evaluated using a bending beam rheometer (BBR). Anderson et al. (1990) concluded that the BBR is the best instrument for measuring low-temperature properties of binders. Furthermore, both $S(t)$ and the m -value, the properties obtained by utilizing the BBR, have been correlated with the low-temperature thermal cracking of binders (Bahia et al. 1992). Bending beam results were obtained at a test temperature of -15°C (5°F), in addition to the SHRP Superpave test temperatures -6°C through -30°C ($+21^{\circ}\text{F}$ and -22°F respectively). The beam specimens were produced and the bending beam rheometer was utilized as specified in AASHTO Designation TP1. The beam is subjected to a force of 980 mN for 240 seconds and deflection is measured by computer. In order to pass the SHRP Performance Grade test at a given temperature, individual PAV aged samples must have a stiffness less than 300 MPa and an m -value greater than 0.3 at a time of 60 seconds after the load is applied (Asphalt Institute 1995). Figure A-1 illustrates the variety and arrangement of the SHRP Superpave asphalt binder tests.

BROOKFIELD ROTATIONAL VISCOMETER

A Brookfield rotational viscometer Model RVF 7 was used to obtain the high-temperature ($>121^{\circ}\text{C}$) (250°F) viscosities of the neat asphalt and asphalt-rubber binders. Torque is applied to a spindle that extends into the thermostatically controlled sample. Resistance to rotation is balanced by a spring and spring compression is measured on a dial and is proportion to viscosity, η , by a constant relating the spindle size and the rotational speed. The high temperature viscosity must be less than 30 poise in order to pass the Performance Grade specification, Figure A-1, however this requirement is optional under the Superpave guidelines (Asphalt Institute 1995). Given the historical compaction problems at installation this requirement is imperative for asphalt rubber blends.

Note: Tests performed at various temperatures
DSR measurements at 10 rad/s

Figure A-1: Superpave Asphalt Binder Tests

CORBETT ANALYSIS

A description of the traditional Corbett (1969) analysis can be found in the standard method ASTM D4124. Corbett analysis separates the components of an asphalt according to polarity. Some modifications of the Corbett procedure were implemented to reduce sample size and increase efficiency as suggested by Thenoux et al. (1988).

DIRECT TENSION

The Direct Tension Test is a relatively new method of determining low temperature properties. Narrow rods of sample are pulled apart and their elongation and the exerted forces are measured. The deformation continues until the specimen breaks. The ductility of samples is related to their brittleness and stiffness. Failure stress is also an important consideration. The direct tension test measures directly those properties that the bending beam test obtains by correlation. The direct tension test was performed at various SHRP temperatures, -12°C through -30°C (+10°F and -22°F respectively), and aided in determining the performance grade of various source asphalts and laboratory blends. Test specimens were prepared in accordance with AASHTO TP3. The test rate of deformation was 0.1 millimeters per minute. The Superpave requirement for passage is that the beam break above 1% shear (Asphalt Institute 1995). This test is used to evaluate PAV Aged materials, Figure A-1, and is currently optional. It is specifically intended for those materials that pass the bending beam test on m-value but fail the stiffness criteria with a stiffness of greater than 300 MPa (passing), but less than 600 MPa.

DYNAMIC SHEAR RHEOMETER

The intermediate-temperature rheological properties are tested with a Carri-Med CSL-500 dynamic shear rheometer (DSR) configured in the parallel plate geometry. This instrument may be operated in either a constant stress-mode (its natural mode) or a constant-strain mode over a temperature range from 0°C (32°F) to 90°C (194°F). This instrument is operated in the constant-

stress oscillation mode for analysis of neat asphalt samples but the constant-strain mode is necessary for analyses of asphalt-rubber samples.

The behavior of asphalt samples is non-Newtonian at intermediate oscillatory frequencies. However, by utilizing the constant-stress mode, a limiting complex viscosity, η_o^* , can usually be obtained at low frequencies. For highly aged samples, the low frequencies are obtained by utilizing temperatures greater than the reference temperature and employing the time-temperature superposition principle (Ferry 1985). For asphalt-rubber samples, however, at low frequencies, a limiting complex viscosity can not be obtained. To complicate matters further, the strains induced in the asphalt-rubber binders at low frequencies are quite large and may cause partial destruction of the bonds formed between the asphalt and rubber during the curing process. Therefore, it is necessary to operate the rheometer in the constant-strain mode for asphalt-rubber samples.

To analyze the asphalt-rubber samples in this study, it was necessary to determine the strain level which corresponds to the linear viscoelastic region. Theoretically, the linear viscoelastic region exists in the strain level range from 0% to some maximum percent strain level. However, a rheometer cannot accurately measure linear behavior at and slightly above the 0% strain level, thus narrowing the range of the linear viscoelastic region. In reality, the measureable linear viscoelastic region exists from a strain level range of slightly above 0%, a minimum strain level, to a maximum percent strain level. This range was determined by specifying several different strains and observing the strain response wave. Linear viscoelastic behavior is encountered when the strain response to sinusoidal stress input is also sinusoidal. The strain level for measurement was chosen to be the minimum strain level at which measureable linear viscoelastic behavior occurred. This minimum strain level was found to be highly sample dependent and ranged from approximately 0.5% to 200%, depending upon the temperature.

An additional complication to the measurement of asphalt-rubber properties is the presence of the rubber particles. As a result, it is necessary to determine a suitably larger gap width for the parallel plate geometry. This gap width was found to be strictly a function of the rubber particle size and rubber content. The gap width for a given rubber size and content was determined by measuring the rheological properties of a given asphalt-rubber at multiple gap settings. To insure the elimination of the 'gap effect', the gap width was chosen such that the rheological properties taken at as wide

or wider gap widths, were independent of the gap width. The dynamic shear rheometer was used to determine high and intermediate temperature properties of aged and unaged blends and source asphalts.

In the evaluation of the Superpave Performance Grade, the use the DSR is threefold, to evaluate the original, unaged binder or binder blend and the RTFOT aged material, both for $G^*/\sin \delta$, and to evaluation the PAV aged material for $G^*\sin \delta$. All of these tests are performed at 10 rad per second in oscillation mode and at various test temperatures. The requirements for these tests are shown in Figure A-1, and in order of increasing degree of aging are: greater than 1.0 kPa, greater than 2.2 kPa, and less than 5 MPa (Asphalt Institute 1995).

ENVIRONMENTALLY CONTROLLED AGING ROOM

The long term aging environment was maintained at 140°F (60°C) and 40% relative humidity throughout this endeavor. Because the temperature is not highly elevated, this aging process is thought to best approximate the real road aging kinetics, and is therefore more desirable than higher temperature, higher pressure aging methods like the POV. But because the temperature is lower, the aging rate is also lower and aging takes considerably longer than the POV. Thus, there is a trade off between aging data quickly obtained that must be extrapolated to lower temperatures, and slower aging that requires far less correction, but much more time to age.

Cookie sheet sized trays containing 100 gram quantities of sample were aged and the samples were sufficient to perform low temperature tests such as bending beam rheometer and later direct tension tests. Smaller 1 to 2 gram sample quantities were aged on trays described under the POV section below, and FTIR and DSR characterizations were performed.

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

A Mattson Galaxy series 5020 Spectrometer at 4 cm^{-1} resolution and 64 scans is used to measure the infrared absorbance spectra of asphalt samples. In particular, the Attenuated Total Reflectance, ATR, method with a Zinc Selenide prism is used (Jemison et al., 1992). To quantify the

changes in the spectra, the carbonyl content is defined as the integrated absorbance from 1820 to 1650 cm^{-1} with respect to the baseline at the absorbance of 1820 cm^{-1} . This area is called the *Carbonyl Area* or *CA*. The above range of wave numbers includes the following carbonyl compounds: esters, ketones, aldehydes, and carboxylic acids. The primary absorbance peak for the oxidized asphalt is located at 1700 cm^{-1} and corresponds to ketone formation. The carbonyl area has been shown to be a good measure of oxidation (Liu et al. 1996).

At low aging pressures of 2 and 0.2 atm oxygen and for thick ($\approx 1\text{ mm}$) films, oxygen diffusion may be significant. To partially eliminate this diffusion problem, only the exposed surface, *ES*, of the film is analyzed for kinetic data. For analysis, a quarter of the material in the aluminum tray is removed and the *ES* placed on the prism face. For samples that have been aged in thinner films, diffusion is probably not significant, so it is possible to measure the spectra of a stirred sample. To insure good contact at the sample/prism interface, the sample is compressed. Heating of the sample is avoided, if possible.

For measuring the spectrum of asphaltenes, the solid material is dissolved in THF and the solution deposited on the ATR prism drop by drop allowing the THF to evaporate. When the film on the prism is sufficiently thick, the heat gun is used to remove latent THF.

GEL PERMEATION CHROMATOGRAPHY (GPC)

GPC analyses are performed using a Waters 712 sample processor and a Waters 600E multisolvent delivery system. Three columns with pore sizes of 1000Å, 100Å, and 50Å are connected in series. The 1000Å and 100Å columns are 30.5 cm (1 foot) in length and are packed with ultrastyrigel particles. The 50Å column is 61.0 cm (2 feet) in length and is packed with PLgel particles. Helium-sparged HPLC grade tetrahydrofuran (THF) at a flow rate of 1 mL/min is used as the carrier solvent to efficiently separate the asphalt and asphalt-rubber binders. A Waters 410 Differential Refractometer and a Viscotek H502 Viscometer is used to monitor sample elution. The column and detector temperatures are controlled at 40°C (104°F). Samples were prepared by dissolving 0.20 to 0.25 grams, depending upon the rubber content, in 10 mL of HPLC grade THF,

and filtering through a PTFE syringe filter with a membrane pore size of 0.45 μm (0.45 micron). Thus, sample preparation removes all rubber particles greater than 0.45 microns, because asphalt is soluble in THF and most rubber is not.

MICRODUCTILITY MEASUREMENTS

A detailed description of the microductility concept can be found in Chapter 2.

MIXING APPARATUS

To produce the asphalt-rubber binders, asphalts and rubbers are 'cured' or mixed together at high temperatures ($> 177^{\circ}\text{C}$ (350°F)). Curing, for the purpose of this report, is defined as an increase in viscosity without oxidation, with oxidation being measured by the carbonyl peak area of the infrared spectrum. The curing process is performed by one of two mixing devices. Low and intermediate curing involve mixing at high temperatures with a 5.1 cm (2") diameter blade driven at variable speeds, 500-1550 rpm by a variable speed motor. For low curing, the mixer speed is usually 500 rpm at a temperature of 177°C (350°F). Intermediate curing, also called high shear mixing, is performed at 1550 rpm at temperatures up to 260°C (500°F). High cure blends are performed using a Silverson L4RT Laboratory Mixer capable of maintaining constant rotational speeds. This mixer is fitted with a 5.7 cm (2.25") slotted disintegrating head and has the capacity to be run at 10,000 rpm. For the blends discussed in Chapter 2, the Silverson mixer was operated at up to 8000 rpm and 260°C (500°F). All blends were cured in either 1 quart or 1 gallon paint cans, depending on sample size, under a nitrogen blanket to prevent the binder from oxidizing.

PENDANT DROP

A pendant drop is based on a drop hanging from any solid surface. The drop elongates as it grows larger (Figure A-2). This elongation is caused by the variation in hydrostatic pressure that becomes appreciable compared to that given by the curvature at the apex (Adamson, 1990). The way the drop hangs does not affect the applicability of the pendant drop method or the precision of the results. The only condition that must be satisfied is that the drop be a solid of revolution (Andreas et al., 1938). Worthington (1881; 1885) first showed how the surface tension of a liquid could be evaluated from the shape of the drop. He suggested that the experimenter trace on paper the magnified image of the liquid pendant drop. Digital cameras and imaging technology have greatly increased the value of this method by automating the imaging process (López de Ramos et al., 1993). A typical pendant drop apparatus is shown in Figure A-3. The device used was located at the University of Tulsa, and was employed as a check on the Wilhelmy Plate results. Special thanks to Dr. R. Cerro at the University of Tulsa for providing the instrument (López de Ramos et al., 1993).

PRESSURE AGING VESSEL (PAV)

The pressure aging vessel was used to age 50 gram samples of RTFOT aged blends and source asphalts for 20 hours at an air pressure of 2070 kPa (300 psi) and temperatures of 90°C and 100°C (194°F and 212°F, respectively). This test was performed to simulate long term aging, comparable to road conditions, and was used for Superpave grading, Figure A-1 (Asphalt Institute 1995). The procedure followed in operating this vessel was in accordance with AASHTO PP1.

Figure A-2: Geometry of a Pendant Drop

Figure A-3: Pendant Drop Apparatus

PRESSURE OXYGEN VESSEL (POV)

The original POV unit is described by Lau (1992) and Davison et al. (1992). In order to improve on aging simulation capacity, four additional units were constructed and a central control panel was installed as shown in Figure A-4. Later, to eliminate temperature gradient problems with the initial design, the vessels were placed in glycol/water baths. Originally, designed for oxygen aging, the POV may employ any available cylinder gas, or combination thereof, over a wide range of temperatures and pressures.

Figure A-5 shows a schematic of one of the POVs. The vessels are located behind a steel wall in an explosion proof hood. Each vessel is contained in an aluminum barrel filled to the bottom of the top flange with a mixture of triethylene glycol and water. The vessel is monitored and controlled from a panel outside the explosion proof hood. The control panel houses a compound pressure gauge to monitor the pressure, a variable transformer to control the amount of electrical power to the heating elements in the water/triethylene glycol bath, a temperature controller which controls the temperature of the bath, and a recorder to monitor the temperature within the POV. A stirrer is employed in the bath to insure that the temperature distribution in the bath is uniform. A vacuum pump is used to evacuate the vessels before charging with oxygen or to remove oxygen depleted air once per day. Three valves per vessel, as labeled in Figure A-4, are used for venting to atmospheric pressure, evacuating to low pressure to remove the gas inside the vessel, and charging with oxygen. The oxygen feed valve isolates the POVs from the oxygen cylinder when closed. Two additional vessels were later constructed, of the same bath and structural design, but these vessels are fitted with a cover flange that is vented to the atmosphere, whereas a rupture disk is in place on the POVs. The two new vessels allow aging at high temperatures, but exclusively in an atmospheric air environment. The air supply in the vessel can be rejected to the atmosphere by means of a small pump.

