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16. Abstract

This project was a comprehensive study of methods for incorporating ground tire rubber in asphalt and of the resulting properties and potential pavement serviceability. Potential benefits include improved pavement durability through reduced rates of oxidative hardening, improved Superpave performance grade on both the high and low end grades, and utilization of a waste material. The degree of performance grade improvement depends upon the amount of rubber and the extent of the cure. In general, higher cure results in less increase in both high and low end improvement. However, higher cure also results in improved stability to storage settling and improved high-temperature (hot-mix temperature) viscosity and thus improved mix compaction in dense-graded mixes. A higher degree of curing can be achieved by higher shear and higher temperature, but also by air curing, which also can produce significant increases in the upper end performance grade. Over-curing can result in reducing significantly the benefit of rubber on performance grade, but the positive effect on reducing hardening rates remains. Field tests of a high-cure asphalt rubber material at two levels of rubber in the binder (13.5 and 17.6 wt%) were placed in Bryan, Texas, in summer 1998. Economic analysis indicates a favorable life-cycle benefit if only a 15 to 20 percent improvement in pavement life is achieved, a level which is likely, based on laboratory aging tests. Field tests of two additional rubber contents in the binder (8 and 12 wt%) were placed in League City, Texas, in June 2000.

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A COMPREHENSIVE LABORATORY AND FIELD STUDY OF HIGH-CURE CRUMB-RUBBER MODIFIED ASPHALT MATERIALS

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DISCLAIMER

This research was performed in cooperation with the Texas Department of Transportation (TxDOT) and the U.S. Department of Transportation, Federal Highway Administration (FHWA). The contents of this report reflect the views of the authors, who are responsible for the facts and accuracy of the data presented herein. The contents do not necessarily reflect the official view or policies of the FHWA or TxDOT. This report does not constitute a standard, specification, or regulation, nor is it intended for construction, bidding, or permit purposes. Trade names are used solely for information and not for product endorsement. The engineer in charge of this project was Charles James Glover, Ph.D., P.E. (Texas, 48732).

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CHAPTER 1. INTRODUCTION

This project began in August 1994, jointly sponsored by the Department of Energy (DOE) and the Texas Department of Transportation (TxDOT). Initially, a primary goal was to develop an effective means of implementing the Intermodal Surface Transportation Efficiency Act (ISTEA) requirement concerning ground tire rubber. The mandate stipulated that rubber be incorporated in asphalt binders, eventually to the level of 20 percent utilization of a 20 percent ground tire rubber binder (or any equivalent usage of rubber, e.g., 100 percent utilization of 4 percent rubber in the binder). To do so would have a tremendous impact on tire waste and on energy usage across the nation.

With the simultaneous demise of the ISTEA mandate and increased pressures to reduce federal spending, the DOE abruptly announced in July 1996 that it would cease funding the project, even though results to that time were very positive toward a successful utilization of ground tire rubber in asphalt. In fact, results even that early in the project suggested that not only would rubber utilization reduce waste and energy usage, but also would have a very positive impact on pavement performance through improved durability, thereby potentially leading to significant enhancements in pavement life-cycle cost.

It was on this basis of a potential for life-cycle cost benefit that TxDOT personnel decided to continue the project in spite of losing the support of the DOE. This support has led to the most complete study to date of techniques for rubber utilization, the impact of rubber content on Superpave™ (Superpave is a registered trademark of the National Academy of Sciences) Performance Grade (PG), and four high-cure asphalt rubber field test pavements. These test pavements consisted of rubber compositions, as a percent of the total amount of binder in the mix, from 8 percent up to 17.6 percent, plus two non-rubber (control) sections. This was a total of six test strips in two TxDOT pavement projects, each with the same binder content (approximately 5 percent) as the rest of its respective TxDOT pavement project. To reiterate, in spite of significant rubber content in the binder (even at the very high level of 17.6 percent), pavement compaction was no problem and thus total binder content was virtually no different from that used in conventional, non-rubber pavements. Additionally, the binder at the two higher contents met the Texas Settling test for binder storage stability. These compaction and settling characteristics were the result of the high-cure process used for blending the rubber and binder which was developed in this study.

A word about definitions is appropriate at this point. The term “asphalt rubber” has been defined by American Society for Testing and Materials (ASTM) to mean “a blend of asphalt cement, reclaimed tire rubber, and certain additives in which the rubber component is at least 15 percent by weight of the total blend and has reacted in the hot asphalt cement sufficiently to cause swelling of the rubber particles.” Unfortunately, this definition, if used exclusively, limits the use of this seemingly generic term to a very specific product, a high-rubber content, low-cure material. At the same time, it says nothing about its properties. Throughout this report, we use the term asphalt rubber in a much more generic sense to mean simply asphalt which contains rubber without any implication about its physical properties or cure state or type of rubber material or mesh size, etc. The discussion in the report which accompanies the term will further clarify the specific type of material and the experiment of interest. The term high-cure asphalt rubber, likewise will refer to a generic rubber containing asphalt material but does emphasize that it is a high cure (meaning cure at conditions of temperature and shear that will significantly reduce the particle size and digest the rubber into the asphalt to a significant degree).

PROBLEM STATEMENT

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. As such, it consists of a wide variety of materials: aromatics, heterocyclic aromatics, saturates, and a variety of oxygen-containing compounds in the form of carbonyls, and others. All of these species may range in molecular mass from several hundred to a few thousand. Furthermore, many (most) of these compounds are reactive to oxidation in the pavement, which results in physical changes to the asphalt binder over its service lifetime.

Together with these complexities of composition, asphalt faces considerable challenges in performance. Ideally, the pavement mix/binder must be capable of placement and compaction to provide an even and strong ride surface and appropriate mix density (air voids); the binder, together with the mix design, must be able to withstand loading to prevent permanent deformation (wheelpath rutting); the binder must be able to withstand low temperatures and the resulting thermal stresses which develop as the pavement contracts; the binder must be able to withstand repeated loading and unloading without exhibiting fatigue failure (cracking); and, finally, the ideal binder will be able to sustain these performance criteria over an extended period of time, meaning that either it must resist oxidative aging or have a limited response to it.

Producing improved binders to meet these service requirements most certainly can be achieved, but requires an improved understanding of the complex relationship between the composition and its performance over time, and of the impact of potential additives on performance. Due to the large number of components, their complex interactions, and their changes over time due to oxidation, this understanding is extremely challenging, indeed. Much research work over many years has been directed at achieving such an understanding, focused primarily on physical properties of binders, but also on chemical properties and on the interactions between the two. Nevertheless, much remains to be done and accomplished.

As a means of establishing the properties that a good binder should have, a set of new asphalt testing and evaluation specifications, known as Superpave, has been developed. This endeavor, part of the Strategic Highway Research Program, is ambitious as climates from the hot southern plains to the frigid northeastern hills, to the varied western extremes, all must be considered. Adapting asphalt production to this variability in requirements is the major challenge of the Superpave program.

The Superpave PG specifications provide a guide relating statistical temperature realities and pavement needs and are a significant start to categorizing a given asphalt for preferred use and for comparison with others. The major benefit of this grading process is a new standardization of testing procedures and methodology, 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 Superpave PG, or the supercritical fractionation of a generic asphalt to adjust the relative amounts of different chemical types (resins versus saturates versus asphaltenes, e.g.) are other considerations. Another idea utilized is to alter the elastic properties of the asphalt binder to allow 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 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 led to government disinterest, this concept is still well worth examination for economic and enhanced performance reasons. 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 performance objective of adding tire rubber 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, prohibitively high cost.

Ultimately, efforts to improve binder performance must include economic factors as well as composition. The key question is if the inevitable additional processing cost, which translates into a higher binder cost and hence a higher mix cost, is warranted by the amount of enhanced performance which is obtained. This requires a life-cycle cost analysis over the life of the project for competing treatment methods. As such, it should include initial installation cost, maintenance, lane closure costs, and perhaps salvage (recycle) value. Of these, the initial installation will be the prime consideration, as well as a reasonable estimate of expected life.

In response to these issues of economically improving binder with ground tire rubber, this project is a rather thorough and comprehensive evaluation of the use of ground tire rubber in asphalt binders to include laboratory studies of processing the rubber with the binder, compatibility with asphalt materials, durability of the binder as it is affected by oxidation, life-cycle project cost, and Superpave performance properties. It also includes field testing processes for curing asphalt and rubber blends and field tests of rubber-containing asphalt binder pavements.

Waste and Energy Considerations

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 percent 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.

Previous Rubber Results

The use of scrap tire rubber as a modifier for asphalt cement is not new to the paving industry in the United States. It has been developing for over 25 years. Crumb-rubber modifier (CRM) has been used primarily in four types of paving applications (Estakhri et al., 1990): asphalt chip seals, stress-absorbing membrane interlayers, crack and joint sealing, and rubber modified hot-mix asphalt pavements.

The use of CRM in hot-mix asphalt concrete has much broader variability and potential than the first three applications discussed above (Heitzman, 1992). However, there is much less research and experience with this application than with the first two. The mandate to use CRM put state highway engineers in a very difficult position. They were required to build CRM asphalt pavements without the needed experience, design procedures, specifications, and construction guidelines. The recyclability of CRM pavements is also unknown. A survey of state highway engineers in all 50 states revealed that no state attempted to recycle pavements containing CRM (Button et al., 1992).

Most earlier uses of tire rubber in asphalt concrete used the dry method in which up to 3 percent rubber was added to the aggregate prior to mixing with the asphalt. This is less expensive than alternatives and gets rid of tire rubber but with very inconsistent results on the road. The increasingly preferred method is to blend finely ground rubber with the asphalt at temperatures from 180-220 °C for an hour or more before mixing with aggregate. During the hot blending, the rubber swells and may be somewhat degraded but has a greater effect on properties and is less inclined to settle.

A number of studies have been conducted to relate such variables as rubber content, rubber source, particle size, mixing time, and temperature to asphalt rubber properties as well as to mix design. Some of these are: Piggott et al., 1977; Oliver, 1979; Huff and Vallerga, 1979; Lalwani et al., 1982; Stephens, 1982; Jimenez, 1982; Shuler, 1982; Shuler et al., 1985a; Shuler et al., 1985b; Hugo and Nachenius, 1989. Most of these works and others have been reviewed by Roberts et al., 1989. These studies show that rubber increases viscosity, especially at higher temperatures. It takes less rubber to achieve the same effect as the particle size decreases. The effectiveness increases with mix time and temperature until a maximum is reached. At some point, especially at higher temperature, the viscosity begins to decrease as the rubber is digested.

Studies also show that cryogenically ground rubber is much less effective than rubber ground at ambient temperature. This is probably a surface area effect. This is borne out by a simple study by Oliver (1979) in which ground rubber was placed in water, boiled to remove air, and allowed to settle. The settled rubber volume was found to correlate with elastic recovery. The percent recovery increased markedly as the bulk density (reciprocal of the volume on settling) decreased. As the particle size was constant, the volume would tend to increase with increasing surface roughness. Natural rubber is more effective than synthetic rubber, but as the latter is much more prevalent, the two are likely to be mixed in any commercially prepared product and be predominantly synthetic.

No study thus far considers the properties of the asphalt in any detail. In general rubber is added to a pavement grade asphalt and if the resulting mixture is too thick, it is thinned with some lighter fraction, perhaps even kerosene, but preferably an aromatic oil. Huff and Vallerga (1979) note that asphalts low in aromatic oil produced an asphalt rubber product with poor adhesive properties. They describe a process patented by Arizona Refining Co. in which about 20 percent rubber is mixed at 350-400 °F in the asphalt which is first tested for compatibility. If the asphalt compatibility is poor, 2-6 percent of a highly aromatic oil (Lube extract) is added.

Very similar problems are encountered in the additions of elastomers to asphalt. Bredail et al. (1991) studied the compatibility of styrene-butadiene-styrene (SBS) block co-polymer additive with asphalt. In general, only those asphalts having over 80 percent aromatics were compatible. Low asphaltenes were particularly important and it was preferable that the asphaltene be of lower molecular size. Addition of aromatic oil improved the compatibility.

Serfass et al. (1992) report SBS compatibility with asphalt in terms of the asphalt colloidal instability index IC, which is

$$IC = \frac{\text{Asphaltenes} + \text{Saturates}}{\text{Resins} + \text{Aromatics}}$$

with results similar to these above; i.e., the lower this index the better. They also noted that adhesion could be a problem with SBS modified asphalts.

In spite of the promise of rubber addition to roads, a number of problems are reported. Most of these stem from compaction difficulties: high voids, or to counter this, high mix temperatures which cause emission problems and further harden the asphalt, or high binder content that increases cost and can lead to flushing and rutting. Too high a viscosity can also lead to poor adhesion and ravelling. These difficulties would be reduced or eliminated if the asphalt rubber blend had a viscosity nearer to that normally encountered at hot-mix temperature and if this is combined with proper mix design.