Asphalt samples are prepared in aluminum trays. The dimensions of the trays are 7.0 cm (2.75 in) by 3.5 cm (1.38 in). Typical film thicknesses of less than 1 mm (0.039 in) are used to minimize potential diffusion problems at low pressure; however, diffusion studies may be performed with thicker films. After preparing the asphalt samples, loading the sample rack, and allowing the temperature in the POV to reach equilibrium, the operator places the rack inside the POV and bolts

Figure A-4: Pressure Oxygen Vessel Control Panel

Figure A-5: Pressure Oxygen Vessel and Control Panel

the cover flange to the top. The vent valves, oxygen feed valves, and vacuum valves are closed. A vacuum pump evacuates the air in the vessel to a pressure of 0.03 atm absolute. The vessels are slowly pressurized to the desired level by manipulating the oxygen cylinder regulator and oxygen feed valves for pure oxygen aging, or by slowly opening the atmospheric venting valve for aging with air (note 0.2 atm oxygen is equivalent to atmospheric air aging). Once the desired oxygen pressure is reached, the cylinder, regulators, and feed valves are closed.

During the experiment, samples are periodically removed. To obtain samples, the pressure in the vessel is decreased by slowly venting off the oxygen to the atmosphere until the pressure gauge reads zero. The operator removes the top insulation, unbolts the cover flange, and collects the samples. Samples to be aged further are loaded back into the vessel, and the process is repeated. The aged samples are saved for chemical and physical analysis.

ROLLING THIN FILM OVEN TEST (RTFOT)

The rolling thin film oven test was part of the Superpave Performance Grade testing and was used to age 35 gram samples of unaged blends and source asphalts, eight bottles at a time, for 85 minutes in atmospheric air, and at a temperatures of 163°C (325°F) (Asphalt Institute 1995). These tests were performed to simulate the short term, high temperature aging incurred during the hot mix process, see Figure A-1. The operating procedure for this test is specified by ASTM D 2872-88.

SUPERCRITICAL FRACTIONATION

A brief description of the supercritical fractionation process, operating conditions, and apparatus modifications follow. The following description is taken primarily from the TxDOT Study 1249 (Davison et al, 1992) report with appropriate modifications. The unit operates at a constant pressure above the critical pressure of the solvent. The SC fractionation unit separates heavy petroleum products into up to four fractions according to solubility in SC solvents. The temperatures of the separators determine the density of the solvent and, consequently, the solvent power in each vessel. Components of the feed precipitate when no longer soluble in the solvent. The lightest, most-

soluble materials are removed by decompression during solvent recovery.

Figures A-6 and A-7 illustrate the SC unit schematically. The solvent is pumped to the operating pressure in vessels S1-S3 by MP1. Several hours are required to bring the temperatures to the desired steady-state values. The steady-state operating temperature in S4 determines the steady state pressure for S4. Once steady-state conditions are achieved, MP2 is activated, introducing feed material into the circulating solvent stream. The temperature in each separator determines the solubility in the SC solvent. The insoluble material collects in the bottom of the separators and is periodically transferred from the separator to its corresponding collector to avoid potential plugging problems while the soluble material travels to the next separator. Finally, the overhead mixture from S3 passes through the control valve, where the pressure is reduced to a significantly subcritical value. At these gaseous conditions, none of the asphaltic material is soluble and complete separation of the solvent is achieved. The solvent then passes overhead, is condensed in WC1 and flows back into the solvent reservoir. For this effort, n-pentane is the solvent used for supercritical fractionation.

The four asphalts fractionated during this effort were fractionated in two passes through the unit. The lightest fraction from the first pass, S4 product, was fed through the unit a second time on a subsequent day, yielding eight fractions that may be analyzed. According to petroleum separation and distillation conventions, the lightest fraction from the second pass is designated as fraction F1 and the heaviest fraction from the first pass is designated as fraction F8 (fraction F5 is the feed material for the second pass through the unit). So, for example, F3 is the second pass product of Separator 2 and F7 is the first pass product of Separator 2. Typically, several first pass runs are made to product sufficient F5 material to make a second pass run worthwhile.

WHATMAN 42 TEST

The extent to which the rubber may "dissolve" into the asphalt was determined with the following procedure. A 1.0 gram asphalt-rubber sample was dissolved in 50 ml of THF. The asphalt-rubber/THF solution was sonicated for 30 minutes. The solution was then strained through a preweighed Whatman 42 paper filter. This filter is rated to retain fine crystalline particles. The

Figure A-6: Supercritical Unit Process Diagram

S0	Solvent Tank	S1-S4	Separators
C1-C4	Collectors	A1	Asphalt Tank
In-line Filter/mixer		Valve
Control Valve		Thermocouple
Tubing Wall Temperature Thermocouple		Temperature Monitor and Controller
Pressure Controller		Pressure Gauge
Heating Tape Heater		Metering Pump
Dual Purpose Heater/Cooler		Water Cooled Condenser

Figure A-7: Legend for Supercritical Extraction Unit Diagram

filter was then heated in the oven at 367K (200°F) for 1 hour, removed from the oven and placed at ambient conditions for 6 hours, and finally weighed. The difference between filter masses, along with the initial sample mass, and percent rubber content of the initial sample were used to determine the amount of rubber that dissolved into the asphalt during the curing process.

WILHELMY PLATE TECHNIQUE

The Wilhelmy plate method was first proposed by Wilhelmy (1863) to determine the surface tension of a liquid using a maximum pull; the maximum value of the force is recorded from a balance. It was believed that at the maximum force the contact angle would be zero, and the surface tension of the liquid could be calculated. With the advent of computers and micro control motors, the method has become much more valuable. An experimenter can now continuously monitor the force versus height of the plate (Neuman and Good, 1979) and calculate the advancing and receding contact angles.

In the Wilhelmy plate method, a plate is suspended by a micro-balance over a beaker of liquid. The beaker rests on a computer-controlled elevator mechanism that raises or lowers the fluid bath by the operator's design, while the entire apparatus is operated on a vibrationless table. The balance measures the total gravity-buoyancy-surface tension force of the hanging plate as the liquid is slowly moved in relation to the plate. First, the liquid is raised to contact the plate, then continued raising partially submerges the plate as force data measurements continue to be taken. At some point the process is reversed and the liquid is slowly lowered, with measurements also being taken. A number of cycles are performed to assure reproducible data (Elphinstone 1997).

APPENDIX B

CURING STUDY DATA

For low cure blends, as in Table B-1, please refer to Chapters 2 and 3 for discussion. For high cure blends, as in Tables B-2 and B-3, please refer to Chapters 4 for discussion.

Table B-1. η^* and δ Values for Low-Cure Blends

	SHRP ABM-1		10/90, TG -10/ SHRP ABM-1, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		18/82, TG -10/ SHRP ABM-1, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	3.653e8	23.67	4.002e8	27.21	2.564e8	30.66
283	7.586e7	63.02	7.229e7	58.48	5.354e7	55.17
298	2.672e6	83.66	3.082e6	70.24	3.076e6	59.76
313	1.130e5	88.45	2.422e5	65.80	4.252e5	53.07
333	2,051	89.66	7,278	84.20	17,240	76.80
363	44.66	90.17	152.7	88.02	384.6	83.00
TS =	18,170		16,550		14,850	
	10/90, TG -40/ SHRP ABM-1, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		18/82, TG -40/ SHRP ABM-1, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour			
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)		
273	3.361e8	25.59	2.364e8	34.50		
283	6.806e7	57.98	4.383e7	55.61		
298	2.867e6	72.10	2.401e6	61.72		
313	2.148e5	71.52	2.739e5	57.50		
333	7,028	81.95	15,190	72.67		
363	159.6	87.90	656.8	81.10		
TS =	16,370		14,280			

Table B-1. η^* and δ Values for Low-Cure Blends (Cont.)

	SHRP ABL-2		10/90, TG -10/ SHRP ABL-2, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		18/82, TG -10/ SHRP ABL-2, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	2.906e7	55.39	3.869e7	49.31	4.808e7	40.71
283	5.455e6	62.92	8.343e6	54.43	1.235e7	45.80
298	4.288e5	71.20	9.439e5	56.54	1.900e6	45.07
313	38,820	79.42	1.288e5	63.85	4.252e5	46.36
333	1,645	87.77	7,306	81.01	35,220	68.20
363	60.23	90.12	249.3	88.18	1,146	84.56
TS =	14,650		13,210		11,570	
	10/90, TG -40/ SHRP ABL-2, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		18/82, TG -40/ SHRP ABL-2, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour			
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)		
273	3.552e7	48.69	2.970e7	33.39		
283	7.693e6	54.26	8.091e6	43.17		
298	8.877e5	55.91	1.341e6	44.20		
313	1.251e5	64.30	3.084e5	46.46		
333	6,005	79.77	33,910	60.11		
363	209.6	88.12	1,689	80.52		
TS =	13,340		10,660			

Table B-1. η^* and δ Values for Low-Cure Blends (Cont.)

	Made AC-5		10/90, TG -10/ Made AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		20/80, TG -10/ Made AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	1.991e8	46.54	3.743e7	48.25	7.982e7	50.83
283	2.088e7	76.34	7.656e6	53.74	1.029e7	63.04
298	7.484e5	86.08	9.102e5	53.93	8.847e5	56.36
313	37,960	89.09	1.475e5	57.04	1.477e5	55.35
333	936.8	89.85	3,291	83.42	7,460	72.21
363	26.36	91.01	112.9	86.34	363.9	82.63
TS =	17,770		14,160		13,480	
	10/90, TG -40/ Made AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		20/80, TG -40/ Made AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour			
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)		
273	1.025e8	53.44	3.506e7	62.30		
283	1.127e7	71.33	5.248e6	66.18		
298	6.329e5	71.95	4.556e6	62.01		
313	61,270	71.11	74,290	59.83		
333	2,639	81.33	4,824	72.00		
363	105.3	86.45	393.3	81.61		
TS =	15,250		12,760			

Table B-1. η^* and δ Values for Low-Cure Blends (Cont.)

	Diamond Shamrock (DS) AC-5		5/95, TG -10/ DS AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		10/90, TG -10/ DS AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	4.926e7	42.37	4.958e7	46.11	4.959e7	45.57
283	1.155e7	55.51	1.141e7	54.59	1.311e7	51.09
298	5.505e5	72.92	5.972e5	67.87	8.400e5	62.30
313	22,000	84.76	29,320	79.99	55,240	64.64
333	447.9	89.74	1,189	85.90	1,801	85.00
363	24.41	91.58	52.19	89.62	101.0	87.09
TS =	16,830		15,750		15,070	
	15/85, TG -10/ DS AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		20/80, TG -10/ DS AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour			
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)		
273	3.947e7	43.61	3.224e7	41.59		
283	9.564e6	49.91	7.995e6	46.06		
298	7.651e5	57.05	8.369e5	51.29		
313	65,140	61.12	88,980	58.52		
333	3,057	77.81	5,011	77.30		
363	112.2	85.23	356.1	82.16		
TS =	14,390		12,930			

Table B-1. η^* and δ Values for Low-Cure Blends (Cont.)

	5/95, TG -40/ DS AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		10/90, TG -40/ DS AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	5.415e7	42.48	4.114e7	45.23
283	1.362e7	51.34	1.062e7	51.89
298	6.881e5	67.61	6.644e5	62.92
313	32,130	80.23	40,820	74.37
333	839.6	87.01	1,542	84.91
363	44.79	89.77	88.95	88.10
TS =	16,200		14,990	
	15/85, TG -40/ DS AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		20/80, TG -40/ DS AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	3.279e7	43.59	2.011e7	45.53
283	9.045e6	49.76	5.452e6	49.54
298	6.982e5	57.82	4.806e5	55.84
313	53,380	68.70	52,080	62.47
333	1,419	83.24	3,811	76.07
363	130.3	87.46	315.5	83.04
TS =	14,640		12,570	

The η^* and δ values in Table B-2 are reported at 1.0 rad/sec and have units of poise and degrees, respectively. The temperature susceptibility (TS) is E_v/R and has units of K^{-1} .

Table B-2. η^* and δ Values for the Silverson Blends

Curing Study of 2/5/96, 10/90, TG -10WT/Exxon AC-10, Silverson, 4000 rpm, 505K (450°F), N ₂								
	Exxon AC-10		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	6.469e7	56.44	3.621e7	58.24	2.991e7	60.63	3.351e7	60.26
10°C	1.058e7	70.91	6.420e6	66.30	5.810e6	67.56	6.237e6	68.03
25°C	5.325e5	82.30	4.398e5	69.91	3.960e5	70.89	3.965e5	72.04
40°C	30,540	87.73	41,040	75.15	39,000	76.51	35,740	76.86
60°C	952.0	89.95	2,213	85.22	1,942	85.75	1,826	85.69
90°C	34.06	90.92	93.86	89.07	88.24	89.19	90.39	89.35
TS=	16,348		14,373		14,281		14,413	

	2 ½ hour		3 ½ hour		5 hour		6 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	3.038e7	60.92	3.695e7	60.52	3.375e7	61.36	2.821e7	63.00
10°C	5.467e6	68.36	6.532e6	69.27	5.949e6	69.46	5.326e6	69.51
25°C	3.427e5	71.96	3.584e5	74.50	3.806e5	74.13	3.444e5	74.21
40°C	35,170	76.36	31,660	78.02	34,970	77.75	32,290	78.25
60°C	1,686	86.02	1,687	85.82	1,711	85.93	1,694	85.53
90°C	80.06	89.69	81.33	89.56	83.09	89.47	81.64	89.18
TS=	14,392		14,626		14,491		14,316	

Table B-2. η^* and δ Values for the Silverson Blends (Cont.)

Curing Study of 2/13/96, 10/90, TG -10WT/Exxon AC-10, Silverson, 4000 rpm, 533K (500°F), N ₂								
	Exxon AC-10		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	6.47e7	56.44	2.820e7	62.02	3.048e7	62.99	2.531e7	64.69
10°C	1.06e7	70.91	5.159e6	69.64	5.182e6	70.43	4.782e6	71.37
25°C	5.32e5	82.30	3.430e5	72.96	3.080e5	75.01	2.775e5	76.28
40°C	30,540	87.73	33,170	76.76	26,680	79.36	24,660	79.14
60°C	952.0	89.95	1,747	85.26	1,593	85.77	1,470	85.58
90°C	34.06	90.92	81.36	88.77	77.69	89.27	73.75	89.10
TS=	16,348		14,286		14,426		14,321	

	2 ½ hour		3 ½ hour		5 hour		6 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	2.927e7	63.88	3.186e7	63.72	2.823e7	65.28	3.119e7	64.83
10°C	5.275e6	71.71	5.279e6	71.51	5.132e6	72.46	5.562e6	72.47
25°C	2.939e5	76.70	2.944e5	76.90	3.031e5	78.42	3.319e5	78.49
40°C	25,180	79.16	25,450	79.55	25,730	81.30	27,690	81.72
60°C	1,420	85.00	1,430	84.63	1,397	85.29	1,414	85.21
90°C	72.30	88.98	76.02	88.61	69.71	89.20	69.77	89.04
TS=	14,515		14,529		14,517		14,633	

Table B-2. η^* and δ Values for the Silverson Blends (Cont.)

Curing Study of 2/23/96: 10/90, TG -10WT/Exxon AC-10, Silverson, 8000 rpm, 533K (500°F), N ₂								
	Exxon AC-10		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	6.47e7	56.44	2.668e7	63.63	2.394e7	64.60	2.846e7	64.05
10°C	1.06e7	70.91	5.075e6	70.27	4.796e6	70.89	5.105e6	71.68
25°C	5.33e5	82.30	3.246e5	73.57	2.915e5	74.86	2.951e5	76.40
40°C	30,540	87.73	30,150	78.13	26,460	79.65	25,580	80.01
60°C	952.0	89.95	1,431	86.66	1,326	86.83	1,285	86.47
90°C	34.06	90.92	69.63	89.31	64.42	89.55	64.93	89.89
TS=	16,348		14,459		14,446		14,614	

	2 ½ hour		3 ½ hour		5 hour		6 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	2.846e7	67.74	3.135e7	64.56	4.186e7	62.65	3.710e7	63.95
10°C	4.915e6	72.72	5.664e6	72.28	6.826e6	71.61	6.686e6	71.98
25°C	2.927e5	77.25	3.117e5	77.96	3.319e5	78.42	3.560e5	78.67
40°C	25,100	80.81	25,510	81.41	25,790	81.96	27,500	82.56
60°C	1,289	86.50	1,273	86.48	1,247	86.65	1,276	86.82
90°C	64.10	90.36	62.46	90.52	61.60	90.44	60.58	89.86
TS=	14,606		14,784		15,116		15,030	

Table B-2. η^* and δ Values for the Silverson Blends (Cont.)

Curing Study of 2/24/96, 10/90, TG -40B/Exxon AC-10, Silverson, 4000 rpm, 533K (500°F), N ₂								
	Exxon AC-10		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	6.469e7	56.44	3.319e7	62.21	2.577e7	64.11	3.279e7	62.96
10°C	1.058e7	70.91	5.953e6	70.07	5.462e6	70.99	5.962e6	71.26
25°C	5.325e5	82.30	3.527e5	75.01	3.170e5	76.19	3.088e5	77.62
40°C	30,540	87.73	30,140	78.44	26,210	79.39	24,410	80.02
60°C	952.0	89.95	1,448	85.63	1,369	85.30	1,296	85.04
90°C	34.06	90.92	75.02	89.48	71.96	89.60	66.63	89.15
TS=	16,348		14,641		14,470		14,780	

	2 ½ hour		3 ½ hour		5 hour		6 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	3.752e7	62.95	3.720e7	62.97	3.978e7	63.12	3.826e7	63.17
10°C	6.278e6	71.82	6.403e6	71.90	6.690e6	72.02	6.625e6	71.73
25°C	3.222e5	78.28	3.390e5	78.84	3.370e5	79.56	3.390e5	79.59
40°C	24,810	80.63	26,730	81.56	24,700	83.01	24,010	83.49
60°C	1,266	85.02	1,212	85.21	1,167	85.55	1,212	86.15
90°C	65.34	89.43	62.79	89.19	60.45	89.34	60.09	89.44
TS=	14,936		14,995		15,121		15,081	

Table B-2. η^* and δ Values for the Silverson Blends (Cont.)

Curing Study of 2/27/96, 10/90, TG -10WT/(EXX/SUN AC-5), Silverson, 4000 rpm, 533K (500°F), N ₂								
	EXX/SUN AC-		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	2.236e7	69.96	2.270e7	65.63	1.708e7	68.04	1.999e7	67.51
10°C	4.380e6	76.76	3.766e6	71.26	3.149e6	72.55	3.405e6	72.58
25°C	2.352e5	84.46	2.241e5	73.11	1.884e5	75.99	1.930e5	75.57
40°C	14,380	88.70	21,600	76.89	17,290	80.15	18,490	79.37
60°C	561.0	89.96	1,054	86.12	953.7	85.82	955.6	85.91
90°C	24.73	90.86	57.30	90.04	57.45	89.10	53.97	89.09
TS=	15,577		14,461		14,198		14,402	

	2 ½ hour		3 ½ hour		5 hour		6 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	1.996e7	68.50	2.294e7	67.78	2.367e7	67.74	2.359e7	67.72
10°C	3.334e6	74.19	3.733e6	73.95	3.949e6	73.92	4.156e6	74.21
25°C	1.899e5	77.30	2.097e5	77.80	2.102e5	78.52	2.270e5	79.06
40°C	17,460	79.85	17,930	79.86	18,180	81.07	18,500	81.96
60°C	879.1	85.97	894.0	85.35	898.4	85.53	906.0	85.71
90°C	49.69	89.60	51.18	89.67	51.20	89.42	48.24	89.00
TS=	14,501		14,640		14,687		14,770	

Table B-2. η^* and δ Values for the Silverson Blends (Cont.)

Curing Study of 2/29/96, 20/80, TG -10WT/Exxon AC-10, Silverson, 4000 rpm, 533K (500°F), N ₂								
	Exxon AC-10		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	6.469e7	56.44	1.870e7	59.18	1.450e7	63.78	1.414e7	64.94
10°C	1.058e7	70.91	3.646e6	63.08	2.858e6	67.35	2.758e6	68.42
25°C	5.325e5	82.30	3.377e5	59.89	2.349e5	67.38	2.255e5	67.99
40°C	30,540	87.73	55,980	58.44	31,250	70.01	30,090	69.15
60°C	952.0	89.95	2,903	80.20	2,120	80.38	2,075	80.04
90°C	34.06	90.92	215.0	85.45	141.6	87.94	147.8	87.79
TS=	16,348		12,700		12,885		12,818	

	3 ½ hour		6 ½ hour	
Temp	η^*	δ	η^*	δ
0°C	1.642e7	66.24	1.753e7	66.75
10°C	2.899e6	70.15	3.295e6	70.94
25°C	2.090e5	71.10	2.179e5	72.99
40°C	26,020	72.66	24,760	74.54
60°C	1,944	79.96	1,807	81.31
90°C	138.6	87.34	126.3	88.14
TS=	13,035		13,263	

Table B-2. η^* and δ Values for the Silverson Blends (Cont.)

Curing Study of 3/3/96, 10/90, TG -10WT/Fina Demex Resin (FNDMRS), Silverson, 4000 rpm, 505K (450°F), N ₂								
	FNDMRS		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	3.377e7	73.23	1.751e7	72.37	1.728e7	73.32	1.625e7	73.72
10°C	5.374e6	81.05	3.201e6	73.33	2.723e6	74.91	2.655e6	74.99
25°C	1.836e5	86.72	1.724e5	72.22	1.430e5	74.00	1.320e5	75.19
40°C	8,742	88.24	14,460	76.29	12,570	77.50	11,380	79.18
60°C	238.6	90.10	599.3	87.04	594.7	87.19	499.8	87.43
90°C	14.16	95.26	44.53	87.58	44.69	89.29	35.74	89.32
TS=	16,833		14,648		14,538		14,746	

	3 ½ hour		6 ½ hour	
Temp	η^*	δ	η^*	δ
0°C	1.590e7	74.71	1.359e7	75.74
10°C	2.757e6	76.33	2.489e6	77.09
25°C	1.415e5	75.87	1.316e5	75.89
40°C	11,530	79.52	11,320	78.46
60°C	475.0	87.20	482.9	87.15
90°C	36.66	89.70	34.89	89.89
TS=	14,760		14,621	

Table B-2. η^* and δ Values for the Silverson Blends (Cont.)

Curing Study of 3/7/96, 10/90, TG -10WT/Fina Demex Resin (FNDMRS), Silverson, 4000 rpm, 533K (500°F), N ₂								
	FNDMRS		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	3.377e7	73.23	1.631e7	74.90	1.512e7	75.25	1.342e7	76.36
10°C	5.374e6	81.05	2.440e6	78.07	2.627e6	77.57	2.305e6	77.65
25°C	1.836e5	86.72	1.008e5	77.21	1.103e5	77.90	1.075e5	77.19
40°C	8,742	88.24	9,121	79.61	9,430	80.01	9,598	78.85
60°C	238.6	90.10	501.5	86.83	430.5	87.08	437.8	86.74
90°C	14.16	95.26	36.73	90.15	32.73	91.34	34.40	89.81
TS=	16,833		14,654		14,815		14,608	

	3 ½ hour		6 ½ hour	
Temp	η^*	δ	η^*	δ
0°C	1.520e7	76.91	1.569e7	76.75
10°C	2.563e6	79.69	2.567e6	80.09
25°C	97,820	81.86	1.048e5	82.76
40°C	7,859	82.58	7,757	83.84
60°C	460.7	86.36	372.8	86.71
90°C	33.00	90.22	26.58	90.59
TS=	14,766		15,083	

Table B-2. η^* and δ Values for the Silverson Blends (Cont.)

Curing Study of 3/8/96, 10/90, TG -10WT/Fina Demex Resin (FNDMRS), Silverson, 8000 rpm, 533K (500°F), N ₂								
	FNDMRS		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	3.377e7	73.23	1.502e7	75.76	1.446e7	76.65	1.723e7	75.24
10°C	5.374e6	81.05	2.450e6	77.79	2.179e6	79.25	2.678e6	78.12
25°C	1.836e5	86.72	1.109e5	78.41	89,990	80.28	1.079e5	79.61
40°C	8,742	88.24	9,107	82.18	8,097	82.46	8,601	82.05
60°C	238.6	90.10	453.2	87.76	445.2	87.46	426.8	87.25
90°C	14.16	95.26	33.96	90.50	32.79	90.70	27.02	92.03
TS=	16,833		14,726		14,652		15,094	

	3 ½ hour		6 ½ hour	
Temp	η^*	δ	η^*	δ
0°C	1.783e7	75.45	3.139e7	72.99
10°C	2.819e6	78.98	4.265e6	79.13
25°C	1.112e5	81.92	1.408e5	83.40
40°C	8,052	83.43	8,910	85.07
60°C	350.9	87.43	348.3	88.10
90°C	25.42	90.77	23.64	91.00
TS=	15,294		16,006	

Table B-2. η^* and δ Values for the Silverson Blends (Cont.)

Curing Study of 3/9/96, 10/90, TG -40B/Fina Demex Resin (FNDMRS), Silverson, 4000 rpm, 533K (500°F), N ₂								
	FNDMRS		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	3.377e7	73.23	1.407e7	75.47	1.560e7	75.78	1.327e7	76.94
10°C	5.374e6	81.05	2.516e6	77.85	2.658e6	78.54	2.215e6	79.49
25°C	1.836e5	86.72	1.027e5	78.69	1.007e5	80.31	96,380	80.18
40°C	8,742	88.24	8,171	81.01	7,995	81.71	7,916	80.48
60°C	238.6	90.10	426.2	86.43	397.1	86.41	382.4	86.11
90°C	14.16	95.26	32.86	89.89	30.37	91.52	29.73	90.59
TS=	16,833		14,744		14,943		14,764	

	3 ½ hour		6 ½ hour	
Temp	η^*	δ	η^*	δ
0°C	1.687e7	76.17	1.843e7	76.22
10°C	2.638e6	80.05	2.824e6	80.44
25°C	94,600	82.88	99,230	84.58
40°C	7,184	82.97	7,030	85.26
60°C	346.5	86.01	327.9	86.93
90°C	25.61	91.73	24.63	91.42
TS=	15,202		15,368	

Table B-2. η^* and δ Values for the Silverson Blends (Cont.)

Curing Study of 3/10/96, 10/90, TG -10WT/Fina AC-5, Silverson, 4000 rpm, 533K (500°F), N ₂								
	Fina AC-5		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	4.939e7	64.69	2.824e7	66.25	2.302e7	68.26	2.643e7	68.09
10°C	9.220e6	74.71	4.828e6	72.66	4.225e6	73.63	4.836e6	74.02
25°C	3.695e5	84.57	2.353e5	74.74	1.956e5	76.73	2.183e5	77.89
40°C	16,090	88.17	18,190	78.74	15,040	78.67	15,990	80.45
60°C	507.9	89.60	851.1	86.29	813.0	86.29	748.3	86.09
90°C	22.62	91.66	56.22	88.81	52.58	89.43	48.54	89.15
TS=	16,709		14,877		14,726		15,013	

	3 ½ hour		6 ½ hour	
Temp	η^*	δ	η^*	δ
0°C	2.610e7	68.30	3.458e7	66.91
10°C	4.629e6	74.90	5.970e6	74.57
25°C	2.066e5	79.76	2.379e5	81.07
40°C	14,160	81.90	14,510	83.88
60°C	693.4	85.89	684.5	86.54
90°C	45.69	89.25	42.86	89.93
TS=	15,069		15,488	

Table B-2. η^* and δ Values for the Silverson Blends (Cont.)