OBJECTIVES OF THE PROJECT

As described in the project proposal, the objective of this study is twofold: 1) to learn to tailor asphalts and recycle agents for compatibility with ground tire rubber and 2) to establish a realistic aging test for asphalt-rubber pavements. In the context of the problem statement discussion, these objectives address the issues of producing a blend of asphalt and rubber which is stable to settling and which possesses good physical properties as well as understanding the impact of aging on these physical properties. Of particular interest to TxDOT was to develop asphalt-rubber materials suitable for dense-graded mixes. Thus, this project has addressed production methods, Superpave PG properties, field tests, and economics for type C and D mixes.

APPROACH TO THE PROBLEM SOLUTION

This project involved a combination of laboratory and field tasks. Laboratory tasks consisted of binder material testing and evaluation (fractionate asphalt material, reblend fractions to produce aromatic asphalts, determine optimal rubber-asphalt curing parameters, age blends); evaluating mixture characteristics (compaction characteristics, deformation and failure of compacted mixes); and adhesion testing (adhesion tests, water susceptibility). In the field, tasks consisted of placing test sections for long-term evaluation of high-cure asphalt rubber materials and performance and economic evaluations.

In order to achieve an asphalt rubber blend suitable for dense-graded mixes, the biggest drawbacks were found to be the heterogeneity of the sample and the high viscosity at the hot-mix conditions. Consequently, a large effort was conducted to evaluate the curing of rubber with asphalt materials. Parameters studied were asphalt composition, curing shear rate and type of mixer, curing temperature, curing time, rubber content, rubber particle size, and rubber type.

OUTLINE OF THE REPORT

This report consists of seven chapters, including this introduction. The chapters provide an implementation-oriented review of the results of this work, as opposed to a project task-oriented review.

Chapter 2 is a report of the extensive laboratory studies on methods for producing an acceptable asphalt rubber binder for dense mixes. This includes three laboratory production methods which exclude air from the process and one study which includes air in the process (air enhances the curing process).

Chapter 3 presents studies on issues related to performance properties of CRMA. These properties include Superpave PG properties (even though the PG system was not designed for asphalt-rubber or other modified materials), the effect of curing on storage stability of the resulting binder, the effect of asphalt composition on curing, and low-temperature direct tension. Additionally, two methods for tracking curing during a commercial process are presented. Highly cured ground tire rubber provides improvement to both the high- and low-temperature ends of the PG spectrum.

Chapter 4 addresses long-term pavement durability issues. This includes a proposed model for the effect of rubber on physical properties and their changes which accompany oxidative aging as well as data and discussion which address the challenges of developing an aging test for CRMA materials. The addition of rubber reduces the rate of oxidative hardening of the binder in the pavement, thereby leading to improved durability.

Chapter 5 presents details of the field implementation projects, constructed in 1998 and 2000. The test sections constructed in the summer of 1998 contained binder which was 13.5 percent and 17.6 percent rubber. These sections test the probable economic upper limits of rubber content that might be used in applications for ease of pavement construction and pavement durability. The test sections placed June 2000 contained binder with 8 percent and 12 percent rubber, levels more likely to be used in practice. Additionally, the 2000 sections used a custom-designed asphalt base, designed to have improved durability to oxidation in its own right.

Chapter 6 provides capitalized cost calculations of the economics of using CRMA. A projected increase in pavement life of 25 percent provides significant incentive for ground tire rubber utilization by this method with a 15 to 20 percent life extension just matching the capitalized cost of the conventional binder. By contrast, these calculations show that a low-cure, high-rubber content “asphalt rubber” binder would require a life extension of from 30 percent to 60 percent over the conventional dense-graded mix to match capitalized costs.

Finally, Chapter 7 summarizes conclusions and presents recommendations for further study and implementation.

CHAPTER 2. LABORATORY STUDIES OF PRODUCTION METHODS FOR CRUMB-RUBBER MODIFIED ASPHALT

Achieving proper curing of ground tire rubber in asphalt is essential to producing a durable pavement. No-cure (as in the dry process), low-cure (as in the traditional wet process), and various levels of intermediate- and high-cure processes, and all with different levels of rubber content and mesh size, produce asphalt-rubber binders and pavements with widely different properties and durability. The pavements may be very difficult to compact, thereby requiring a higher binder content (and more expense) and leading to high air voids and a tendency to ravel, or they may be as easy to compact as conventional pavements with the same binder content. In general, the cure process will be designed so as to optimize high-temperature viscosity, low-temperature ductility and stiffness, and, perhaps, rubber particle settling.

This project encompassed a comprehensive effort to determine the effects of cure level (temperature, level of shear, with and without air oxidation), rubber content, and asphalt composition on the curing process, as measured by asphalt-rubber binder properties. The work is reported as low-cure, intermediate-cure, and high-cure investigations, plus a study of the effect of air oxidation on curing and binder properties, a study on curing to meet Texas Settling test, and an investigation of the effect of asphalt composition. The three sections on curing, as well as the section of the effect of oxidative curing, have been reported previously in the scientific literature. These reports are reproduced here in their entirety for ease of reference and completeness in this final project report. Appropriate citations are given at the start of each of these sections.

Some comments about the content of Chapter 3 as it relates to that of Chapter 2 are appropriate. As described above, Chapter 2 deals with curing methods. As will be seen, this includes the effect of curing on physical properties and settling, including performance grade properties. As such, Chapter 2 presents early studies of this project on curing methods.

Chapter 3 presents more extensive studies of curing. First is a more detailed study which focuses specifically and in more detail on performance grade properties and on different levels of cure. Second is further studies on high-cure methods and especially settling stability. This study also includes some effects of asphalt composition. The next study also deals with high-cure, composition and settling, but now the objective is to understand the impact of Corbett composition on curing efficiency. The final curing study addresses meeting the optional high-temperature viscosity specification and the Texas Settling test. Incorporated within the study are techniques for tracking the cure process. This is essential for industrial process quality control.

Considering all studies of both Chapters 2 and 3 together reveals an extensive body of work on curing asphalt and rubber and on a wide array of resulting modified binder properties.

PHYSICAL PROPERTIES OF ASPHALT-RUBBER BINDER

(Pages 2-2 through 2-22 reprinted from Billiter, T.C., Davison, R.R., Glover, C.J., and Bullin, J.A., “Physical Properties of Asphalt-Rubber Binder,” **Petroleum Sci. and Technol.**, Volume 15, Numbers 3&4, 1997, pp. 205-236 by courtesy of Marcel Dekker, Inc.)

Abstract

This study was performed to determine how the rheological properties of asphalt-rubber binders are affected by various parameters. Properties studied were asphalt composition, rubber dissolution, and the low-, intermediate-, and high-temperature rheological properties, measured with the bending beam rheometer, dynamic shear rheometer, and rotational viscometer, respectively. The rheological properties of the asphalt-rubber binder were determined to be dependent on the rubber content (weight percent), rubber particle size, and base asphalt composition. By controlling these variables, an asphalt-rubber binder with improved low-temperature cracking resistance, improved mid-temperature rutting resistance and temperature susceptibility, and a non-detrimental high-temperature compaction viscosity, all relative to the base asphalt, can be produced.

Introduction

Rubber modifiers have been used in bituminous materials for years. In fact, the use of natural rubber in bituminous material was patented in England in the early 1840s (Allison, 1967). Rubber alone has also been tried, with extensive testing of rubber roads (without asphalt) in both Great Britain (Dempster, 1979) and the United States (Allison, 1967) in the 1920s. More recently, engineers have blended both natural and synthetic rubber with asphalt in hopes of producing a more elastic binder. Tire rubber, a combination of both natural and synthetic rubber, has been studied widely, primarily due to its abundance and low cost. Specifically, the use of scrap tire rubber (crumb rubber) as a modifier for asphalt has been developing for more than 25 years (Heitzman, 1992).

There is much research indicating that crumb rubber can improve certain characteristics of asphalt pavements (Blumenthal, 1991). The obvious benefit of adding rubber to asphalt is that the rubber imparts elasticity to the binder (Gagle et al., 1973; Lalwani et al., 1982; Nadkarni et al., 1985; Nielson and Bagley, 1978; Shuler et al., 1985b), which helps increase pavement fatigue life (Takallou et al., 1986) or fatigue resistance (Takallou and Takallou, 1991), as well as reduce reflective cracking (Takallou and Takallou, 1991). This elasticity also makes the pavement more flexible (Dempster, 1978; McQuillen et al., 1988; Roberts et al., 1991), thus improving the pavement's susceptibility to low-temperature cracking (Dempster, 1978; Ferry, 1985; McQuillen et al., 1988; Nielson and Bagley, 1978; Ohta, 1983). It has been reported that rubber also imparts tensile strength (Lalwani et al., 1982; Nielson and Bagley, 1978), ductility (Allison, 1967; Gagle et al., 1973), toughness (Lalwani et al., 1982; Nielson and Bagley, 1978; Ohta, 1983), resiliency (Lalwani et al., 1982; Nielson and Bagley, 1978; Takallou et al., 1986), tenacity (Allison, 1967;

Ohta, 1983) and thus, durability (Lalwani et al., 1982; Takallou and Takallou, 1991) to the binder. Asphalt-rubber binder has a higher softening point than asphalt (Lalwani et al., 1982; Ohta, 1983), which improves resistance to rutting (Roberts et al., 1991). The improved adhesion (Dempster, 1978; Huff and Vallerga, 1979; Nielson and Bagley, 1978) of asphalt-rubber binder promotes chip retention (Allison, 1967) when it is used as a chip seal. Rubber-modified pavement improves skid resistance (Dempster, 1978; Takallou and Takallou, 1991) even under icy conditions (McQuillen et al., 1988). Furthermore, the practice of utilizing rubber in asphalt is environmentally friendly since it eliminates solid waste and reduces traffic noise (McQuillen et al., 1988). On the other hand, the addition of rubber increases the viscosity of the binder at high temperatures (Ohta, 1983), which can make compaction more difficult (Allison, 1967). The high compaction viscosity can lead to high air void content (Jimenez, 1982) and thus, high rates of oxidation (Linden et al., 1989) which, overtime, leads to pavement brittleness (McDonald, 1975). Because of the compaction problems, engineers often increase the hot-mix temperature when they use rubber (Roberts et al., 1991). Overall, the long-term savings in maintenance and road replacement will offset the high initial costs of using CRM (Takallou and Takallou, 1991), thus making the utilization of asphalt-rubber more than worthwhile (Dempster, 1978).

The process of adding rubber to asphalt can be divided into two categories: the dry process and the wet process. The dry process defines any method of adding rubber to the heated aggregate before the addition of asphalt, whereas the wet process defines any method that adds the rubber to the asphalt before the addition of aggregate (Heitzman, 1992). Henceforth, this work will be concerned with the wet process and will refer to the material produced by the wet process as asphalt-rubber binder. Additionally, the authors will follow the lead of Shuler et al. (1985) by stating that the term asphalt-rubber in this paper indicates that a chemical and physical change has occurred in the two constituents that compose blended asphalt-rubber. These changes allow a distinction to be made between asphalt-rubber and a simple mixture of asphalt cement and solid ground tire rubber. Furthermore, the reaction of asphalt and rubber during the wet process is affected by the reaction time and temperature, the type and amount of mechanical energy, weight percentage and mesh size of rubber, and the aromatic content of the asphalt (Heitzman, 1992).

There is little doubt that proper use of crumb rubber in asphalt can improve performance. Some researchers (Chehovits et al., 1982; Estakhri et al., 1993; Roberts et al., 1991; Stroup-Gardiner et al., 1993 to name a few) have done thorough investigations, but none have considered the full range of variables that affect the cost and performance of asphalt rubber.

Experimental Design

The experimental design is shown in Table 2-1. As can be seen, this factorial includes two types of rubber, four asphalts, two rubber mesh sizes, and four rubber concentrations. Even so, the study does not include all curing variables, but is limited to a curing time of 1.0 hour at 177 °C (350 °F), which is widely used in industry (Takallou and Takallou, 1991). The asphalt-

Table 2-1. Experimental Design Plan.

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%
Asphalt #3	Rouse	-40	5%, 10%, 15%, 20%
	Tire Gator	-10	5%, 10%, 15%, 20%
		-40	5%, 10%, 15%, 20%
Asphalt #4	Rouse	-40	5%, 10%, 15%, 20%
	Tire Gator	-10	5%, 10%, 15%, 20%
		-40	5%, 10%, 15%, 20%

rubber products were evaluated in terms of high-temperature viscosities (>121 °C [>250 °F]), intermediate-temperature rheological properties (0 °C - 90 °C, [32 °F - 194 °F]), and low-temperature creep stiffness at -15 °C (5 °F).