Curing Study of 3/13/96, 20/80, TG -10WT/Fina Demex Resin (FNDMRS), Silverson, 4000 rpm, 533K (500°F), N ₂								
	FNDMRS		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C	3.377e7	73.23	4.157e6	75.33	4.166e6	75.25	4.804e6	75.93
10°C	5.374e6	81.05	8.869e5	72.97	9.488e5	72.95	8.719e5	74.00
25°C	1.836e5	86.72	58,910	72.03	68,610	71.31	61,980	73.03
40°C	8,742	88.24	8,324	72.46	8,538	73.21	8,572	73.54
60°C	238.6	90.10	665.3	82.60	626.4	83.07	605.9	83.10
90°C	14.16	95.26	66.43	88.61	66.91	87.66	61.15	89.45
TS=	16,833		12,440		12,521		12,538	

	3 ½ hour		6 ½ hour	
Temp	η^*	δ	η^*	δ
0°C	6.305e6	75.61	9.574e6	75.62
10°C	1.224e6	75.72	1.563e6	76.94
25°C	75,880	76.42	84,030	78.52
40°C	9,134	76.43	9,119	79.21
60°C	560.8	83.39	454.0	84.53
90°C	51.34	88.79	40.54	89.07
TS=	13,236		13,973	

Table B-2. η^* and δ Values for the Silverson Blends (Cont.)

Curing Study of 3/18/96, 10/90, TG -10WT/SC Asphalt, Silverson, 4000 rpm, 505K (450°F), N ₂								
	SC Asphalt		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C			1.160e8	55.53	9.543e7	57.27	1.084e8	57.58
10°C	8.186e6	77.12	1.615e7	72.70	1.382e7	72.44	1.592e7	72.92
25°C	2.340e5	86.99	7.751e5	75.30	6.460e5	73.61	7.310e5	76.48
40°C	9,518	87.82	49,130	77.73	47,070	75.06	47,100	77.31
60°C	369.0	89.74	1,572	85.97	1,708	85.81	1,610	85.84
90°C	15.50	92.16	70.98	87.99	77.38	89.36	76.61	88.83
TS=	17,032		16,146		15,788		16,007	

	3 ½ hour		6 ½ hour	
Temp	η^*	δ	η^*	δ
0°C	8.132e7	60.93	7.693e7	63.19
10°C	1.268e7	74.05	1.180e7	75.20
25°C	5.725e5	78.39	5.824e5	77.97
40°C	34,170	79.87	40,850	78.22
60°C	1,350	85.99	1,374	86.07
90°C	67.74	89.46	67.08	89.28
TS=	15,857		15,768	

Table B-2. η^* and δ Values for the Silverson Blends (Cont.)

Curing Study of 3/19/96: 10/90, TG -10WT/SC Asphalt, Silverson, 4000 rpm, 533K (500°F), N ₂								
	SC Asphalt		½ hour		1 hour		1 ½ hour	
Temp	η^*	δ	η^*	δ	η^*	δ	η^*	δ
0°C			7.929e7	62.63	6.530e7	64.87	7.372e7	64.63
10°C	8.186e6	77.12	1.149e7	75.55	1.042e7	76.11	1.137e7	76.16
25°C	2.340e5	86.99	5.371e5	78.25	5.109e5	79.86	5.094e5	80.10
40°C	9,518	87.82	34,140	79.89	32,600	79.79	30,930	80.88
60°C	369.0	89.74	1,432	86.04	1,206	85.87	1,212	85.47
90°C	15.50	92.16	69.96	89.21	62.44	88.87	61.84	89.08
TS=	17,032		15,725		15,705		15,846	

	3 ½ hour		6 ½ hour	
Temp	η^*	δ	η^*	δ
0°C	9.767e7	61.93	1.205e8	58.68
10°C	1.388e7	76.44	1.605e7	75.71
25°C	5.351e5	82.07	6.516e5	82.99
40°C	30,260	82.20	33,500	83.61
60°C	1,131	84.91	1,223	85.18
90°C	58.05	89.88	58.94	88.90
TS=	16,244		16,447	

Table B-3. Percentage of Crumb Passing Whatman 42 Paper Filter for the Silverson Blends

Curing Time (hours)	Curing Study of 2/5/96, 10/90, TG -10WT/ Exxon AC-10, Silverson, 4000rpm, 505K (450°F), N ₂	Curing Study of 2/13/96, 10/90, TG -10WT/ Exxon AC-10, Silverson, 4000rpm, 533K (500°F), N ₂	Curing Study of 2/23/96, 10/90, TG -10WT/ Exxon AC-10, Silverson, 8000rpm, 533K (500°F), N ₂	Curing Study of 2/24/96, 10/90, TG -40B/ Exxon AC-10, Silverson, 4000rpm, 533K (500°F), N ₂	Curing Study of 2/27/96, 10/90, TG -10WT/ EXX/SUN AC-5, Silverson, 4000rpm, 533K (500°F), N ₂
0.5	37.5	47.7	59.1	58.2	61.1
1.0	38.5	66.7	65.2	67.7	70.3
1.5	38.9	69.5	68.0	71.9	75.4
2.5	48.4	70.0	72.3	73.4	76.6
3.5	49.2	75.1	74.5	81.4	77.3
5.0	52.5	78.6	78.5	86.5	79.2
6.5	62.3	81.9	86.5	89.0	82.3

Table B-3. Percentage of Crumb Passing Whatman 42 Paper Filter for the Silverson Blends (Cont.)

Curing Time (hours)	Curing Study of 2/29/96, 20/80, TG -10WT/ Exxon AC-10, Silverson, 4000rpm, 533K (500°F), N ₂	Curing Study of 3/3/96, 10/90, TG -10WT/ Fina Demex Resin, Silverson, 4000rpm, 505K (450°F), N ₂	Curing Study of 3/7/96, 10/90, TG -10WT/ Fina Demex Resin, Silverson, 4000rpm, 533K (500°F), N ₂	Curing Study of 3/8/96, 10/90, TG -10WT/ Fina Demex Resin, Silverson, 8000rpm, 533K (500°F), N ₂	Curing Study of 3/9/96, 10/90, TG -40B/ Fina Demex Resin, Silverson, 4000rpm, 533K (500°F), N ₂
0.5	43.0	37.5	65.4	78.0	68.1
1.0	52.3	39.2	78.0	83.6	79.0
1.5	56.2	46.4	83.2	90.1	83.0
2.5	59.8	64.3	85.7	91.4	85.2
3.5	63.9	66.1	88.1	93.3	87.5
5.0	67.0	69.3	90.8	95.2	93.0
6.5	71.1	73.1	94.1	98.1	93.5

Table B-3. Percentage of Crumb Passing Whatman 42 Paper Filter for the Silverson Blends (Cont.)

Curing Time (hours)	Curing Study of 3/10/96, 10/90, TG -10WT/ Fina AC-5, Silverson, 4000rpm, 533K (500°F), N ₂	Curing Study of 3/13/96, 20/80, TG -10WT/ Fina Demex Resin, Silverson, 4000rpm, 533K (500°F), N ₂	Curing Study of 3/18/96, 10/90, TG -10WT/ SC Asphalt, Silverson, 4000rpm, 505K (450°F), N ₂	Curing Study of 3/19/96, 10/90, TG -10WT/ SC Asphalt, Silverson, 4000rpm, 505K (500°F), N ₂
0.5	52.8	60.6	31.1	62.4
1.0	67.1	70.5	40.4	78.5
1.5	75.9	72.4	52.9	84.8
2.5	79.1	74.6	63.5	85.4
3.5	83.1	82.0	67.2	86.2
5.0	89.7	84.0	68.3	87.4
6.5	89.9	84.9	69.6	89.6

APPENDIX C
AGING STUDY DATA

Table C-1. η^* and δ Values for the Unaged Phase 3 and 4 Blends

	Exxon AC-5		5/95, TG -40B/ Exxon AC-5, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hour		10/90, TG -40B/ Exxon AC-5, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	3.241e7	64.67	3.685e7	56.68	2.549e7	60.80
283	4.689e6	76.18	6.729e6	67.12	3.755e6	69.18
298	2.163e5	85.02	4.295e5	75.65	2.985e5	71.97
313	1.345e4	88.80	3.573e4	80.66	3.316e4	75.03
333	636.3	89.62	1,597	86.61	1,734	83.91
363	26.18	90.82	60.66	89.15	95.05	86.80
TS =	15,766		14,938		13,899	

	5/95, RS -40/ Exxon AC-5, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hour		10/90, RS -40/ Exxon AC-5, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hour		10/90, TG -40B/ Exxon AC-5, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	2.365e7	64.24	2.060e7	62.23	1.947e7	63.66
283	3.812e6	71.99	3.798e6	69.09	3.848e6	68.77
298	2.371e5	76.52	2.467e5	72.16	2.674e5	70.89
313	2.129e4	81.39	2.692e4	75.78	2.911e4	76.44
333	1,073	87.06	1,557	85.06	1,498	86.17
363	52.36	88.70	77.08	88.82	74.00	88.98
TS =	14,579		13,965		13,990	

Table C-1. η^* and δ Values for the Unaged Phase 3 and 4 Blends (Cont.)

	20/80, TG -40B/ Exxon AC-5, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hour		Exxon AC-5, Polar Aromatics		Exxon AC-5, Naphthene Aromatics	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	1.459e7	58.43			1.405e6	87.36
283	3.260e6	60.04	3.599e8	25.28	3.032e5	85.80
298	3.547e5	57.51	3.884e7	69.55	1.766e4	86.81
313	6.216e4	63.01	1.775e6	84.97	1,503	88.97
333	4,661	79.85	2.452e4	89.33	84.51	88.98
363	337.8	83.90	291.5	89.37	7.227	103.4
TS =	11,867		18,583		13,894	

	Exxon AC-5, Saturates	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	521.9	82.08
283	151.9	80.88
298	19.31	86.72
313	9.437	89.56
333	1.467	92.08
363		
TS =	8,748	

Table C-1. η^* and δ Values for the Unaged Phase 3 and 4 Blends (Cont.)

	Exxon AC-10		5/95, TG -40B/ Exxon AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hour		10/90, TG -40B/ Exxon AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	6.496e7	56.44	1.169e8	38.40	9.251e7	42.34
283	1.058e7	70.91	2.452e7	55.18	1.850e7	57.28
298	5.325e5	82.30	1.834e6	68.93	1.288e6	68.47
313	3.054e4	87.73	1.513e5	75.98	1.171e5	73.70
333	952.0	89.85	5,922	85.08	5,306	82.77
363	34.06	90.92	141.0	89.32	159.1	87.11
TS =	16,348		15,235		14,830	

	5/95, RS -40/ Exxon AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hour		10/90, RS -40/ Exxon AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hour		10/90, TG -40B/ Exxon AC-10, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	9.654e7	42.77	5.980e7	48.14	3.922e7	56.44
283	2.003e7	57.66	1.138e7	60.35	7.884e6	65.56
298	1.583e6	69.31	8.600e5	68.45	5.263e5	69.19
313	1.345e5	76.13	8.825e4	72.05	5.378e4	73.66
333	5,109	84.05	4,895	82.12	2,554	85.07
363	131.1	88.97	157.8	87.96	101.2	89.39
TS =	15,109		14,271		14,411	

Table C-1. η^* and δ Values for the Unaged Phase 3 and 4 Blends (Cont.)

	20/80, TG -40B/ Exxon AC-10, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	2.748e7	52.67
283	6.343e6	58.10
298	6.162e5	56.89
313	9.468e4	61.37
333	8,107	78.16
363	437.0	84.63
TS =	12,249	

	Fina AC-10		5/95, TG -40B/ Fina AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hour		10/90, TG -40B/ Fina AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	9.510e7	45.57	9.540e7	43.67	7.565e7	44.62
283	1.816e7	63.51	1.728e7	60.70	1.542e7	58.37
298	9.296e5	78.94	7.701e5	73.82	8.673e5	68.78
313	4.336e4	86.95	4.480e4	79.22	6.944e4	72.55
333	944.0	89.77	2,225	86.90	3,913	82.19
363	32.27	91.20	89.76	87.00	132.7	88.47
TS =	17,012		15,692		14,863	

Table C-1. η^* and δ Values for the Unaged Phase 3 and 4 Blends (Cont.)

	5/95, RS -40/ Fina AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hour		10/90, RS -40/ Fina AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hour		10/90, TG -40B/ Fina AC-10, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	9.401e7	44.13	6.473e7	46.28	7.453e7	44.69
283	1.677e7	61.05	1.220e7	59.96	1.747e7	57.68
298	8.144e5	72.93	6.278e5	69.32	9.876e5	67.93
313	5.178e4	78.65	5.103e4	73.60	7.528e4	72.84
333	1,773	87.96	2,437	84.78	2,820	84.58
363	63.28	89.55	99.30	88.90	107.8	89.33
TS =	16,065		15,063		15,253	

	20/80, TG -40B/ Fina AC-10, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	5.109e7	43.25
283	1.338e7	51.16
298	1.090e6	55.41
313	1.410e5	58.48
333	7,856	77.35
363	450.0	84.87
TS =	13,120	

Table C-1. η^* and δ Values for the Unaged Phase 3 and 4 Blends (Cont.)

	Fina Demex Resin		10/90, TG -40B/ Fina Demex Resin, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hour		20/80, TG -40B/ Fina Demex Resin, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hour	
Temp (K)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)	η^* at 1.0 rad/sec (poise)	δ at 1.0 rad/sec (degrees)
273	3.377e7	73.23	3.384e7	64.88	1.938e7	62.67
283	5.374e6	81.05	5.872e6	72.63	4.061e6	63.09
298	1.836e5	86.72	2.683e5	73.67	3.045e5	60.23
313	8,742	88.24	2.176e4	76.61	3.876e4	64.60
333	238.6	90.10	1,385	71.69	2,368	82.37
363	14.16	95.26	52.10	88.68	236.7	81.22
TS =	16,883		14,970		12,800	

Table C-2. CA, η^* , and δ Values for Phase 1 Blends Aged at 367K (200°F) with 3.4 atm Nitrogen

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
Diamond Shamrock (DS) AC-5	0.0	0.4288	548.4	89.46
	1.0	0.3925	645.4	89.50
	2.0	0.3835	655.5	89.20
	3.0	0.4282	747.7	87.03
	4.0	0.4901	561.5	89.20
	5.0	0.4065	600.9	89.08
10/90, TG -40/ DS AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	0.0	0.4328	1,455	85.02
	1.0	0.4641	1,579	84.95
	2.0	0.4208	1,656	84.29
	3.0	0.4540	1,484	84.78
	4.0	0.5000	1,446	86.19
	5.0	0.5230	2,090	81.51
20/80, TG -40/ DS AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	0.0	0.4742	3,583	76.17
	1.0	0.4602	4,044	74.05
	2.0	0.3628	4,097	72.60
	3.0	0.5612	5,096	71.28
	4.0	0.5972	4,511	73.55
	5.0	0.5658	3,932	74.11

Table C-2. CA, η^* , and δ Values for Phase 1 Blends Aged at 367K (200°F) with 3.4 atm Nitrogen (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
SHRP ABM-1	0.0	0.8170	2,409	89.85
	1.0	0.8075	2,569	88.89
	2.0	0.7601	2,608	89.58
	3.0	0.7918	2,677	88.63
	4.0	0.9188	2,601	89.43
	5.0	0.8832	2,435	89.63
10/90, RS -40/ SHRP ABM-1, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	0.0	0.7356	6,195	84.56
	1.0	0.8596	6,041	84.24
	2.0	0.8096	6,075	83.94
	3.0	0.7521	6,510	82.79
	4.0	0.8808	6,415	83.51
	5.0	0.8865	5,720	83.58
18/82, RS -40/ SHRP ABM-1, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	0.0	0.7780	15,750	76.64
	1.0	1.0198	15,780	76.55
	2.0	0.7572	17,980	74.33
	3.0	0.7558	15,280	75.08
	4.0	0.7645	16,550	75.63
	5.0	0.9043	15,370	75.51

Table C-3. CA, η^* , and δ Values for Phase 2 Blends Aged with 20 atm Oxygen

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Diamond Shamrock (DS) AC-5		0.0	0.419	548.4	89.46
	355K (180°F)	2.0	1.155	3,984	82.18
		4.0	1.359	6,624	81.50
		6.0	1.544	12,830	76.80
		8.0	1.720	21,810	74.15
		10.0	1.714		
		12.0	1.850	63,550	67.11
	367K (200°F)	1.0	1.148	4,488	84.14
		2.0	1.471	9,543	80.23
		3.0	1.625	19,550	75.53
		4.0	1.852	37,570	71.19
		5.0	1.886	60,580	67.18
20/80, TG -10/ DS AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		0.0	0.433	5,011	77.60
	355K (180°F)	2.0	1.096	15,170	65.98
		4.0	1.430	21,110	61.65
		6.0	1.534	21,960	61.84
		8.0	1.758	51,770	54.05
		10.0	1.860	56,190	53.44
		12.0	2.010	90,260	47.73

Table C-3. CA, η^* , and δ Values for Phase 2 Blends Aged with 20 atm Oxygen (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
20/80, TG -10/ DS AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	367K (200°F)	1.0	1.207	8,021	71.41
		2.0	1.461	19,380	64.52
		3.0	1.780	31,590	59.92
		4.0	2.064	64,330	53.37
		5.0	2.134	122,000	47.14
20/80, TG -40/ DS AC-5, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	355K (180°F)	0.0	0.474	3,583	76.17
		2.0	1.103	6,664	73.34
		4.0	1.320	10,050	68.96
		6.0	1.509	13,590	64.20
		8.0	1.704	25,560	63.74
		10.0	1.756	28,050	64.53
		12.0	1.970	51,680	58.59
	367K (200°F)	1.0	1.243	7,132	73.13
		2.0	1.522	12,380	68.42
		3.0	1.773	23,590	62.81
		4.0	1.964	54,830	55.00
		5.0	2.109	76,850	52.93

Table C-3. CA, η^* , and δ Values for Phase 2 Blends Aged with 20 atm Oxygen (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
SHRP ABM-1		0.0	0.817	2,409	89.85
	355K (180°F)	2.0	2.399	14,830	88.32
		4.0	2.761	22,720	87.90
		6.0	3.147	27,140	85.39
		8.0	3.206	49,800	86.32
		10.0	3.547	68,850	85.58
		12.0	3.646	76,450	84.88
	367K (200°F)	1.0	2.488	15,730	88.60
		2.0	2.912	24,290	87.93
		3.0	3.347	36,370	86.91
		4.0	3.654	54,020	85.76
		5.0	3.671	74,900	84.85
18/82, TG -10/ SHRP ABM-1, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		0.0	0.909	17,240	76.80
	355K (180°F)	2.0	2.302	39,910	63.87
		4.0	2.503	45,890	63.26
		6.0	2.938	37,790	65.76
		8.0	3.251	50,590	64.87
		10.0	3.322	55,700	65.96
		12.0	3.765	68,490	64.43

Table C-3. CA, η^* , and δ Values for Phase 2 Blends Aged with 20 atm Oxygen (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
18/82, TG -10/ SHRP ABM-1, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	367K (200°F)	1.0	2.606	26,660	68.86
		2.0	2.951	38,160	67.87
		3.0	3.417	36,160	68.65
		4.0	3.777	51,020	71.46
		5.0	3.875	62,390	68.66
18/82, TG -40/ SHRP ABM-1, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour	355K (180°F)	0.0	0.778	15,190	72.67
		2.0	2.383	28,560	65.44
		4.0	2.750	27,870	66.07
		6.0	2.992	32,930	66.34
		8.0	3.314	39,420	69.52
		10.0	3.325	47,990	69.49
		12.0	3.634	56,460	68.39
	367K (200°F)	1.0	2.414	24,510	67.63
		2.0	3.078	26,220	68.90
		3.0	3.386	34,300	70.29
		4.0	3.747	47,320	71.21
		5.0	3.953	61,700	70.60

Table C-3. CA, η^* , and δ Values for Phase 2 Blends Aged with 20 atm Oxygen (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
18/82, RS -40/ SHRP ABM-1, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		0.0	0.773	21,180	73.12
	355K (180°F)	2.0	2.192	30,690	64.05
		4.0	2.514	31,150	63.44
		6.0	2.905	27,230	63.02
		8.0	3.309	39,350	66.87
		10.0	3.562	45,170	68.89
		12.0	3.744	52,280	66.65
	367K (200°F)	1.0	2.302	28,890	63.12
		2.0	3.029	28,300	66.08
		3.0	3.398	28,060	69.63
		4.0	3.701	43,740	69.94
		5.0	3.845	51,260	69.15
5/95, TG -40/ SHRP ABM-1, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		0.0	0.802	3,958	86.62
	355K (180°F)	2.0	2.701	17,650	81.78
		4.0	3.075	22,630	82.72
		6.0	3.382	27,710	83.62
		8.0	3.649	34,980	63.68
		10.0	3.789	38,890	83.65
	367K (200°F)	1.0	2.595	16,580	83.23
		2.0	3.197	22,070	84.90
		3.0	3.372	25,580	84.35
		5.0	3.998	36,070	84.79
		6.0	4.232	43,150	84.53

Table C-3. CA, η^* , and δ Values for Phase 2 Blends Aged with 20 atm Oxygen (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
10/90, TG -40/ SHRP ABM-1, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		0.0	0.736	7,028	81.95
	355K (180°F)	2.0	2.611	19,940	77.45
		4.0	3.031	23,400	78.95
		6.0	3.354	26,790	80.64
		8.0	3.648	33,190	80.93
		10.0	3.793	35,990	81.93
	367K (200°F)	1.0	2.541	19,520	77.56
		2.0	3.161	19,350	80.15
		3.0	3.347	22,770	82.43
		5.0	4.068	33,100	81.95
		6.0	4.345	34,650	82.79
15/85, TG -40/ SHRP ABM-1, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		0.0	0.722	10,360	82.38
	355K (180°F)	2.0	2.573	25,940	74.15
		4.0	3.064	26,730	73.68
		6.0	3.290	27,410	75.61
		8.0	3.719	35,610	76.69
		10.0	3.902	34,350	77.58
	367K (200°F)	1.0	2.538	25,510	70.98
		2.0	3.138	23,870	75.25
		3.0	3.366	21,430	79.02
		5.0	4.084	28,350	79.77
		6.0	4.357	30,690	80.38

Table C-3. CA, η^* , and δ Values for Phase 2 Blends Aged with 20 atm Oxygen (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
SHRP ABM-1 Fraction		0.0	0.514	201.8	89.87
	355K (180°F)	2.0	2.007	2,557	89.42
		4.0	2.461	3,361	89.79
		6.0	2.734	3,980	89.51
		8.0	2.973	5,163	89.46
		10.0	3.067	5,014	89.37
	367K (200°F)	1.0	1.943	2,423	89.26
		2.0	2.375	2,717	89.05
		3.0	2.753	3,882	89.02
		5.0	3.179	4,258	89.30
		6.0	3.420	4,458	89.40
5/95, TG -40/ SHRP ABM-1 Fraction, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		0.0	0.837	1,259	85.88
	355K (180°F)	2.0	2.054	2,882	86.13
		4.0	2.472	3,331	87.51
		6.0	2.686	3,602	88.27
		8.0	2.951	4,741	88.74
		10.0	3.134	4,800	88.04
	367K (200°F)	1.0	1.952	3,483	82.94
		2.0	2.429	3,345	87.42
		3.0	2.808	3,727	87.81
		5.0	3.308	4,676	88.81
		6.0	3.509	5,511	89.10

Table C-3. CA, η^* , and δ Values for Phase 2 Blends Aged with 20 atm Oxygen (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
10/90, TG -40/ SHRP ABM-1 Fraction, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		0.0	1.212	2,147	78.57
	355K (180°F)	2.0	2.015	3,049	81.63
		4.0	2.458	3,230	84.86
		6.0	2.711	3,492	86.54
		8.0	3.037	3,909	88.06
		10.0	3.176	4,053	87.87
	367K (200°F)	1.0	2.000	3,099	81.64
		2.0	2.455	2,978	85.09
		3.0	2.763	3,337	87.40
		5.0	3.321	3,086	88.30
		6.0	3.646	4,284	88.69

Table C-3. CA, η^* , and δ Values for Phase 2 Blends Aged with 20 atm Oxygen (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
SHRP AAA-1 Fraction		0.0	0.453	287.6	89.78
	355K (180°F)	2.0	0.907	797.5	89.66
		4.0	1.298	1,358	89.56
		6.0	1.741	3,232	89.67
		8.0	2.278	7,049	88.78
		10.0	2.610	16,110	88.00
	367K (200°F)	1.0	0.907	1,018	89.40
		2.0	1.356	1,944	89.74
		3.0	1.988	4,375	89.43
		5.0	2.964	20,840	86.90
		6.0	3.589	74,390	82.59
5/95, RS -40/ SHRP AAA-1 Fraction, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		0.0	0.516	462.5	88.05
	355K (180°F)	2.0	0.9089	968.0	87.58
		4.0	1.210	1,353	86.94
		6.0	1.507	2,078	87.90
		8.0	2.108	2,479	88.10
		10.0	2.454	11,260	87.88
	367K (200°F)	1.0	0.930	1,066	86.53
		2.0	1.294	1,388	86.69
		3.0	1.723	2,633	88.96
		5.0	3.360	29,470	85.66
		6.0	3.950	181,900	76.92

Table C-3. CA, η^* , and δ Values for Phase 2 Blends Aged with 20 atm Oxygen (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
10/90, RS -40/ SHRP AAA-1 Fraction, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		0.0	0.527	609.1	86.23
	355K (180°F)	2.0	0.939	1,146	85.49
		4.0	1.239	1,553	83.63
		6.0	1.446	1,885	84.87
		8.0	1.904	2,389	87.75
		10.0	2.404	5,459	87.93
	367K (200°F)	1.0	0.905	1,197	84.79
		2.0	1.298	1,468	83.20
		3.0	1.731	2,191	87.14
		5.0	4.015	35,120	84.24
		6.0	5.290	354,200	72.07
15/85, RS -40/ SHRP AAA-1 Fraction, Sears, 500 rpm, 450K (350°F), N ₂ , 1 hour		0.0	0.534	965.9	83.70
	355K (180°F)	2.0	0.951	1,689	82.24
		4.0	1.223	1,906	80.68
		6.0	1.495	2,199	80.03
		8.0	1.865	2,499	85.17
		10.0	2.077	3,804	85.22
	367K (200°F)	1.0	0.961	1,642	82.04
		2.0	1.327	1,982	78.89
		3.0	1.762	2,175	84.13
		5.0	4.552	25,500	84.21
		6.0	5.844	343,300	73.19

Table C-4. CA, η^* , and δ Values for Phase 3 Blends Aged in the POV

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Exxon AC-5		0.0	0.440	636.3	89.62
	372K (210°F)	5.05	0.766	2,206	89.05
		6.97	0.899	3,066	87.96
		9.93	0.958	4,075	87.86
		11.03	1.079	5,275	87.50
		13.03	1.253	8,616	86.07
5/95, TG -40B/ Exxon AC-5, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours		0.0	0.637	1,597	86.61
	372K (210°F)	5.99	1.043	6,571	82.46
		7.97	1.222	10,920	79.89
		10.00	1.287	13,810	80.37
		13.01	1.500	24,490	77.47
		15.02	1.610	27,200	76.79
10/90, TG -40B/ Exxon AC-5, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours		0.0	0.623	1,734	83.91
	372K (210°F)	5.99	1.108	6,747	79.55
		7.97	1.249	8,666	77.18
		10.00	1.358	10,220	78.19
		13.01	1.537	16,620	75.54
		15.02	1.657	22,920	72.68