Materials

Four asphalts were used in this study. 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. Asphalt #3, an AC-5, was acquired from a refinery in Texas. The final asphalt studied, Asphalt #4, was produced in the laboratory by blending SHRP ABM-1 and a commercially available highly aromatic extending oil to AC-10 viscosity specifications. The highly aromatic extending oil comprised 13 percent by weight of Asphalt #4 and had a viscosity of 5.5 poise at 60 °C (140 °F). Two of these asphalts, SHRP ABL-2 and Asphalt #3 have good low-temperature properties. Asphalt #4 was produced to study the effect of adding a light aromatic fraction to an asphalt with poor low-temperature properties.

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

Experimental Methods

Mixing Apparatus

To produce the asphalt-rubber binders, asphalts and rubbers were ‘cured’ or mixed at high temperatures (> 177 °C [350 °F]). The author defines curing as the application of heat and mixing to an asphalt and crumb rubber mixture in which the rubber may be swelled, disintegrated, dissolved, and/or reduced in molecular size. The curing process, as carried out in this laboratory, involved mixing at high temperatures with a 5.1 cm (2 inch) diameter blade driven at 500 rpm by a variable speed motor. The blends were cured in either one quart or one gallon paint cans, depending on sample size, under a nitrogen blanket to prevent the binder from oxidizing.

Bending Beam Rheometer

Low-temperature properties of the asphalt-rubber binder were 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). All bending beam results were obtained at a beam testing temperature of -15 °C (5 °F). The beam specimens were produced and the bending beam rheometer was utilized as specified in AASHTO Designation TP1. Furthermore, all material tested in this paper was unaged.

Dynamic Shear Rheometer

The intermediate-temperature rheological properties were tested with a Carri-Med CSL-500 dynamic shear rheometer 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 was operated in the constant-stress oscillation mode for analysis of neat asphalt samples but the constant-strain mode was necessary for analysis of asphalt-rubber samples to assure testing in the linear viscoelastic region.

The behavior of asphalt samples is non-Newtonian at intermediate oscillatory frequencies. However, by utilizing the constant-stress mode, a limiting complex viscosity, η^*_0, can usually be obtained at low frequencies. For highly aged samples, the limiting low frequency values are obtained by utilizing temperatures greater than the reference temperature and then shifting the frequency by using 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 and maintain a low strain level.

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 percent to some maximum percent strain level. However, a rheometer cannot accurately measure linear behavior at and slightly above the 0 percent strain level, thus narrowing the range of the measurable linear viscoelastic region. In reality the measurable linear viscoelastic region exists from a strain level range of slightly above 0 percent, a minimum strain level, to a maximum percent strain level. This range was determined by specifying several different strains and observing the strain response. Linear viscoelastic behavior is encountered when a change in the strain level does not change the measured rheological properties. The strain level for measurement was chosen to be the minimum strain level at which measurable linear viscoelastic behavior occurred. This minimum strain level was found to be highly sample dependent and ranged from approximately 0.5 percent to 200 percent, 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 was necessary to determine an acceptable 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.

Brookfield Rotational Viscometer

A Brookfield rotational viscometer Model RVF 7 was used to obtain the high-temperature (>121 °C) [250 °F]) viscosities of the asphalt-rubber binders. Torque is applied to a spindle that is submerged in a binder sample. The binder sample is maintained at the desired temperature by a thermostatically controlled beaker. The relative resistance to rotation is measured for a given rotational speed. The relative resistance, the spindle size, and the rotational speed are then used to calculate the viscosity, η.

Fourier Transform Infrared Spectrometer

A Mattson 5020 Galaxy Series Fourier Transform Infrared (FTIR) Spectrometer was used to measure the infrared spectra. The Attenuated Total Reflectance (ATR) method using a Zinc Selenide prism was utilized to collect the spectrum as described by Jemison et al. (1992). The area under the peak between 1650 and 1820 wavenumbers (cm^{-1}), defined as the carbonyl area, was measured to determine if the asphalt was oxidizing during the curing process. The carbonyl area has been shown to be a good measure of oxidation (Liu et al., 1996).

Gel Permeation Chromatograph

Gel Permeation Chromatograph (GPC) analyses were performed using a Waters 712 sample processor and a Waters 600E multisolvent delivery system. Helium-sparged HPLC grade tetrahydrofuran (THF) at a flow rate of 1 mL/min was used as the carrier solvent to efficiently separate the asphalt-rubber binders. Three columns with pore sizes of 1000 Å, 100 Å, and 50 Å were connected in series. The 1000 Å and 100 Å columns are 30.5 cm (1 foot) in length and are packed with ultrastyragel particles. The 50 Å column is 61.0 cm (2 feet) in length and is packed with PLgel particles. A Waters 410 Differential Refractometer and a Viscotek H502 Viscometer were used to monitor sample elution. The column and detector temperatures were 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 THF and filtering through a poly-tetra-fluoroethylene (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, since asphalt is soluble in THF and rubber is not.

Rubber Dissolution Test

The extent to which the rubber has dissolved into the asphalt was determined with the following gravimetric 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 pre-weighed Whatman 42 slow speed filter. The filter was heated in an oven at 93 ºC (200 °F) for 1 hour, removed from the oven and placed at ambient conditions for six hours, and finally weighed. The difference between the final filter weight and the initial filter weight is the weight of the rubber that did not dissolve into the asphalt. This weight, the initial sample size weight, and percent rubber content of the initial sample were used to determine the amount of rubber that dissolved into the asphalt.

Results and Discussion

The following tables contain the data for the asphalts: SHRP ABM-1, SHRP ABL-2, Asphalt #3, and Asphalt #4, which were blended with either Tire Gator -10, Tire Gator -40, or Rouse -40 mesh particles at levels from 5 to 20 percent rubber.

Figures 2-1 and 2-2 represent low-temperature data in Table 2-2. Figures 2-3, 2-4, and 2-5 give intermediate-temperature data in Table 2-3. Figures 2-6 and 2-7 present high-temperature data in Table 2-4. Figures 2-8 through 2-13 show that the rubber dissolves into the asphalt during the curing process.

Low-Temperature

From examining the data in Table 2-2, Figure 2-1, and Figure 2-2, 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 rubber particles improved the low-temperature properties more than comparable amounts of larger rubber particles. 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 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 Asphalt #4.

Ground rubbers 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, but 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 Asphalt #4 halved the 60 °C (140 °F) viscosity, which alone would improve the -15 °C (5 °F) stiffness. Interestingly, the effect of rubber was also enhanced. Although in general less benefit is expected for a more flexible material, the percent reduction in stiffness was greater with Asphalt #4 than with ABM-1, and the m-value was also improved.

Intermediate-Temperature

From the data in Table 2-3, Figures 2-3, 2-4, and 2-5, 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 Table 2-3 are defined in terms of the Andrade equation (Andrade, 1930), $\ln(\eta) = \text{Constant} - E_v/RT$, in which E_v is a viscosity activation energy and is a measure of temperature susceptibility. The temperature susceptibilities improved, and the complex viscosities at rutting temperatures increased with increasing rubber content. The temperature susceptibility was 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 in Asphalt #4 not only reduced the complex viscosity but also improved the temperature susceptibility somewhat. However, it did not enhance the effect of rubber as it did at low temperature. On the other hand ABL-2 which has excellent low-temperature properties without rubber addition and also has the best temperature susceptibility

Table 2-2. Low-Temperature Data of Asphalt-Rubber Binders Cured for 1 Hour at 177 ^{0}C (350 ^{0}F) and 500 rpm.

Asphalt	Rubber Type and Mesh	Variable	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	1018	719	468	441	214
		m-value	0.24	0.25	0.24	0.28	0.29
Asphalt #4	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	
Asphalt #3	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			0.41

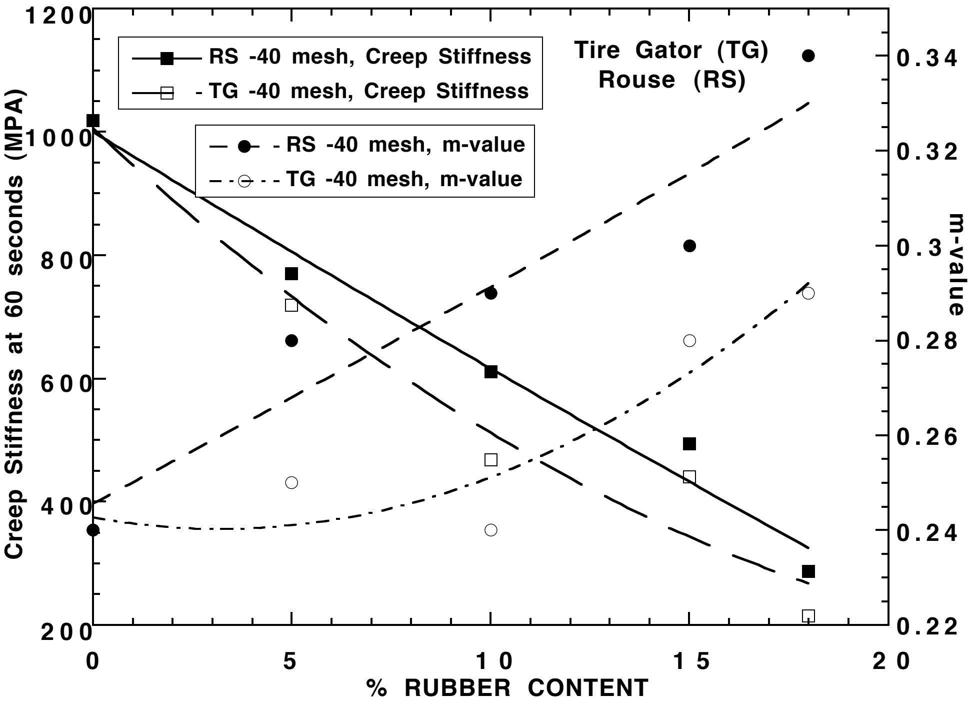

Figure 2-1. Low-Temperature Data for SHRP ABM-1 and Blends.

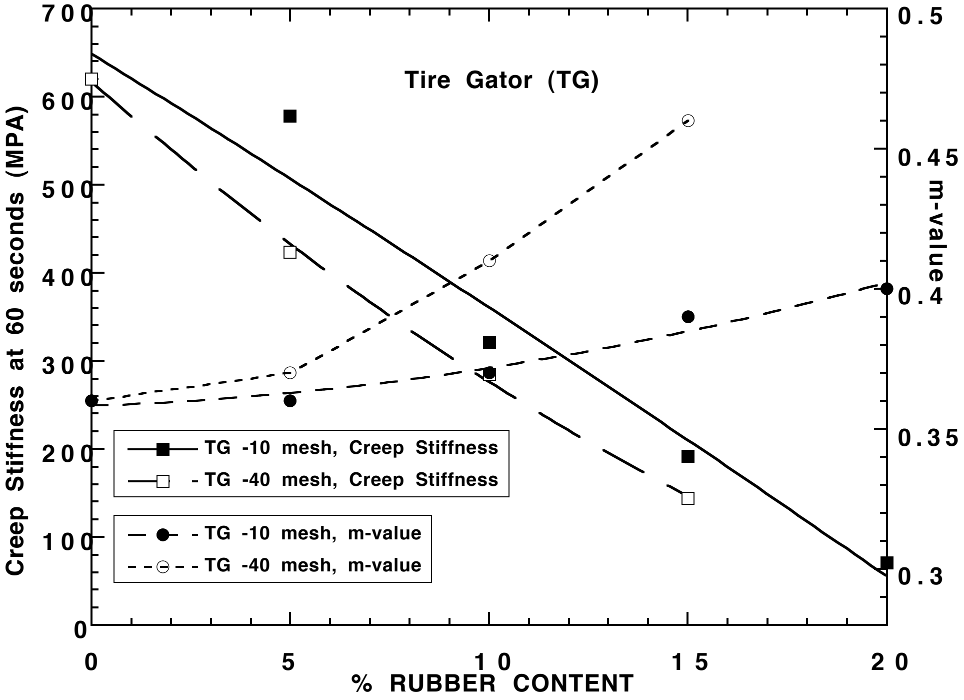

Figure 2-2. Low-Temperature Data for Asphalt #4 and Blends.

Table 2-3. Intermediate-Temperature Data of Asphalt-Rubber Binders Cured for 1 Hour at 177 ^{0}C (350 ^{0}F) and 500 rpm.