Table C-4. CA, η^* , and δ Values for Phase 3 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333 (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
5/95, RS -40/ Exxon AC-5, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours		0.0	0.502	1,073	87.06
	372K (210°F)	5.99	1.013	3,655	83.74
		7.97	1.178	4,786	83.44
		10.00	1.277	6,339	83.12
		13.01	1.404	10,250	81.82
		15.02	1.447	12,940	81.76
10/90, RS -40/ Exxon AC-5, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours		0.0	0.650	1,557	85.06
	372K (210°F)	5.99	1.106	6,070	77.70
		7.97	1.201	7,960	77.23
		10.00	1.371	9,642	76.52
		13.01	1.560	15,100	74.85
		15.02	1.601	16,710	74.98

Table C-4. CA, η^* , and δ Values for Phase 3 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Exxon AC-10		0.0	0.513	952.0	89.85
	372K (210°F)	5.05	0.801	3,690	88.50
		6.97	0.902	5,081	88.06
		9.93	1.126	9,916	86.32
		11.03	1.186	13,690	85.24
		13.03	1.210	14,060	85.43
5/95, TG -40B/ Exxon AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours		0.0	0.766	5,922	85.01
	372K (210°F)	3.98	1.140	28,150	77.71
		5.99	1.286	43,290	75.79
		7.08	1.337	51,000	74.61
		10.05	1.357	57,690	74.39
		11.97	1.522	88,730	71.33
10/90, TG -40B/ Exxon AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours		0.0	0.766	5,306	82.77
	372K (210°F)	3.98		23,480	74.28
		5.99		37,230	71.31
		7.08		43,690	70.64
		10.05		64,640	68.92
		11.97		76,980	67.71

Table C-4. CA, η^* , and δ Values for Phase 3 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
5/95, RS -40/ Exxon AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours		0.0	0.781	5109	84.05
	372K (210°F)	3.98	1.133	22,580	77.96
		5.99	1.187	27,550	77.52
		7.08	1.266	33,570	76.64
		10.05	1.410	47,840	74.49
		11.97	1.551	83,450	72.05
5/95, RS -40/ Exxon AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours		0.0	0.899	4,895	82.12
	372K (210°F)	3.98	1.138	20,110	73.26
		5.99	1.293	29,360	71.17
		7.08	1.332	31,350	71.14
		10.05	1.515	48,900	68.38
		11.97	1.590	55,720	67.51

Table C-4. CA, η^* , and δ Values for Phase 3 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Fina AC-10		0.0	0.465	944.0	89.77
	372K (210°F)	5.05	0.971	10,910	86.39
		6.97	0.989	14,920	85.42
		9.93	1.200	31,620	82.64
		11.03	1.354	46,610	80.98
		13.03	1.512	97,800	75.91
5/95, TG -40B/ Fina AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours		0.0	0.557	2,225	86.09
	372K (210°F)	5.99	1.300	33,060	76.74
		7.97	1.425	53,800	76.02
		10.00	1.628	86,510	73.88
		13.01	1.600	91,330	73.21
		15.02	1.927	169,100	69.43

Table C-4. CA, η^* , and δ Values for Phase 3 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
10/90, TG -40B/ Fina AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours		0.0	0.689	3,913	82.19
	372K (210°F)	5.99	1.037	20,420	73.10
		7.97	1.201	31,070	70.87
		10.00	1.493	45,830	71.80
		13.01	1.580	53,440	71.08
		15.02	1.699	80,750	69.48
5/95, RS -40/ Fina AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours		0.0	0.654	1,773	87.96
	372K (210°F)	5.99	1.275	26,150	78.02
		7.97	1.501	49,230	75.97
		10.00	1.632	82,350	74.34
		13.01	1.856	150,800	69.87
		15.02	1.952	247,400	67.71
10/90, RS -40/ Fina AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours		0.0	0.713	2,437	84.78
	372K (210°F)	5.99	1.325	24,370	72.64
		7.97	1.496	36,960	72.42
		10.00	1.702	54,740	71.36
		13.01	1.857	109,200	67.81
		15.02	2.004	139,100	66.50

Table C-5. CA, η^* , and δ Values for Phase 3 Blends Aged in the ENVRM

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
5/95, TG -40B/ Exxon AC-5, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours	0	0.637	1,597	86.61
	28	0.696	4,177	84.61
	52	0.784	4,888	84.37
	70	0.811	5,799	83.40
	84	0.852	6,163	83.84
	98	0.894	6,677	83.20
	114	0.860	7,769	82.98
	138	0.976	8,660	81.64
	152	1.009	9,850	81.74
	166	1.011	12,120	80.50
	187	1.012	11,700	80.87
	202		13,760	80.11
	215		13,790	80.86
	236		14,040	80.53
	250		14,790	80.63
	271		17,480	80.12
	300		20,350	78.87

Table C-5. CA, η^* , and δ Values for Phase 3 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
10/90, TG -40B/ Exxon AC-5, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours	0	0.623	1,734	83.91
	28	0.733	4,226	81.72
	52	0.814	4,965	81.08
	70	0.770	6,018	79.72
	84	0.874	6,538	79.94
	98	0.909	6,849	79.53
	114	0.975	7,726	78.76
	138	1.055	9,201	78.84
	152	1.087	10,220	78.01
	166	1.033	10,370	77.24
	187	1.040	12,200	76.72
	202		13,670	77.05
	215		14,480	76.08
	236		14,240	73.72
	250		14,080	76.20
	270		15,960	75.69
	300		18,830	74.82

Table C-5. CA, η^* , and δ Values for Phase 3 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
5/95, RS -40/ Exxon AC-5, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours	0	0.502	1,073	87.06
	34	0.637	2,272	86.78
	58	0.698	2,857	86.33
	73	0.724	2,990	85.96
	89	0.828	3,350	85.88
	104	0.860	3,739	85.21
	120	0.875	3,973	84.89
	144	0.951	4,760	84.51
	158	0.985	4,993	84.10
	172	0.942	5,778	83.61
	193	0.959	6,166	82.94
	208		6,862	83.08
	221		7,002	82.79
	242		6,857	82.95
	256		7,067	83.33
	277		8,575	81.42
	306		8,771	82.77

Table C-5. CA, η^* , and δ Values for Phase 3 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
10/90, RS -40/ Exxon AC-5, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours	0	0.649	1,557	85.06
	52	0.796	5,019	80.29
	70	0.846	6,000	79.14
	84	0.882	6,120	79.20
	98	0.910	6,521	78.61
	114	0.943	7,245	78.60
	138	0.987	9,329	76.90
	152	1.045	9,459	76.95
	166	1.060	10,750	75.79
	187	1.083	11,300	75.84
	202		12,620	75.07
	215		13,620	74.93
	236		12,800	74.95
	250		13,720	74.23
	300		17,420	72.80

Table C-5. CA, η^* , and δ Values for Phase 3 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
5/95, TG -40B/ Exxon AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours	0	0.766	5,922	85.01
	23	0.798	11,350	82.14
	42	0.863	14,930	81.41
	57	0.931	17,540	80.70
	81	0.961	20,590	80.02
	96	1.003	22,740	79.39
	112	1.033	25,650	79.25
	127	1.055	28,090	77.42
	143	1.050	31,540	78.85
	167	1.074	37,140	77.30
	181	1.083	45,570	76.44
	195	1.168	48,490	76.21
	216	1.147	50,980	76.57
	231		58,370	75.43
	244	1.205	64,180	75.12
	265		65,380	74.08
	279	1.269	71,430	73.76
	300		83,890	72.75
	329	1.277	85,950	72.52

Table C-5. CA, η^* , and δ Values for Phase 3 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
10/90, TG -40B/ Exxon AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours	0	0.766	5,306	82.72
	33	0.976	12,690	77.18
	52		15,560	76.51
	76	1.068	20,690	74.53
	100		24,040	74.21
	117	1.127	26,110	74.37
	131		27,920	73.09
	146	1.190	30,870	73.69
	162		33,120	72.63
	186	1.170	43,080	71.57
	200		45,900	71.47
	214	1.325	48,600	70.68
	235		57,410	69.32
	250	1.400	56,280	70.33
	263		64,860	68.60
	284	1.291	65,890	68.80
	298		67,560	68.83
	319	1.459	80,970	67.64
	348	1.497	87,830	66.90

Table C-5. CA, η^* , and δ Values for Phase 3 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
5/95, RS -40/ Exxon AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours	0	0.781	5,109	84.05
	23	0.824	10,190	82.03
	42		13,700	80.93
	57	0.914	14,630	80.61
	81		18,790	79.46
	96	1.007	20,110	79.08
	112		22,740	78.53
	127	1.049	22,630	78.76
	143		25,750	77.98
	167	1.143	33,370	76.61
	181		35,780	76.71
	195	1.200	36,030	76.89
	216		45,080	75.24
	231	1.216	48,620	74.87
	244		51,180	74.40
	265	1.300	51,670	75.42
	279		58,860	73.48
	300	1.326	66,400	73.09
	329		70,720	72.59

Table C-5. CA, η^* , and δ Values for Phase 3 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
10/90, RS -40/ Exxon AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours	0	0.899	4,895	82.12
	30	0.950	12,040	76.58
	49	1.014	16,070	75.46
	64	1.046	16,660	75.55
	88	1.091	21,150	73.81
	105	1.134	22,470	72.74
	119	1.132	24,410	71.95
	134	1.172	25,630	72.03
	151	1.176	28,550	71.39
	175	1.240	34,290	70.74
	189	1.243	35,860	70.61
	203	1.282	37,670	70.11
	224	1.317	42,020	69.10
	239	1.329	46,700	68.64
	252	1.342	50,600	67.98
	273	1.380	49,730	68.05
	287	1.402	55,610	66.91
	307	1.427	60,490	66.36
	336	1.424	69,740	66.05
	350	1.443		

Table C-5. CA, η^* , and δ Values for Phase 3 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
5/95, TG -40B/ Fina AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours	0	0.557	2,225	86.09
	28	0.803	10,360	82.57
	52		13,340	81.23
	70	0.908	16,940	80.30
	84	0.998	18,560	80.00
	98		22,290	78.68
	114	1.077	25,190	78.93
	138	1.161	33,140	77.74
	152		36,800	77.27
	166	1.232	41,090	77.32
	187		47,600	77.53
	202	1.300	49,800	76.12
	215		58,256	75.64
	236	1.345	67,240	75.40
	250		72,870	74.19
	271	1.397	88,880	74.11
	300		88,150	73.64
	314	1.447		

Table C-5. CA, η^* , and δ Values for Phase 3 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
10/90, TG -40B/ Fina AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours	0	0.689	3,913	82.19
	28	0.831	14,130	76.52
	52		18,190	74.88
	69	0.978	21,860	73.35
	84		24,960	73.21
	98	1.088	29,030	71.85
	114		29,790	71.88
	138	1.217	37,190	71.21
	152		41,800	70.46
	166	1.311	44,230	70.54
	187		51,250	71.30
	202	1.358	58,740	69.56
	215		65,490	68.34
	236	1.451	71,000	68.17
	250		70,730	69.53
	271	1.522	86,520	67.00
	300		91,330	67.34
	314	1.585		

Table C-5. CA, η^* , and δ Values for Phase 3 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
5/95, RS -40/ Fina AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours	0	0.654	1,773	87.96
	34	0.777	10,360	80.95
	58		14,660	80.21
	73	0.961	17,800	79.19
	89		17,360	79.28
	104	1.055	21,060	78.59
	120		23,530	77.54
	144	1.188	31,050	77.22
	158		36,250	76.35
	172	1.262	38,860	77.36
	193		48,910	75.67
	208	1.336	50,480	75.15
	221		55,620	74.89
	242	1.416	61,630	74.79
	256		72,020	73.63
	277	1.457	78,880	73.24
	306		91,680	72.22
	320	1.510		

Table C-5. CA, η^* , and δ Values for Phase 3 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
10/90, RS -40/ Fina AC-10, Sears, 500 rpm, 464K (375°F), N ₂ , 12 hours	0	0.713	2,437	84.78
	34	0.950	11,710	76.86
	58		16,000	74.99
	73	1.028	19,310	74.11
	89		20,210	74.03
	104	1.089	22,500	76.63
	120		24,320	72.25
	144	1.225	32,580	70.76
	158		35,090	70.08
	172	1.400	35,720	70.52
	193		42,460	70.26
	208	1.421	43,290	69.01
	221		46,940	68.61
	242	1.448	53,780	68.72
	256		60,000	67.75
	277	1.496	69,010	67.62
	306		77,670	66.96
	320	1.562		

Table C-6. CA, η^* , and δ Values for Phase 4 Blends Aged in the POV

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Exxon AC-5		0.0	0.440	636.3	89.62
	353K (176°F)	11.9	0.748	2,208	88.95
		15.9	0.816	2,964	88.59
		19.9	0.826	3,328	88.38
		23.9	0.937	4,028	87.80
		27.9	0.942	4,505	87.89
	358K (185°F)	10.0	0.807	2,347	88.44
		17.2	0.984	3,685	88.25
		24.1	1.127	5,837	87.01
		31.2	1.253	8,503	86.07
		38.3	1.353	11,820	85.24
	363K (194°F)	10.0	0.932	4,072	88.11
		13.0	1.038	5,781	87.26
		16.0	1.145	7,683	86.16
		19.0	1.263	11,650	85.60
		22.0	1.296	13,210	85.03

Table C-6. CA, η^* , and δ Values for Phase 4 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
10/90, TG -40B/ Exxon AC-5, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours	353K (176°F)	0.0	0.512	1,498	86.17
		22.2	1.065	6,616	79.09
		29.2	1.195	8,474	77.24
		36.2	1.281	8,714	78.20
		43.3	1.351	9,679	78.43
		50.2	1.457	12,000	76.66
	358K (185°F)	10.0	0.944	4,478	81.61
		17.1	1.111	5,207	80.39
		24.1	1.246	7,377	78.67
		31.2	1.411	8,421	78.61
		38.3	1.575	8,724	77.05
	363K (194°F)	10.0	1.031	4,263	80.75
		17.2	1.318	5,091	79.91
		24.1	1.509	8,106	79.23
		29.1	1.597	11,880	77.35
		35.3	1.800	19,100	75.67