Asphalt	Rubber Type and Mesh	Variable (η* and G* in poise at 60 ^{0}C (140 ^{0}F) and δ in degrees)	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, delta	89.7	84.2	76.8
		Temperature Susceptibility	18,170	16,500	14,230
	TG -40	η* or G* at 1.0 rad/sec	2,051	7,028	15,190
		δ, delta	89.7	82.0	72.7
		Temperature Susceptibility	18,170	16,370	14,280
Asphalt #4	TG -10	η* or G* at 1.0 rad/sec	936	3,291	7,460
		δ, delta	89.9	83.4	72.2
		Temperature Susceptibility	17,770	14,230	12,430
	TG -40	η* or G* at 1.0 rad/sec	936	2,639	4,824
		δ, delta	89.9	81.3	72.0
		Temperature Susceptibility	17,770	15,250	13,740

Table 2-3. Intermediate-Temperature Data of Asphalt-Rubber Binders Cured for 1 Hour at 177 ^{0}C (350 ^{0}F) and 500 rpm. (Continued)

Asphalt	Rubber Type and Mesh	Variable (η* and G* in poise at 60 ^{0}C (140 ^{0}F) and δ in degrees)	Rubber Concentration		
			0%	10%	18% or 20%
Asphalt #3	TG -10	η* or G* at 1.0 rad/sec	448	1,801	5,011
		δ, delta	89.3	85.0	77.6
		Temperature Susceptibility	18,160	16,380	14,550
	TG -40	η* or G* at 1.0 rad/sec	448	1,542	3,811
		δ, delta	89.3	84.9	76.1
		Temperature	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, delta	87.7	81.0	68.2
		Temperature	14,650	13,210	10,610
	TG -40	η* or G* at 1.0 rad/sec	1,645	6,005	33,910
		δ, delta	87.7	79.8	60.1
		Temperature	14,650	13,340	10,660

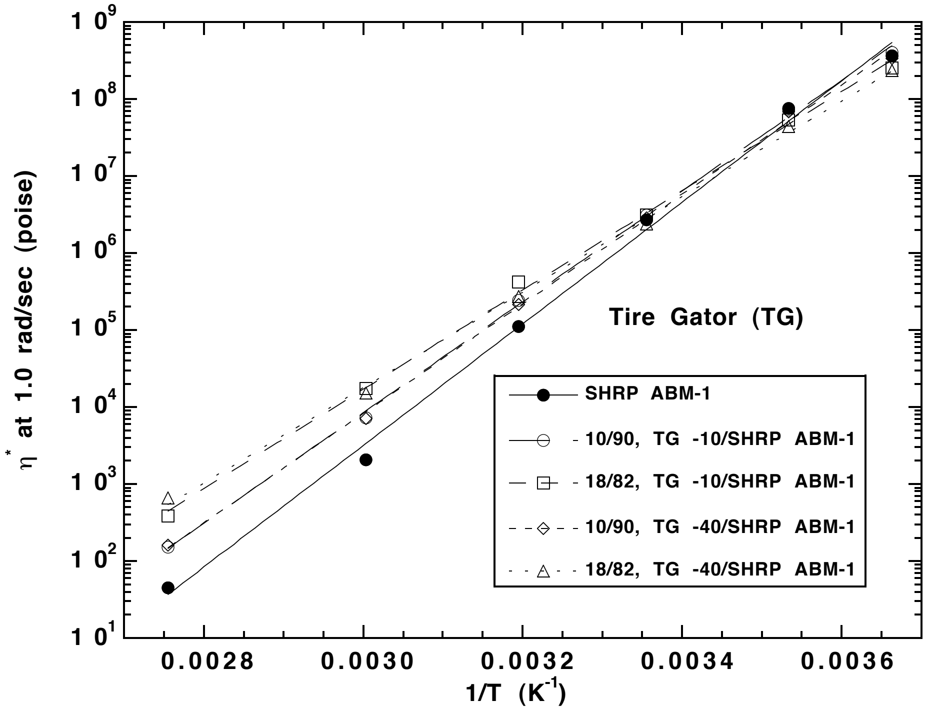

Figure 2-3. Intermediate-Temperature Data for SHRP ABM-1 and Blends.

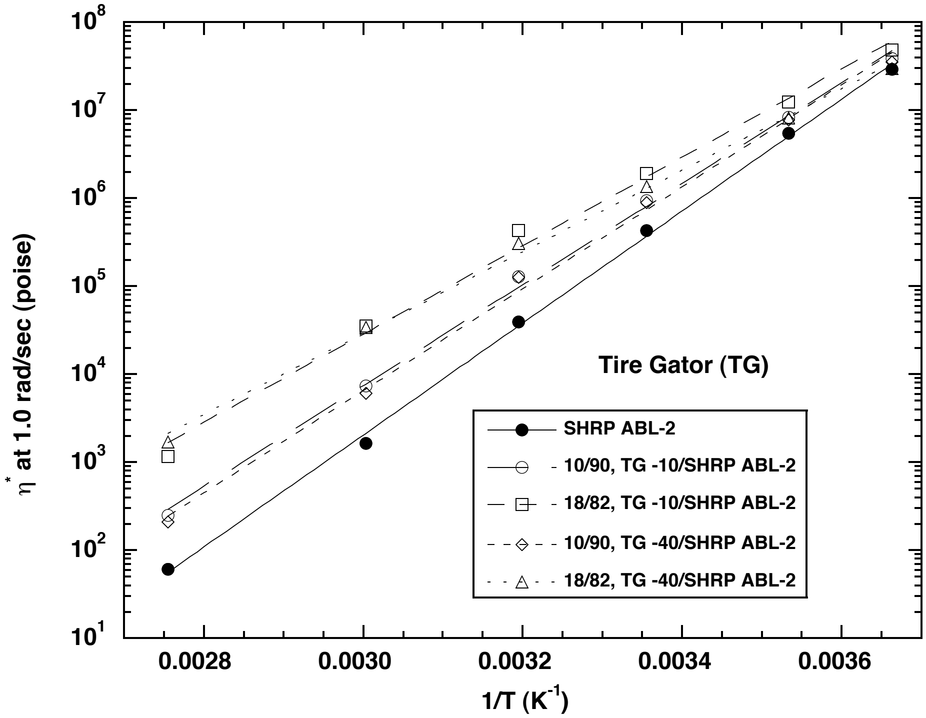

Figure 2-4. Intermediate-Temperature Data for SHRP ABL-2 and Blends.

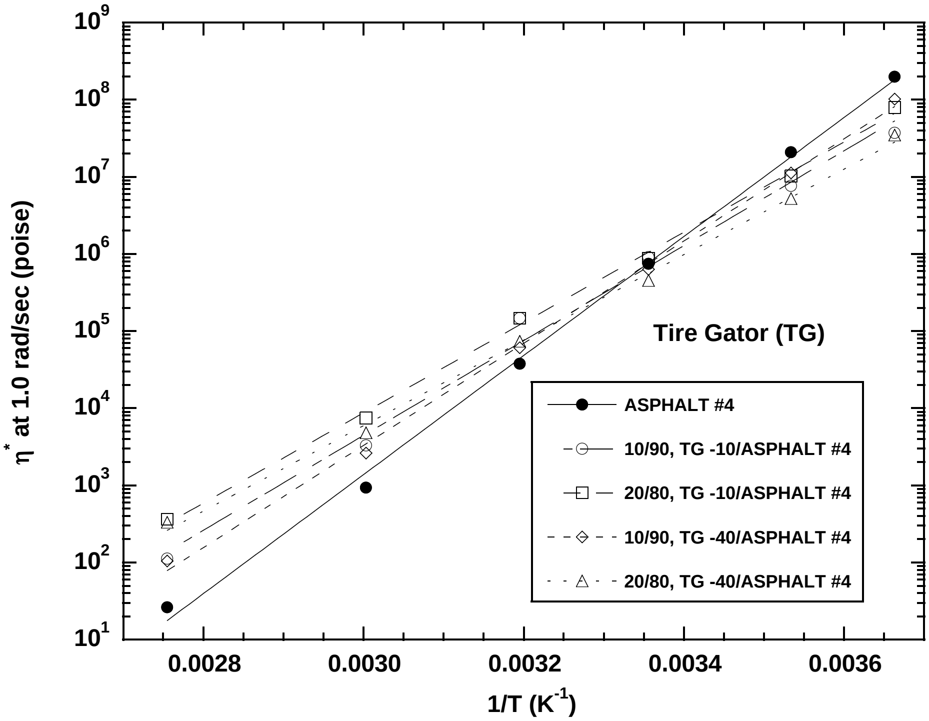

Figure 2-5. Intermediate-Temperature Data for Asphalt #4 and Blends.

without rubber shows the most improvement after its addition. However, it resulted from considerable increase in complex viscosity at higher temperatures rather than a decrease at low temperature. This would appear to be undesirable, but asphalt-rubber is highly non-Newtonian. The ABL-2 asphalt-rubber blends have the lowest phase angle at 60 °C (140 °F) of any of the other material. In spite of the lack of complex viscosity reduction at 0 °C (32 °F), the -15 °C (5 °F) bending beam results are still the best. Also the high complex viscosity at 90 °C (194 °F) is not reflected in high viscosities at hot-mix temperatures, Table 2-4.

High-Temperature

The data of Table 2-4, Figure 2-6, and Figure 2-7 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. Only Asphalt #4 shows any particle size effect at 10 percent rubber, but at 18 and 20 percent, the viscosity increase is much larger for the -40 mesh rubber. The addition of the light aromatic in Asphalt #4 is seen to be beneficial at high temperature. Because of better temperature susceptibility, Asphalt #4 has approximately the same viscosity at high temperature as ABM-1 although at 60 °C (140 °F) it is less than half as viscous as ABM-1. On the addition of 20 percent -40 mesh rubber, however, Asphalt #4 has a considerably lower viscosity than ABM-1 containing 18 percent -40 mesh rubber.

Table 2-4. High-Temperature Viscosities (in poise) of Asphalt-Rubber Binders Cured for 1 Hour at 177 ^{0}C (350 ^{0}F) and 500 rpm.

Asphalt	Rubber Type and Mesh	Rubber Concentration	Temperature, °C				
			149	160	171	182	193
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
Asphalt #4	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

Table 2-4. High-Temperature Viscosities (in poise) of Asphalt-Rubber Binders Cured for 1 Hour at 177 ^{0}C (350 ^{0}F) and 500 rpm. (Continued)

Asphalt	Rubber Type and Mesh	Rubber Concentration	Temperature, °C				
			149	160	171	182	193
Asphalt #3	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

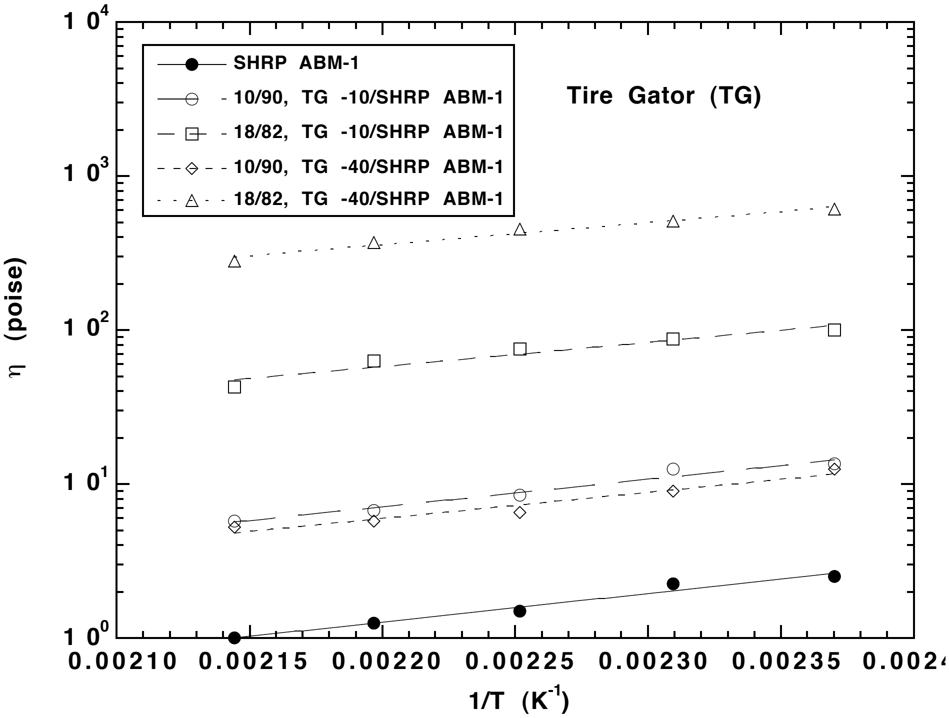

Figure 2-6. High-Temperature Data for SHRP ABM-1 and Blends.