Table C-6. CA, η^* , and δ Values for Phase 4 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
20/80, TG -40B/ Exxon AC-5, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours		0.0	0.554	4,661	79.85
	353K (176°F)	22.2	1.174	12,510	69.73
		29.2	1.279	14,760	67.39
		36.2	1.365	17,520	65.83
		43.3	1.444	19,440	65.31
		50.2	1.583	18,190	66.12
	358K (185°F)	9.9	0.918	10,060	72.94
		16.7	1.088	10,900	70.85
		24.0	1.266	13,200	67.77
		30.9	1.447	15,450	67.05
		36.8	1.514	17,100	66.34
	363K (194°F)	10.0	1.135	9,360	71.52
		17.2	1.380	10,930	68.66
		24.1	1.702	16,780	66.15
		29.1	1.743	21,560	64.41
		35.3	1.935	31,590	62.08

Table C-6. CA, η^* , and δ Values for Phase 4 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Exxon AC-10		0.0	0.513	952.0	89.85
	353K (176°F)	11.9	0.776	3,819	87.77
		15.9	0.836	4,642	88.39
		19.9	0.898	5,700	87.67
		23.9	0.961	6,417	87.53
		27.9	1.011	7,112	87.32
	358K (185°F)	10.0	0.845	4,469	88.28
		17.2	1.003	7,179	87.47
		24.1	1.126	11,540	86.23
		31.2	1.293	16,870	84.80
		38.3	1.417	19,975	83.80
	363K (194°F)	10.0	0.982	8,210	87.22
		13.0	1.040	9,246	86.64
		16.0	1.190	15,680	85.06
		19.0	1.283	22,120	83.81
		22.0	1.357	29,470	82.46

Table C-6. CA, η^* , and δ Values for Phase 4 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
10/90, TG -40B/ Exxon AC-10, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours		0.0	0.534	2,554	85.07
	353K (176°F)	22.2	1.090	12,380	77.71
		29.2	1.211	16,170	76.11
		36.2	1.311	16,870	75.66
		43.3	1.382	20,540	75.48
		50.2	1.438	24,880	74.00
	358K (185°F)	10.0	0.921	7,673	80.29
		17.1	1.102	9,821	78.43
		24.1	1.218	14,440	76.33
		31.2	1.389	17,420	76.37
		38.3	1.568	21,230	75.64
	363K (194°F)	10.0	0.979	8,082	77.96
		17.1	1.283	10,210	78.35
		24.1	1.462	18,680	76.52
		29.1	1.654	26,350	75.00
		35.3	1.821	43,730	72.06

Table C-6. CA, η^* , and δ Values for Phase 4 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
20/80, TG -40B/ Exxon AC-10, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours		0.0	0.638	8,107	78.16
	353K (176°F)	22.2	1.169	21,320	66.79
		29.2	1.300	24,400	65.29
		36.2	1.353	30,830	61.50
		43.3	1.443	31,310	62.73
		50.2	1.566	34,890	62.57
	358K (185°F)	9.9	0.985	17,620	69.47
		16.7	1.148	18,610	67.99
		24.0	1.314	22,630	65.34
		30.9	1.461	26,070	64.13
		36.8	1.579	33,080	63.82
	363K (194°F)	10.0	1.139	15,320	68.50
		17.1	1.374	18,380	67.27
		24.1	1.627	27,080	64.89
		29.1	1.778	33,980	63.53
		35.3	1.899	51,120	61.62

Table C-6. CA, η^* , and δ Values for Phase 4 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Fina AC-10		0.0	0.465	944	89.77
	353K (176°F)	11.9	0.866	9,051	86.36
		15.9	0.974	12,570	85.99
		19.9	1.064	15,060	85.38
		23.9	1.121	21,240	84.24
		27.9	1.215	29,870	82.69
	358K (185°F)	10.0	1.013	12,450	85.72
		17.2	1.107	17,550	85.14
		24.1	1.286	43,200	81.53
		31.2	1.459	79,980	78.36
		38.3	1.545	86,770	77.47
	363K (194°F)	10.0	1.1347	29,550	83.49
		13.0	1.2808	53,510	80.77
		16.0	1.3903	93,100	77.64
		19.0	1.5020	139,700	75.10
		22.0	1.5322	187,800	73.04

Table C-6. CA, η^* , and δ Values for Phase 4 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
10/90, TG -40B/ Fina AC-10, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours		0.0	0.587	2,820	84.58
	353K (176°F)	22.2	1.275	35,100	70.16
		29.2	1.418	48,650	69.77
		36.2	1.535	67,250	69.36
		43.3	1.581	80,660	67.79
		50.2	1.653	115,000	66.00
	358K (185°F)	10.0	1.090	16,870	74.90
		17.1	1.279	24,890	73.23
		24.1	1.447	42,230	72.08
		31.2	1.613	52,420	71.07
		38.3	1.905	58,290	72.73
	363K (194°F)	10.0	1.020	24,010	72.71
		17.2	1.253	31,040	73.48
		24.1	1.453	68,380	70.54
		29.1	1.642	107,300	68.45
		35.3	1.796	168,600	65.17

Table C-6. CA, η^* , and δ Values for Phase 4 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
20/80, TG -40B/ Fina AC-10, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours		0.0	0.762	7,856	77.35
	353K (176°F)	22.2	1.371	57,590	57.02
		29.2	1.504	63,000	56.34
		36.2	1.626	81,410	55.40
		43.3	1.779	95,210	54.72
		50.2	1.730	102,800	55.01
	358K (185°F)	9.9	1.162	34,420	62.66
		16.7	1.334	46,260	59.28
		24.0	1.418	51,350	58.55
		30.9	1.787	65,530	58.50
		36.8	1.918	80,210	57.46
	363K (194°F)	10.0	1.325	31,680	61.45
		17.2	1.673	42,720	61.31
		24.1	1.898	74,520	58.10
		29.1	2.107	118,400	56.39
		35.3	2.354	177,800	54.25

Table C-6. CA, η^* , and δ Values for Phase 4 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Fina Demex Resin		0.0	0.407	238.6	90.10
	353K (176°F)	11.9	0.763	1,374	89.05
		15.9	0.815	1,392	89.28
		19.9	0.884	1,614	89.07
		23.9	0.943	1,805	89.11
		27.9	0.998	2,050	89.45
	358K (185°F)	10.0	0.812	1,276	89.33
		17.2	0.916	1,605	89.37
		24.1	1.073	2,286	89.34
		31.2	1.178	2,639	89.41
		38.3	1.326	2,962	89.21
	363K (194°F)	10.0	0.932	1,904	89.24
		13.0	0.975	2,251	89.35
		16.0	1.055	2,719	89.13
		19.0	1.167	3,337	89.42
		22.0	1.245	4,001	89.12

Table C-6. CA, η^* , and δ Values for Phase 4 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
10/90, TG -40B/ Fina Demex Resin, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours		0.0	0.490	1,385	71.69
	353K (176°F)	22.2	1.027	2,537	84.71
		29.2	1.208	3,145	83.63
		36.2	1.289	3,646	83.35
		43.3	1.402	4,101	83.26
		50.2	1.486	4,459	83.87
	358K (185°F)	10.0	0.943	2,109	81.43
		17.1	1.103	2,613	82.31
		24.1	1.284	3,066	83.33
		31.2	1.452	3,302	84.35
		38.3	1.648	4,059	78.11
	363K (194°F)	10.0	1.033	2,159	83.33
		17.1	1.355	2,469	83.67
		24.1	1.674	3,728	84.67
		29.1	1.893	4,992	84.73
		35.3	1.934	7,380	84.58

Table C-6. CA, η^* , and δ Values for Phase 4 Blends Aged in the POV (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
20/80, TG -40B/ Fina Demex Resin, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours		0.0	0.516	2,368	82.37
	353K (176°F)	22.2	1.147	5,356	76.09
		29.2	1.283	5,738	75.28
		36.2	1.382	6,435	74.35
		43.3	1.519	6,558	74.40
		50.2	1.544	7,198	74.70
	358K (185°F)	9.9	0.892	3,884	77.83
		16.7	1.027	4,281	75.84
		24.0	1.184	4,945	74.50
		30.9	1.379	5,570	75.48
		36.8	1.434	6,080	75.34
	363K (194°F)	10.0	1.155	3,347	77.56
		17.1	1.432	3,981	76.57
		24.1	1.696	5,538	76.46
		29.1	1.825	6,824	76.24
		35.3	2.052	9,071	76.52

Table C-7. CA, η^* , and δ Values for Phase 4 Blends Aged in the ENVRM

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
Exxon AC-5	35	0.624	1,626	89.44
	54	0.723	1,986	89.30
	78	0.764	2,384	89.01
	102	0.816	2,825	89.09
	119	0.822	3,011	88.86
	133	0.839	3,253	88.76
	148	0.843	3,471	88.75
	164	0.866	3,725	88.54
	188	0.907	4,427	88.41
	202	0.926	4,480	88.27
	216	0.963	4,829	87.62
	237	0.978	5,179	88.14
	252		6,219	87.52
	265		6,512	87.34

Table C-7. CA, η^* , and δ Values for Phase 4 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
10/90, TG -40B/ Exxon AC-5, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours	60	0.855	4,942	82.06
	73	0.832	5,239	81.20
	94	0.922	5,550	81.37
	108	0.910	6,025	81.19
	129	1.021	6,580	80.75
	158	1.064	7,452	80.29
	185	1.066		
	221	1.081		
20/80, TG -40B/ Exxon AC-5, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours	60	0.866	11,040	72.78
	73	0.911	11,660	72.77
	94	0.976	12,220	72.51
	108	0.987	12,890	72.49
	129	1.083	12,880	71.49
	158	1.162	14,310	70.68
	185	1.140		
	221	1.207		

Table C-7. CA, η^* , and δ Values for Phase 4 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
Exxon AC-10	35	0.633	2,875	89.22
	54	0.705	3,415	89.05
	78	0.745	4,265	88.80
	102	0.792	4,867	88.50
	119	0.830	5,606	88.55
	133	0.863	5,852	88.35
	148	0.866	6,328	87.97
	164	0.879	6,980	87.97
	188	0.937	8,243	87.59
	202	0.982	9,622	87.35
	216	1.013	8,901	87.24
	237	1.027	11,440	86.97
	252		12,490	86.16
	265		13,320	86.46

Table C-7. CA, η^* , and δ Values for Phase 4 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
10/90, TG -40B/ Exxon AC-10, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours	63	0.886	9,516	79.62
	76	0.880	9,834	79.75
	97	0.962	11,420	79.11
	111	0.952	11,390	78.57
	132	1.060	12,820	78.55
	161	1.100	14,070	77.09
	188	1.068		
	224	1.103		
20/80, TG -40B/ Exxon AC-10, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours	63	0.928	19,090	69.23
	76	0.965	19,520	69.94
	97	1.050	21,180	69.19
	111	1.043	20,090	69.15
	132	1.078	22,220	68.16
	161	1.129	23,320	67.44
	188	1.150		
	224	1.258		

Table C-7. CA, η^* , and δ Values for Phase 4 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
Fina AC-10	35	0.789	6,016	88.17
	54		8,089	87.66
	78	0.930	10,650	87.20
	102	1.001	13,710	86.65
	119	1.033	16,660	85.93
	133	1.077	18,470	85.73
	148	1.107	20,060	85.35
	164	1.185	23,300	85.02
	188	1.200	31,670	83.81
	202	1.256	35,720	82.94
	216	1.245	38,030	82.93
	237	1.310	46,810	82.77
	252	1.286	48,530	81.14
	265	1.254	45,570	81.77
	286	1.335	62,350	79.88

Table C-7. CA, η^* , and δ Values for Phase 4 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
10/90, TG -40B/ Fina AC-10, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours	60	0.980	20,590	75.00
	73	1.041	22,460	74.17
	94	1.128	26,660	73.25
	108	1.137	29,320	72.24
	129	1.243	34,260	71.79
	185	1.260		
	221	1.292		
20/80, TG -40B/ Fina AC-10, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours	60	1.081	35,930	62.22
	73	1.095	42,590	61.60
	94	1.162	43,790	61.19
	108	1.212	49,250	59.95
	129	1.255	53,450	58.69
	158	1.300	65,830	56.82
	185	1.330		
	221	1.380		

Table C-7. CA, η^* , and δ Values for Phase 4 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
Fina Demex Resin	60	0.761	1,240	89.17
	73	0.811	1,331	89.18
	94	0.867	1,543	89.22
	108	0.868	1,636	89.13
	129	0.931	1,771	89.61
	158	0.976	1,793	89.13
	185	0.996		
	221	1.088		

Table C-7. CA, η^* , and δ Values for Phase 4 Blends Aged in the ENVRM (Cont.)