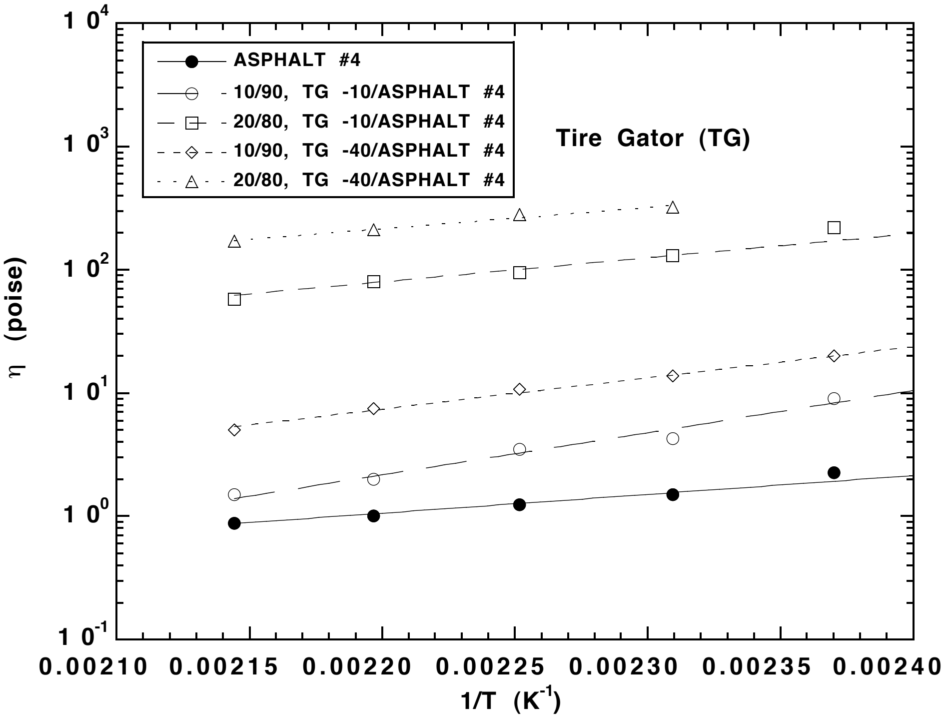

Figure 2-7. High-Temperature Data for Asphalt #4 and Blends.

General

The GPC results, Figures 2-8 through 2-11, show that significant interaction occurs between the asphalt and the rubber during the curing process. The results for Asphalt #3, Figures 2-8 and 2-9, were obtained with the refractive index detector while the results for SHRP ABM-1, Figures 2-10 and 2-11, were obtained with the intrinsic viscosity detector. The data represented in Figures 2-12 and 2-13 correspond to the data represented by the GPC chromatographs in Figures 2-8 through 2-11. Figures 2-12 and 2-13 show that the percentage of rubber dissolved during the curing process for these two asphalts is very different. The lower viscosity, higher aromatic content asphalt, Asphalt #3, dissolved more rubber during the curing process, indicating that asphalt composition is a very important curing variable. The enormous difference between the two chromatographs shows the increase in sensitivity when using the intrinsic viscosity detector for high molecular weight material such as dissolved rubber. The growth of the peak in the retention time of 20 to 23 minutes represents the influx of rubber into the asphalt phase of the binder. The molecular weight distribution in this region varies from 190,000 at a retention time of 20.63 minutes to 9,100 at a retention time of 23.38 minutes. Figures 2-8 and 2-10 show that the higher the percent rubber, the higher the mass transfer of rubber into the asphalt phase. Figures 2-9, 2-11, 2-12, and 2-13 show that the smaller the particle size, the higher the mass transfer of rubber into the asphalt phase. Obvious in Figures 2-9, 2-12, and 2-13, this conclusion is probably supported in Figure 2-11 by the higher shoulder for the smaller particles in the retention time region of 21 to 23 minutes. Figures 2-12 and 2-13 show that the fraction of the total rubber going into solution decreases with increasing rubber content. This is easily explained by the decrease in mass transfer coefficient with increasing viscosity.

The dissolved rubber molecules represented by the data in Figures 2-8, 2-9, 2-10, and 2-11 are all smaller than 0.45 µm (0.45 microns, 4500 **Å**), since each sample was prepared for GPC injection with a filter that has a pore membrane size of 0.45 µm. In fact they are generally smaller than 1000 **Å**, the pore size of the largest GPC column, as the chromatographs show little indication of exclusion. It is apparent that for the rubber particles, which are 400-2000 microns before curing, to be reduced to less than 1000 **Å** during the curing process, the rubber almost certainly is being “devulcanized and depolymerized” during the curing process. Understanding this phenomenon is essential, since 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

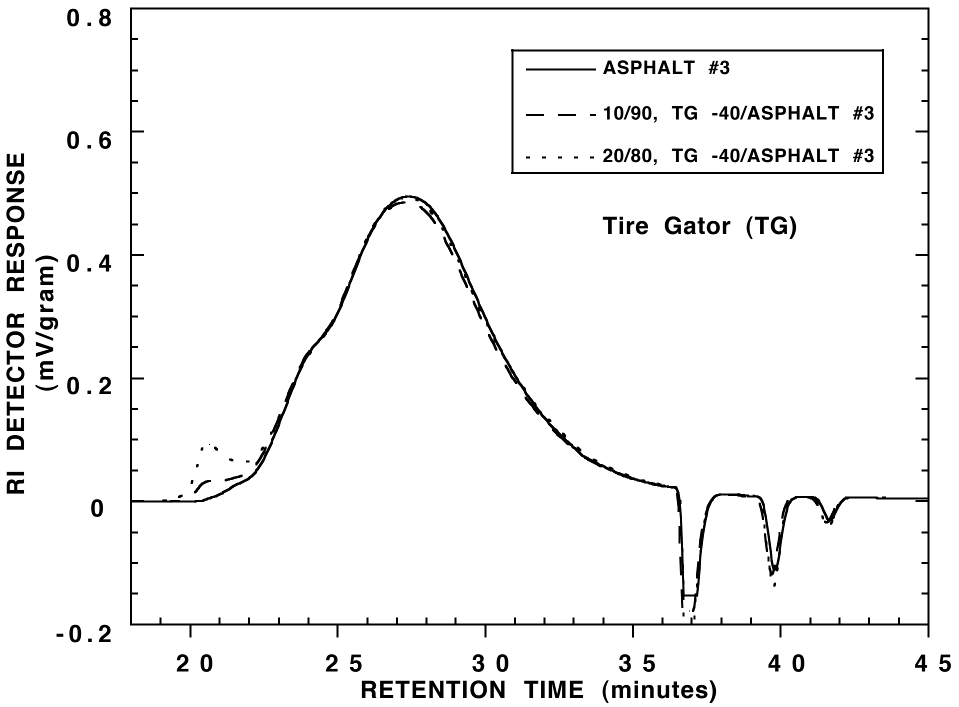

Figure 2-8. GPC Data for Asphalt #3 and Blends - Comparison of Rubber Content.

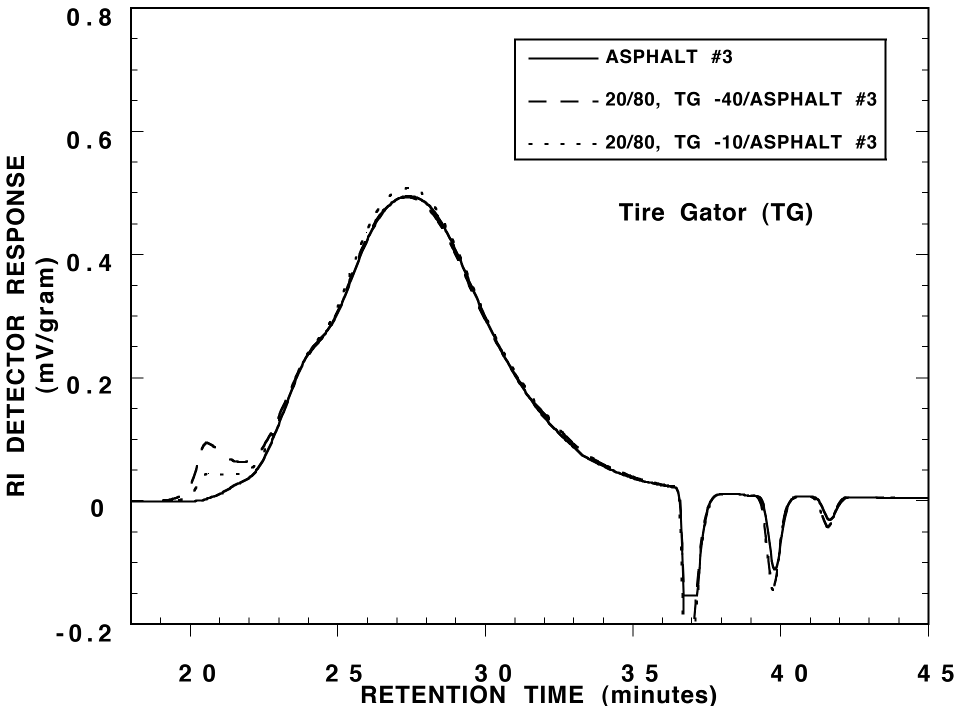

Figure 2-9. GPC Data for Asphalt #3 and Blends - Comparison of Rubber Mesh.

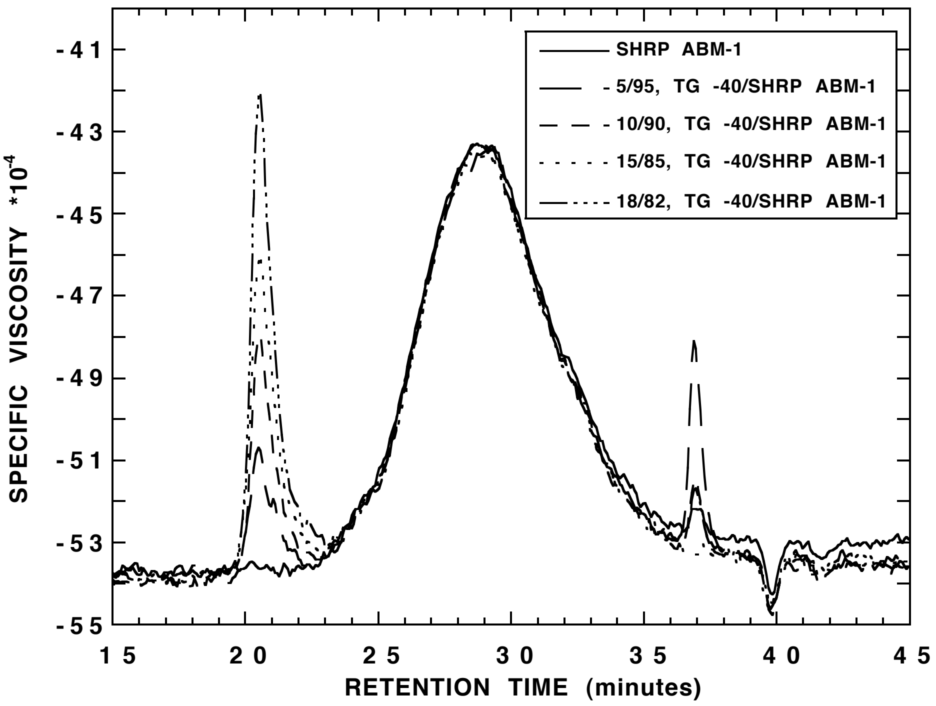

Figure 2-10. GPC Data for SHRP ABM-1 and Blends - Comparison of Rubber Content.

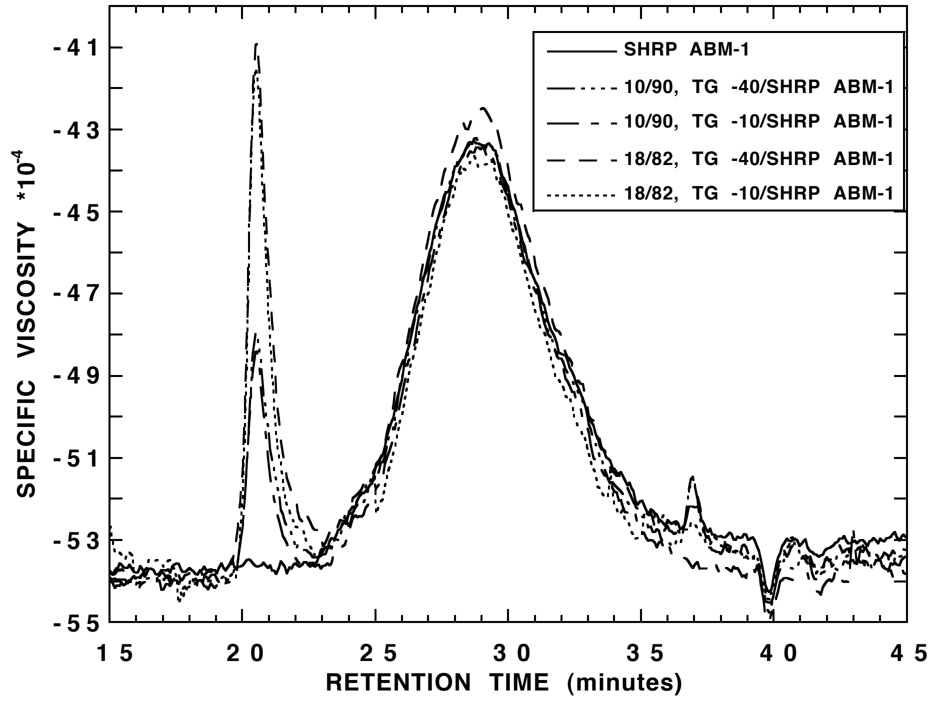

Figure 2-11. GPC Data for SHRP ABM-1 and Blends - Comparison of Rubber Mesh.

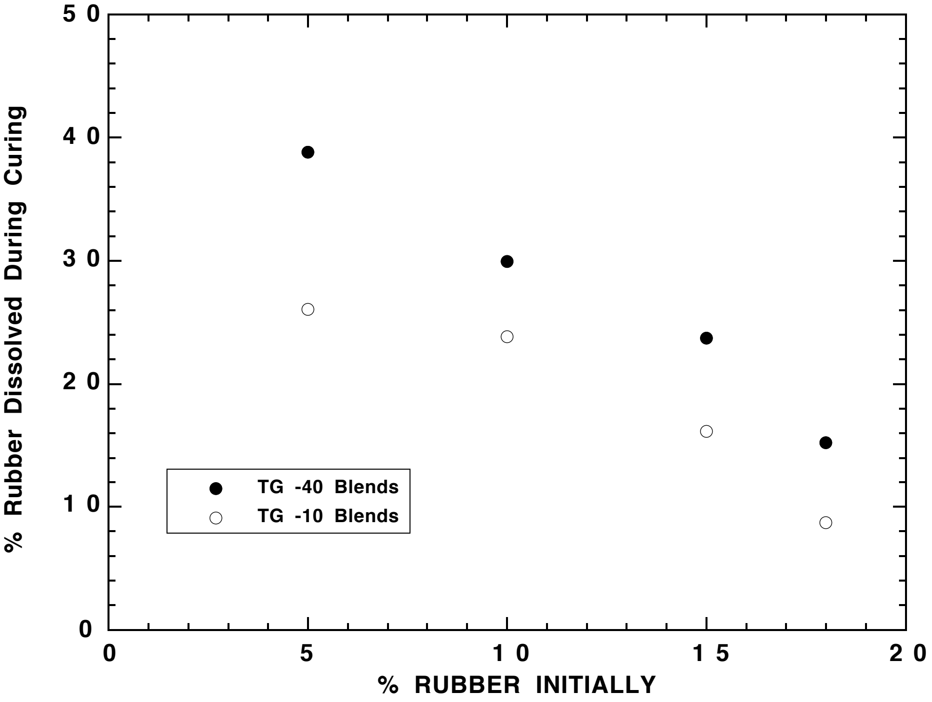

Figure 2-12. Rubber Dissolution Data for SHRP ABM-1 and Blends.

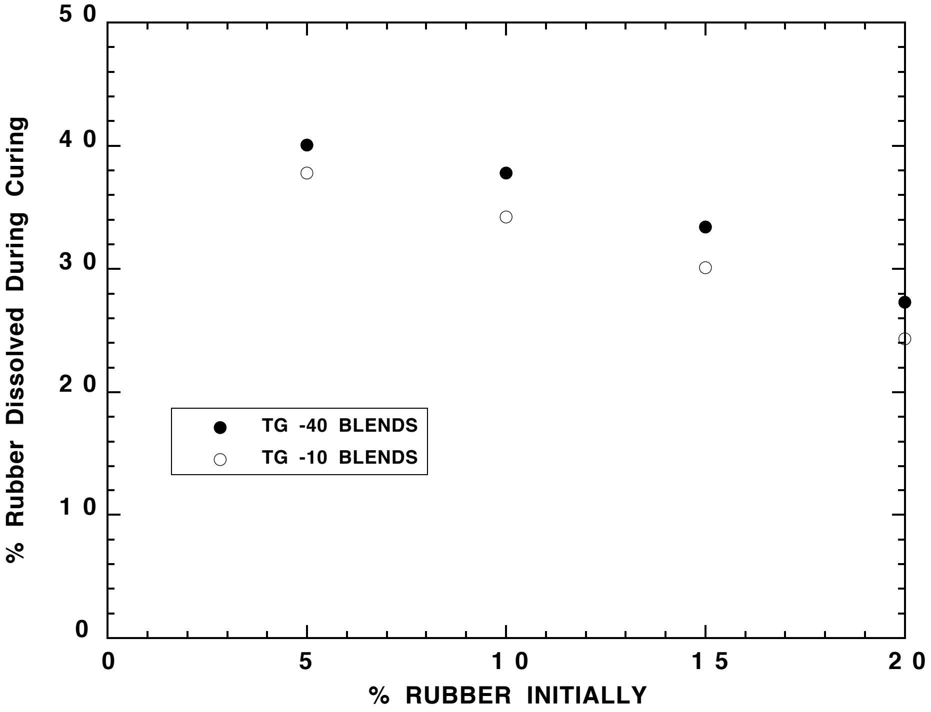

Figure 2-13. Rubber Dissolution Data for Asphalt #3 and Blends.

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 (302 °F) ... ." The process described is very similar to the curing process employed in this work except that the authors used much lower amounts of mechanical energy. Since 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.

Conclusions

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. High-temperature viscosities are greatly increased by rubber addition. The 40 mesh material has a greater effect than 10 mesh at high rubber concentrations.

All of these effects are asphalt dependent. For instance, rubber addition had the largest effect on 60 °C (140 °F) complex viscosity and phase angle δ in asphalt ABL-2. However this resulted in a very high complex viscosity at higher temperature rather than a decrease in complex viscosity at lower temperature, which occurs with ABM-1 and Asphalt #4. From this one might expect poor low-temperature properties, but the bending beam results reveal that this is not so. The low values of phase angle δ associated with ABL-2 mixtures probably are an indication that increasing elasticity will provide good low-temperature flexibility.

The addition of light aromatics to ABM-1 generally improved its properties. The wide variation in asphalt-rubber interactions underscores the importance of considering this fact in choosing an asphalt for use with ground tire rubber. The change of properties as an asphalt cures and the degree of rubber dissolution occurring is a powerful indicator that the 1 hour curing time at 177 °C (350 °F) and relatively low shear, used in this study and generally used in the field, may not be optimum.

INVESTIGATION OF THE CURING VARIABLES OF ASPHALT-RUBBER BINDER

(Pages 2-23 through 2-38 reprinted from Billiter, T. C., Chun, J. S., Davison, R. R., Glover, C. J., and Bullin, J. A., "Investigation of the Curing Variables of Asphalt-Rubber Binder," **Petroleum Sci. and Technol.**, Volume 15, Numbers 5&6, 1997, pp. 445-469, by courtesy of Marcel Dekker, Inc.)

Abstract

A curing study was undertaken to determine the effect of asphalt type, rubber content, rubber mesh size, rubber source, curing time, curing temperature, and rate of mixing on the properties of asphalt-rubber binder. Properties studied were asphalt composition, rubber dissolution, molecular weight distribution, and the low-, intermediate-, and high-temperature rheological properties. These properties were found to be dependent on the above listed variables. Most notable were the curing variables of curing time, curing temperature, and rate of mixing. Increasing the curing time, curing temperature, and rate of mixing increased the amount of rubber dissolution into the asphalt during the curing process. Increased rubber dissolution was determined to improve the low- and intermediate-temperature rheological properties of a binder. Furthermore, after the initial increase in high-temperature viscosity with the addition of rubber, the high-temperature viscosity decreased significantly with increased rubber dissolution.

Introduction

Currently, the standard industry wet process uses a curing temperature of 177 °C (350 °F) for one hour in a low-shear environment to produce asphalt-rubber binder (Takallou and Takallou, 1991). Billiter et al. (1997a) showed at these curing conditions adding rubber to asphalt was beneficial, with the rubber improving the low-temperature creep stiffness at -15 °C (5 °F), the temperature susceptibility in the 0-90 °C (32-194 °F) temperature region, increasing G^* and η^* at 60 °C (140 °F) and 1.0 rad/sec, and decreasing δ at 60 °C (140 °F) and 1.0 rad/sec. On the other hand, they also showed that the addition of rubber greatly increased the viscosity in the compaction temperature region of 149-193 °C (300-380 °F). This increased viscosity can cause compaction problems, with Allison (1967) reporting 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 lead to early road failure. High compaction viscosities can also lead to high air void content for dense-graded mixes (Jimenez, 1982). This can be detrimental, since Linden et al. (1989) reported a correlation between compaction and performance.

If Allison (1967) is correct, then dissolving the rubber would not only produce a homogeneous binder, but one that would have a non-detrimental compaction viscosity. Apparently, the dissolution of rubber into asphalt is possible since Billiter et al. (1997a), Franta (1989), and Zanzotto and Kennepohl (1996) have reported that rubber devulcanizes and depolymerizes during the application of high shear and high temperature in the presence of asphalt. Obviously, the production of a homogeneous asphalt-rubber binder will require the altering of the variables of curing time, curing temperature, and the type and amount of mechanical energy from the industry standard curing time and temperature of one hour and 177 °C (350 °F) at low-shear rates. This work investigates the altering of these variables in an attempt to produce such a homogeneous asphalt-rubber binder.

Materials

Three asphalts were used in this study. Asphalt #1, an AC-10, and Asphalt #2, an AC-5, were acquired from refineries in Texas. Asphalt #3, an AC-10, was produced in the laboratory by blending a commercially available resin and a commercially available recycling agent. The resin is a center cut from a 3-stage supercritical extraction unit. The resin comprised 78 percent by weight of Asphalt #3 and had a viscosity of 40,710 poise at 60 °C (140 °F) and 1.0 rad/sec. The highly aromatic recycling agent comprised 22 percent by weight of Asphalt #3 and had a viscosity of 5.5 poise at 60 °C (140 °F) and 1.0 rad/sec. Asphalt #3 was produced to study the effect of adding a light aromatic fraction to an asphalt.

Minus 10 and -40 mesh rubber were acquired from rubber manufacturer (RM) #1 and -10, 40, and 80 mesh rubber were acquired from RM #2. Sieve analysis showed that for a given mesh size the RM #2 rubber had a finer distribution than the RM #1 rubber.

Experimental Methods

To produce the asphalt-rubber binders, asphalts and rubbers were 'cured' or mixed at high temperatures (177, 191, and 204 °C [350, 375, and 400 °F]). Curing is the application of heat and mixing to an asphalt and crumb-rubber mixture in which the rubber may be swelled, disintegrated, dissolved, and/or reduced in molecular size. The curing process, as carried out in this laboratory, involved mixing at high temperatures with a 5.1 cm (2 in) diameter blade driven at 500 rpm or 1550 rpm by a variable speed motor. The blends were cured in one gallon paint cans under a nitrogen blanket to prevent the binder from oxidizing.

Low-temperature properties of the asphalt-rubber binder were evaluated using a bending beam rheometer. The beam specimens were produced, and the BBR was utilized as specified in AASHTO Designation TP1 (1993) with the exception that the BBR specimens were allowed to sit for 12 hours before removal from the molds. Furthermore, all material tested in this paper was unaged.

The intermediate-temperature rheological properties were tested with a Carri-Med CSL-500 dynamic shear rheometer configured in the parallel plate geometry. This instrument was operated in the constant-strain mode for analyzing asphalt-rubber samples to assure testing in the linear viscoelastic region. The strain level for measurement was chosen to be the minimum strain level at which measurable linear viscoelastic behavior occurred. Furthermore, the gap width was chosen such that the rheological properties taken at as wide or wider gap widths, were independent of the gap width. A more detailed description of the method used with the Carri-Med CSL-500 is given in Billiter et al. (1997a).

A Brookfield rotational viscometer Model RVF 7 was used to obtain the high-temperature (>121 °C [250 °F]) viscosities of the asphalt-rubber binders.

A Mattson 5020 Galaxy Series Fourier Transform Infrared Spectrometer was used to measure the infrared spectra. The Attenuated Total Reflectance method using a Zinc Selenide prism was utilized to collect the spectrum as described by Jemison et al. (1992). The area under the peak between 1650 and 1820 wavenumbers (cm^{-1}), defined as the carbonyl area, was measured to determine if the asphalt was oxidizing during the curing process.

Gel Permeation Chromatograph analyses were performed using a Waters 712 sample processor and a Waters 600E multisolvent delivery system. A Waters 410 Differential Refractometer and a Viscotek H502 Viscometer were used to monitor sample elution. The operating conditions of these units are given in Billiter et al. (1997a). Samples were prepared by dissolving 0.20 to 0.25 grams of binder, depending upon the rubber content, in 10 mL of THF and filtering through a PTFE syringe filter with a membrane pore size of 0.45 µm (0.45 micron).