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
10/90, TG -40B/ Fina Demex Resin, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours	63	0.809	2,280	84.89
	76	0.881	2,520	84.79
	97	0.942	2,657	84.47
	111	1.109	2,708	84.36
	131	1.006	2,848	83.70
	161	1.043	3,350	84.00
	188	1.114		
	224	1.114		
20/80, TG -40B/ Exxon AC-10, Sears, 1550 rpm, 464K (375°F), N ₂ , 6 hours	63	0.887	4,080	78.61
	76	0.886	4,564	78.63
	97	1.000	4,735	78.53
	111	1.053	4,550	78.98
	131	1.055	4,787	78.51
	161	1.108	10,520	74.24
	188	1.182		
	224	1.207		

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 2/5/96, 10/90, TG -10WT/ Exxon AC-10, Silverson, 4000 rpm, 505K (450°F), N ₂ , 6.5 hours		0.0	0.561	1,768	85.60
	353K (176°F)	12.05	0.868	6,085	81.33
		17.09	0.925	7,596	80.05
		22.01	1.031	9,495	79.17
		26.98	1.076	10,530	78.91
		31.97	1.141	11,420	78.80
	358K (185°F)	10.06	0.943	7,903	79.40
		14.89	1.038	9,341	78.87
		18.03	1.122	10,090	78.10
		22.01	1.218	12,950	77.71
		25.98	1.303	14,090	77.31
	363K (194°F)	9.92	1.067	9,072	78.94
		12.88	1.127	12,830	77.51
		15.91	1.255	15,400	76.80
		18.87	1.315	20,630	75.01
		21.99	1.484	24,150	75.65

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 2/13/96, 10/90, TG -10WT/ Exxon AC-10, Silverson, 4000 rpm, 533K (500°F), N ₂ , 6.5 hours		0.0	0.603	1,414	85.21
	353K (176°F)	12.05	0.880	5,683	82.31
		17.09	0.953	6,110	82.73
		22.01	1.025	7,874	82.23
		26.98	1.087	9,661	81.57
		31.97	1.161	10,670	81.20
	358K (185°F)	10.06	0.980	6,862	82.13
		14.89	1.085	8,846	81.66
		18.03	1.163	9,808	81.63
		22.01	1.234	12,320	80.78
		25.98	1.340	13,330	80.69
	363K (194°F)	9.92	1.090	9,676	81.36
		12.88	1.176	11,900	80.30
		15.91	1.272	16,990	79.52
		18.87	1.364	21,200	78.52
		21.99	1.467	19,030	79.16

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 2/23/96, 10/90, TG -10WT/ Exxon AC-10, Silverson, 8000 rpm, 533K (500°F), N ₂ , 6.5 hours		0.0	0.607	1,276	86.82
	353K (176°F)	12.05	0.889	5,101	83.99
		17.09	0.943	6,200	83.46
		22.01	1.013	8,291	82.17
		26.98	1.145	10,170	81.95
		31.97	1.202	11,440	81.40
	358K (185°F)	10.06	1.005	7,492	82.99
		14.89	1.139	9,764	81.64
		18.03	1.219	10,270	82.05
		22.01	1.305	12,680	80.87
		25.98	1.446	15,960	80.75
	363K (194°F)	9.92	1.147	9,247	82.05
		12.88	1.218	11,990	81.11
		15.91	1.377	18,350	79.36
		18.87	1.444	23,560	78.46
		21.99	1.556	28,610	78.33

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 2/24/96, 10/90, TG -40B/ Exxon AC-10, Silverson, 4000 rpm, 533K (500°F), N ₂ , 6.5 hours		0.0	0.570	1,212	86.15
	353K (176°F)	12.05	0.833	4,551	84.27
		17.09	0.923	5,206	83.70
		22.01	1.039	6,950	83.00
		26.98	1.104	8,234	82.29
		31.97	1.181	10,070	82.46
	358K (185°F)	10.06	0.962	6,303	83.16
		14.89	1.071	8,190	81.95
		18.03	1.173	8,929	82.75
		22.01	1.275	10,980	81.83
		25.98	1.357	13,050	81.69
	363K (194°F)	9.92	1.036	8,813	82.35
		12.88	1.125	10,550	81.61
		15.91	1.253	14,950	80.49
		18.87	1.350	17,980	79.48
		21.99	1.461	22,850	79.59

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 2/27/96, 10/90, TG -10WT/ Exx/Sun AC-5, Silverson, 4000 rpm, 533K (500°F), N ₂ , 6.5 hours		0.0	0.639	906.0	85.71
	353K (176°F)	12.05	0.880	3,264	84.22
		17.09	0.984	3,813	83.32
		22.01	1.069	4,909	83.14
		26.98	1.138	5,069	83.36
		31.97	1.178	6,064	83.10
	358K (185°F)	10.06	1.013	4,729	83.01
		14.89	1.138	5,754	82.68
		18.03	1.222	5,640	83.18
		22.01	1.295	7,941	82.10
		25.98	1.413	9,149	81.91
	363K (194°F)	9.92	1.081	5,627	83.48
		12.88	1.168	7,372	81.76
		15.91	1.324	9,214	82.15
		18.87	1.398	12,590	80.01
		21.99	1.527	16,110	79.84

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 2/29/96, 20/80, TG -10WT/ Exxon AC-10, Silverston, 4000 rpm, 533K (500°F), N ₂ , 6.5 hours		0.0	0.643	1,807	81.31
	353K (176°F)	12.05	1.000	7,281	75.56
		17.09	1.050	8,303	74.49
		22.01	1.130	10,350	74.35
		26.98	1.223	12,160	73.50
		31.97	1.270	13,040	73.27
	358K (185°F)	10.06	1.091	8,433	74.95
		14.89	1.196	10,520	74.09
		18.03	1.355	10,740	74.60
		22.01	1.400	14,680	73.25
		25.98	1.535	15,360	73.02
	363K (194°F)	9.92	1.194	11,230	73.80
		12.88	1.273	12,990	72.26
		15.91	1.388	17,960	71.06
		18.87	1.419	22,370	69.48
		21.99	1.518	25,520	69.74

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 3/3/96, 10/90, TG -10WT/ Fina Demex Resin, Silverson, 4000 rpm, 505K (450°F), N ₂ , 6.5 hours		0.0	0.496	482.9	87.15
	353K (176°F)	12.12	0.810	1,013	85.35
		17.06	0.860	1,220	84.17
		22.02	0.931	1,316	83.98
		26.94	1.023	1,226	84.71
		31.90	1.075	1,362	84.26
	358K (185°F)	9.93	0.845	1,350	83.66
		14.12	0.956	1,446	83.90
		17.94	0.989	1,433	83.46
		21.92	1.084	1,554	83.88
		25.91	1.170	1,585	84.10
	363K (194°F)	9.92	0.899		
		12.88	1.010	1,581	84.26
		15.91	1.086	1,811	83.50
		18.87	1.221	1,800	84.55
		21.99	1.296	1,964	85.37

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 3/7/96, 10/90, TG -10WT/ Fina Demex Resin, Silverson, 4000 rpm, 533K (500°F), N ₂ , 6.5 hours		0.0	0.486	372.8	86.71
	353K (176°F)	12.12	0.800	872.7	86.55
		17.06	0.883	991.3	86.52
		22.02	0.953	1,085	87.02
		26.94	1.039	1,133	86.86
		31.90	1.095	1,179	87.21
	358K (185°F)	9.93	0.900	978.7	86.55
		14.12	0.968	1,041	86.30
		17.94	1.033		
		21.92	1.109	1,215	87.09
		25.91	1.199	1,320	87.43
	363K (194°F)	9.92	0.935	1,021	86.67
		12.88	1.050	1,208	86.71
		15.91	1.125	1,325	87.10
		18.87	1.203	1,500	87.25
		21.99	1.340	1,618	88.16

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 3/8/96, 10/90, TG -10WT/ Fina Demex Resin, Silverson, 8000 rpm, 533K (500°F), N ₂ , 6.5 hours		0.0	0.470	348.3	88.10
	353K (176°F)	12.12	0.820	818.0	87.55
		17.06	0.943	965.1	87.64
		22.02	1.040	1,034	87.57
		26.94	1.096	1,144	87.54
		31.90	1.163	1,243	87.86
	358K (185°F)	9.93	0.896	932.9	87.38
		14.12	0.945	1,157	87.34
		17.94	1.087	1,216	87.73
		21.92	1.211	1,380	87.87
		25.91	1.269	1,510	88.02
	363K (194°F)	9.92	0.993	1,205	86.68
		12.88	1.107	1,387	87.31
		15.91	1.198	1,603	87.01
		18.87	1.366	2,102	87.33
		21.99	1.442	2,067	87.87

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 3/9/96, 10/90, TG -40B/ Fina Demex Resin, Silverston, 4000 rpm, 533K (500°F), N ₂ , 6.5 hours		0.0	0.486	327.9	86.93
	353K (176°F)	12.12	0.787	749.6	87.00
		17.06	0.888	840.2	87.44
		22.02	0.993	911.2	87.02
		26.94	1.021	1,019	87.48
		31.90	1.090	1,097	87.68
	358K (185°F)	9.93	0.872	917.8	86.81
		14.12	0.976	986.5	87.14
		17.94	0.998	1,026	87.01
		21.92	1.113	1,217	87.52
		25.91	1.209	1,310	87.89
	363K (194°F)	9.92	0.914	1,046	87.14
		12.88	1.005	1,150	87.36
		15.91	1.076	1,386	87.21
		18.87	1.183	1,643	87.41
		21.99	1.315	1,631	88.12

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 3/10/96, 10/90, TG -10WT/ Fina AC-5, Silverson, 4000 rpm, 533K (500°F), N ₂ , 6.5 hours		0.0	0.540	507.9	89.60
	353K (176°F)	12.12	0.908	2,145	85.13
		17.06	1.011	2,750	85.69
		22.02	1.100	2,940	85.32
		26.94	1.205	3,652	85.63
		31.90	1.299	3,926	85.68
	358K (185°F)	9.93	0.941	2,894	85.16
		14.12	1.106	3,548	84.83
		17.94	1.214	3,956	84.97
		21.92	1.326	5,074	84.57
		25.91	1.407	5,447	84.47
	363K (194°F)	9.92	1.073	3,463	84.26
		12.88	1.165	4,807	83.53
		15.91	1.311	6,255	83.98
		18.87	1.436	7,931	83.95
		21.99	1.570	8,848	83.92

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 3/13/96, 20/80, TG -10WT/ Fina Demex Resin, Silverston, 4000 rpm, 533K (500°F), N ₂ , 6.5 hours		0.0	0.650	454.0	84.53
	353K (176°F)	12.09	0.983	1,357	82.76
		17.10	1.024	1,447	83.32
		22.09	1.118	1,722	82.75
		27.06	1.186	1,824	82.92
		32.28		1,839	83.30
	358K (185°F)	10.25	1.034	1,254	83.27
		14.15	1.153	1,481	83.27
		18.24	1.231	1,561	83.63
		22.09	1.332	1,744	83.61
		26.02	1.417	1,908	83.78
	363K (194°F)	10.25	1.121	1,790	82.50
		13.10	1.226	1,938	83.15
		16.17	1.340	2,315	83.57
		19.44	1.408	2,477	83.14
		22.09	1.455	2,582	83.35

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Supercritical (SC) Asphalt		0.0	0.508	634.6	89.30
	353K (176°F)	22.23	0.920	4,518	89.62
		29.19	1.024	6,222	89.48
		36.16	1.148	7,599	89.32
		43.26	1.210	9,892	89.25
		50.22	1.296	12,130	89.26
	358K (185°F)	10.00	0.767	3,075	89.45
		17.15	0.918	4,459	89.46
		24.14	1.079	7,340	89.52
		31.21	1.232	10,230	89.06
		38.25	1.355	10,580	89.28
	363K (194°F)	10.02	0.820	3,767	89.65
		17.15	1.098	4,508	89.53
		24.13	1.336	11,660	89.22
		29.15	1.450	17,960	88.71
		35.25	1.680	21,060	88.66

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 3/18/96, 10/90, TG -10WT/ SC Asphalt, Silverston, 4000 rpm, 505K (450°F), N ₂ , 6.5 hours		0.0	0.573	1,610	85.84
	353K (176°F)	12.09	0.888	5,106	81.89
		17.10	0.955	5,329	82.05
		22.09	1.017	5,786	81.74
		27.06	1.080	5,971	81.99
		32.28	1.147	6,600	81.25
	358K (185°F)	10.25	0.940	4,224	82.58
		14.15	1.005	5,004	81.53
		18.24	1.120	6,255	80.62
		22.09	1.190	6,456	81.47
		26.02	1.297	7,360	82.17
	363K (194°F)	10.25	1.044	6,972	81.03
		13.10	1.155	7,708	80.94
		16.17	1.225	8,484	81.37
		19.44	1.354	9,115	82.02
		22.09	1.434	9,309	82.10

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Curing Study of 3/19/96, 10/90, TG -10WT/ SC Asphalt, Silverson, 4000 rpm, 533K (500°F), N ₂ , 6.5 hours		0.0	0.587	1,374	86.07
	353K (176°F)	12.09	0.919	3,876	84.13
		17.10	0.972	4,476	84.62
		22.09	1.051	5,303	85.24
		27.06	1.142	5,842	84.85
		32.28	1.210	6,381	84.70
	358K (185°F)	10.25	0.983	3,704	84.82
		14.15	1.089	4,533	85.02
		18.24	1.195	5,399	84.94
		22.09	1.267	6,233	85.10
		26.02	1.379	6,944	85.77
	363K (194°F)	10.25	1.102	6,234	84.94
		13.10	1.225	8,001	84.64
		16.17	1.376	8,682	85.10
		19.44	1.474	9,488	85.72
		22.09	1.551	10,590	85.74

Table C-8. CA, η^* , and δ Values for the Phase 5 Blends (Cont.)

Blend	Aging Temp	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
				η^* (poise)	δ (degree)
Neste-Wright, Liquefied Tire Rubber 10 (LTR10), (Exxon AC-10 Based Asphalt Rubber)		0.0	0.691	457.9	89.00
	353K (176°F)	22.23	1.138	3,529	85.89
		29.19	1.247	4,764	84.92
		36.15	1.367	6,750	83.94
		43.26	1.437	8,085	83.18
		50.22	1.547	10,460	82.27
	358K (185°F)	9.89	1.002	2,103	87.38
		16.72	1.157	3,080	86.28
		23.96	1.294	5,074	84.88
		30.88	1.445	7,332	83.44
		36.80	1.559	10,630	82.33
	363K (194°F)	13.00	1.189	2,410	87.26
		16.00	1.310	3,473	86.34
		19.00	1.363	4,010	85.52
		22.00	1.476	5,660	84.98
		25.00	1.527	6,260	84.74

**Table C-9. CA, η^* , and δ Values for the Supercritical Asphalt
Aged at 333K (140°F) with 1 atm Air**

Blend	Time (day)	CA	At 333K (140°F) and 1.0 rad/sec	
			η^* (poise)	δ (degree)
Supercritical Asphalt	0	0.508	634.6	89.30
	60	0.755	2,828	89.56
	73	0.763	3,100	89.59
	94	0.818	3,760	89.71
	108	0.851	3,884	89.58
	129	0.883	4,359	89.28
	158	0.938	4,879	89.44
	185	0.962		
	221	0.990		