The extent to which the rubber had dissolved into the asphalt was determined with the following gravimetric procedure. The analysis was performed using a preweighed 0.45 µm syringe filter. A 0.2 gram asphalt-rubber sample was dissolved in 10 mL of THF. The asphalt-rubber/THF solution was sonicated for 30 minutes. The solution was then strained through the syringe filter. The filter was heated in a vacuum oven at 100 °C (212 °F) for 3.0 hours, removed from the oven and placed at ambient conditions for 24 hours, and finally weighed. The difference between the final filter weight and the initial filter weight is the weight of the rubber that did not dissolve into the asphalt. This weight, the initial sample size weight, and percent rubber content of the initial sample were used to determine the amount of rubber that dissolved into the asphalt.

Experimental Design

Table 2-5 shows the combinations of temperature, mixer speed, weight percent rubber, rubber mesh size, rubber source, and asphalt that were used in these sets of experiments. The total curing time was 48 hours for the blends cured at 500 rpm, with samples being taken at 3.0, 6.0, 12, 24, 36, and 48 hours. For the 1550 rpm blends, the total curing time was 3.0 hours, with samples being taken at 1.0, 2.0, and 3.0 hours. Experimental Plan (EP) #1, EP #2, and EP #3 were done to study the variable of curing time. EP #3 was done to study the variable of curing temperature, and EP #2 was done to study the variable of mixing power, assuming that power is approximately proportional to the square of the blending speed. The asphalt rubber products were evaluated in terms of high-temperature viscosities (>121 °C [>250 °F]), intermediate-temperature rheological properties (0 °C - 90 °C, [32 °F - 194 °F]), low-temperature creep

Table 2-5. Experimental Plans (EP).

EP	Asphalt	Rubber Source	Mesh Size	Weight Percent	Mixer Speed	Temperature (°C)
#1	#1	RM #2	-10	10	500	191
		RM #1	-10, -40	5, 10		
	#2	RM #2	-10, -40, -80	5, 10		
		RM #1	-10, -40	10		
	#3	RM #2	-40, -80	5, 10		
		RM #1	-10	5, 10		
#2	#1	RM #2	-10	10	500, 1550	191
	#2	RM #1	-40	10		
#3	#1	RM #1	-40	10	500	177, 191, 204

stiffness at -15 °C (5 °F), rubber dissolution, molecular weight distribution, and Fourier Transform Infrared Spectrometer.

Results and Discussion

As discussed in the introduction, previous results in the literature suggest that the dissolution of rubber during the curing process should lead to better binder properties. Consequently, the primary objective of this research was to study the effect of various curing variables on the dissolution of rubber. Specifically, the curing variables of curing time, curing temperature, and rate of mixing are of greatest interest. The results for the variables of asphalt type, rubber content, rubber mesh size, and rubber source are also presented.

Each figure focuses on a particular variable. If a graph is referenced, at least one example of the comparison being made will be presented.

Experimental Plan #1

Comparison of Percent Rubber and Comparison of Mesh Size

The addition of rubber was positive for the low- and intermediate-temperature properties of a binder; the higher the rubber content, within the range studied, the better the results. For a given mesh size, the 10 percent rubber level improved the creep stiffness more than the 5 percent rubber level (Figure 2-14). Obviously, the benefits of the elastic additive were more pronounced at the higher concentration levels, thus producing a more flexible binder. Furthermore, the smaller rubber particles were slightly better at improving low-temperature properties, Figure 2-14. It is theorized that the smaller rubber particles are better able to interact because of their greater surface area per unit mass than the larger rubber particles. The 60 °C (140 °F) and 1.0 rad/sec complex viscosities were higher for the 10 percent blends and for the larger -10 mesh particles (Figure 2-15). The increase in complex viscosity for the larger -10 mesh blends at 60 °C (140 °F) is probably more of a particle effect than a surface area effect, thus explaining the larger -10 mesh rubber particles' enhanced performance. In the intermediate-temperature region, the temperature susceptibility was lower, and therefore better, for the 10 percent blends and the smaller -40 mesh rubber particles (Figure 2-16). The temperature susceptibility of this work is defined in terms of the Andrade equation (Andrade, 1930), $\ln(\eta) = \text{Constant} - E_v/RT$, in which E_v is a viscosity activation energy and is a measure of temperature susceptibility. The higher 10 percent rubber concentration and the larger -10 mesh rubber particles raised and thus, was detrimental for the high-temperature viscosity (Figure 2-17).

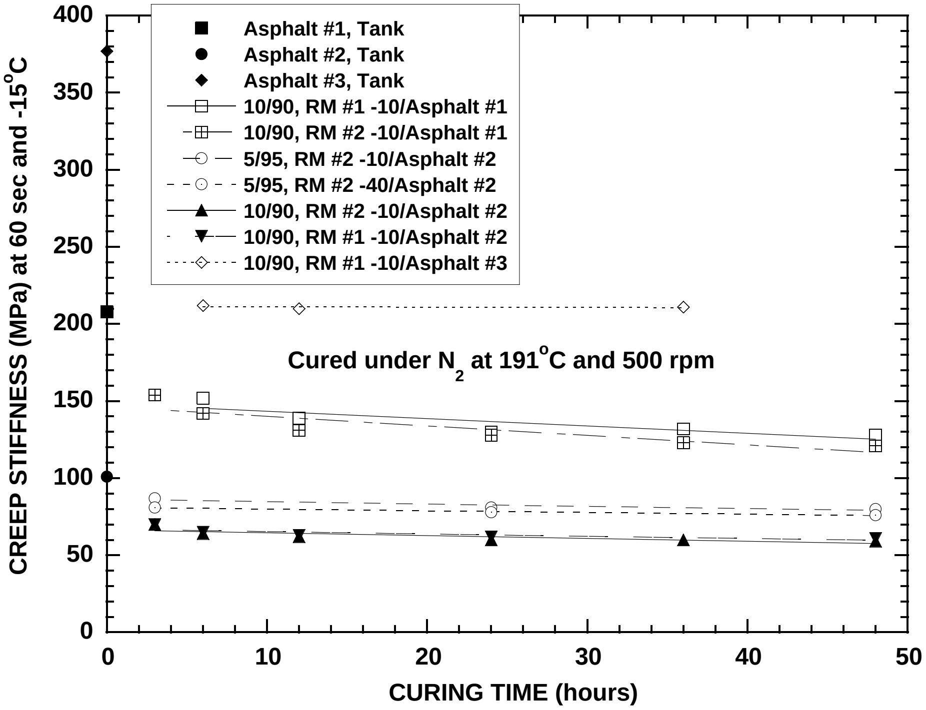

Figure 2-14. Low-Temperature Data.

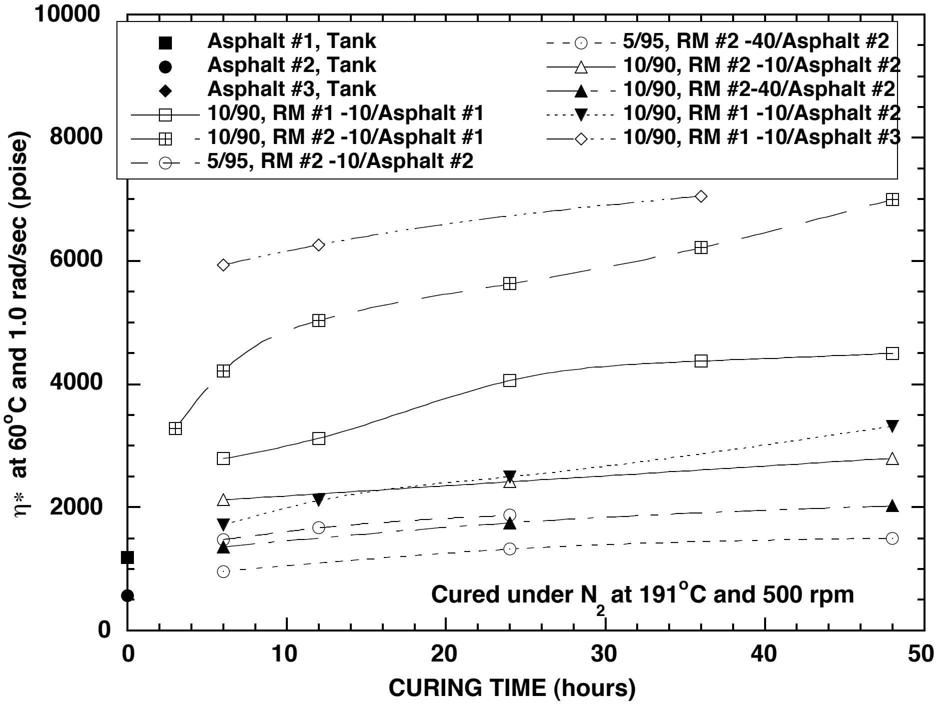

Figure 2-15. Intermediate-Temperature Data - Complex Viscosity.

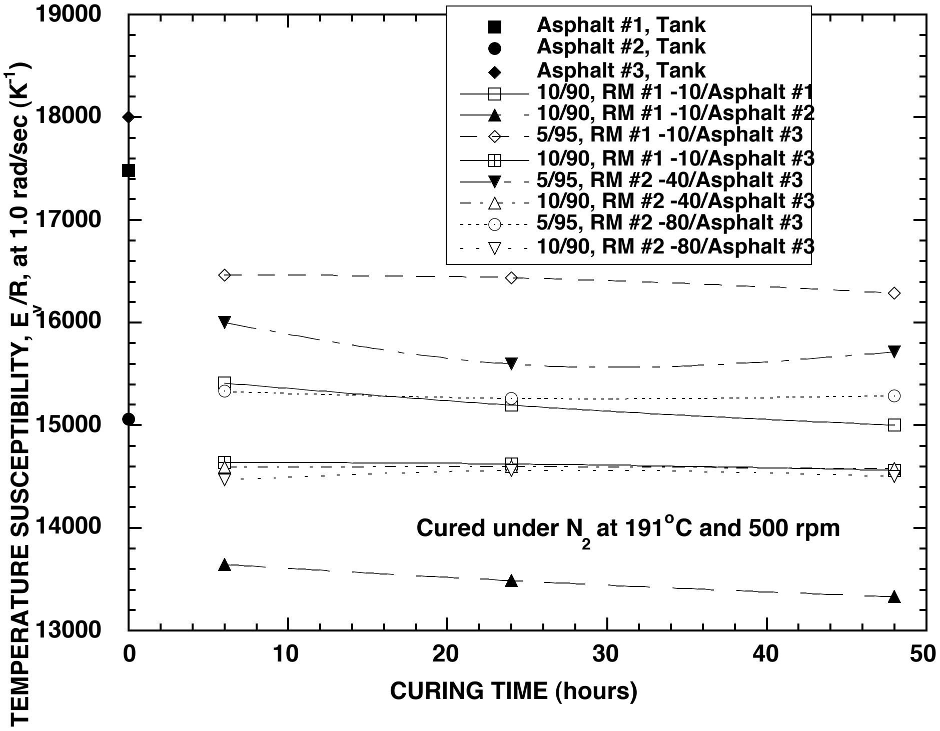

Figure 2-16. Intermediate-Temperature Data - Temperature Susceptibility.

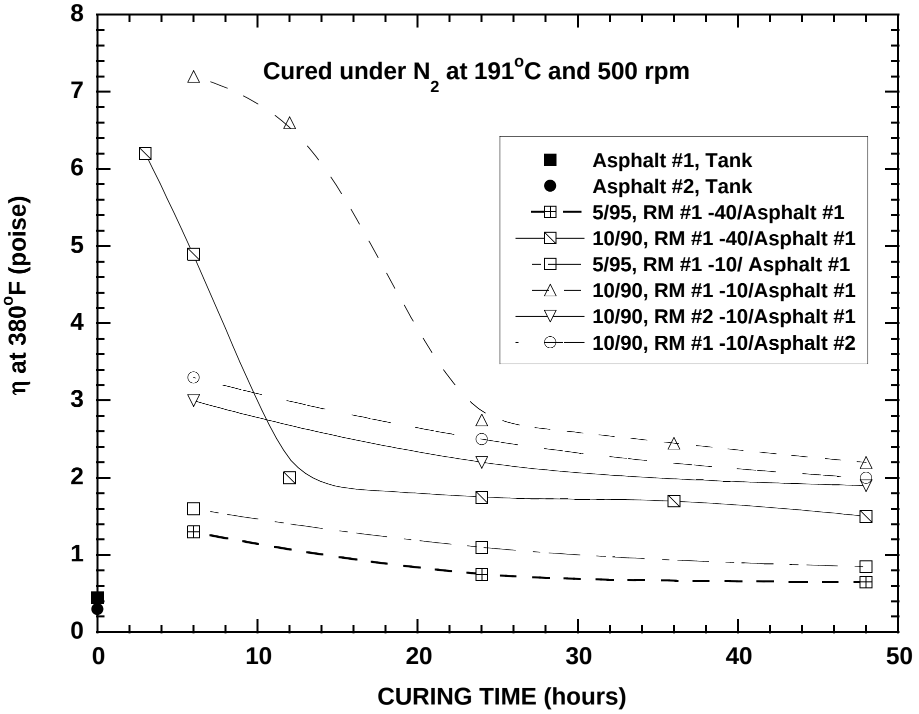

Figure 2-17. High-Temperature Data.

All binder properties were a function of curing time. Creep stiffness, though relatively unaffected, always improved slightly with curing time (Figure 2-14). The 60 °C (140 °F) complex viscosity increased with curing time (Figure 2-15). The high-temperature viscosity decreased with curing time, which is desirable (Figure 2-17). 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: $\eta = \eta_s(1+2.5\varphi)$, where η is the viscosity of the solution, η_s is the viscosity of the solvent, and φ the volume fraction of spheres (Rosen, 1993). Obviously, the higher the percent rubber the higher the effective φ and thus, the higher the viscosity. Furthermore, the significant decrease in high-temperature viscosity with curing time 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 as the particles are devulcanized and depolymerized into the asphalt phase of the solution.

The improvements with curing time in the low- and intermediate-properties, as well as the reduction of high-temperature viscosity, are most certainly explained by the rubber devulcanizing and depolymerizing during the curing process. As noted earlier, the devulcanizing and depolymerizing of rubber during the curing process has been discussed by Billiter et al. (1997a) and Zanzotto and Kennepohl (1996), with support from Franta (1989). This phenomenon is represented in Figures 2-18 and 2-19, which are GPC chromatographs of an Asphalt #1 blend, and in Figure 2-20, which shows the percent rubber passing a 0.45 µm syringe

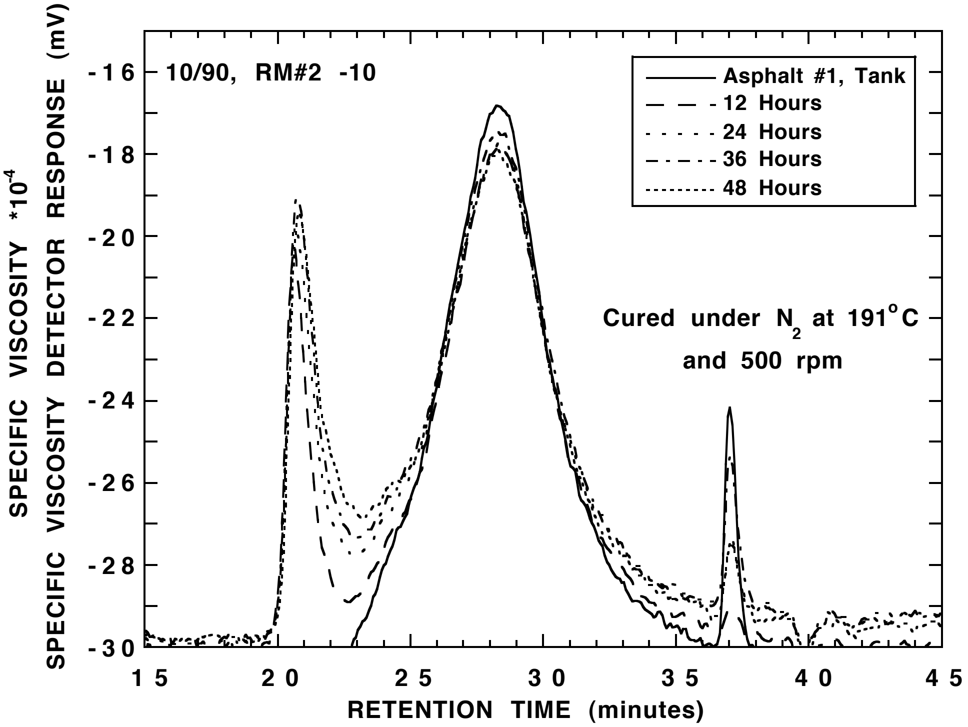

Figure 2-18. GPC Data for Asphalt #1 Blend as Measured by an Intrinsic Viscosity Detector.

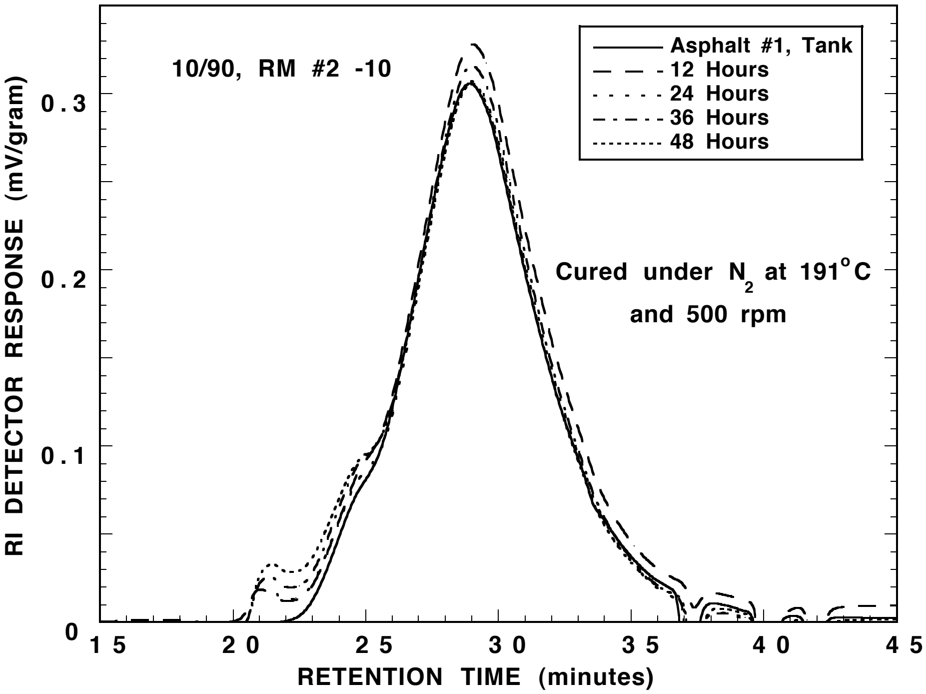

Figure 2-19. GPC Data for Asphalt #1 Blend as Measured by a Refractive Index Detector.

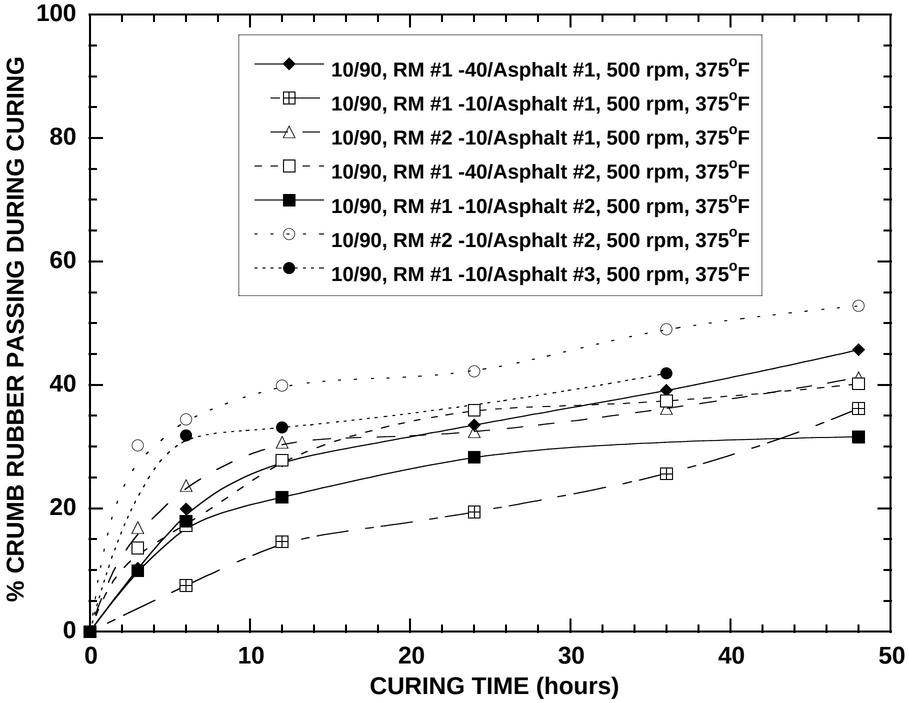

Figure 2-20. Rubber Dissolution Data.

filter versus curing time for a variety of rubber-asphalt combinations. Figure 2-20 shows that, in general, smaller particles dissolve more rapidly than larger ones, as would be expected. Figure 2-18 shows the molecular weight distribution as measured by an intrinsic viscosity detector. Figure 2-18 shows that with curing time there is mass transfer into the asphalt phase of the mixture. The growth of the peak in the 20 to 25 minute retention time region represents the flux of devulcanized and depolymerized rubber into the asphalt phase of the binder. The molecular weight distribution in this region varies from approximately 190,000 at a retention time of 20.66 minutes to 5,970 at a retention time of 24.37 minutes. The dissolved rubber molecules represented by the data in Figure 2-18 are smaller than 0.45 µm (0.45 microns, 4500 Å), since each sample was prepared for GPC injection with a filter that had a pore membrane size of 0.45 µm. In fact they are generally smaller than 1000 Å, the pore size of the largest GPC column, as the chromatographies show little indication of exclusion. The particles are most certainly being devulcanized and depolymerized since they are being reduced from a size of 400-2000 microns to smaller than 1000 Å during the curing process. Figure 2-21 shows the effect of particle size for Asphalt #2. Not only was more -40 mesh rubber dissolving than -10 mesh, but the molecular size distributions of the dissolved rubber were significantly different. Apparently after 24 hours, rubber depolymerization was occurring more rapidly than devulcanzation for the -40 mesh material as the peak height at 20 minutes was higher for the -10 mesh but lower elsewhere.

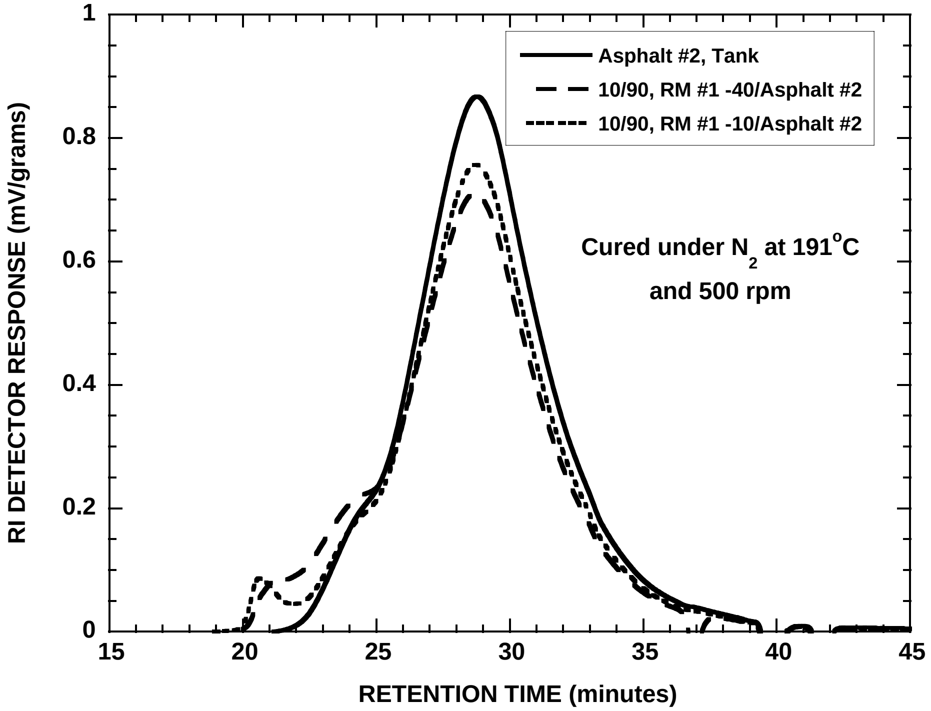

Figure 2-21. GPC Data for Asphalt #2, RM #1 Blends.

GPC analyses were performed using both an intrinsic viscosity detector and a refractive index detector. The difference in how these detectors measure molecular weight distribution can be seen by comparing Figures 2-18 and 2-19. Figures 2-18 and 2-19 represent the molecular weight distribution of a 10/90, RM #2 -10/Asphalt #1 blend at various curing times. These figures show that the refractive index detector (Figure 2-19), has better resolution than the intrinsic viscosity detector (Figure 2-18). However, these figures also show that the intrinsic viscosity detector accentuates the high-molecular weight retention time region much better than the intrinsic viscosity detector. This makes the intrinsic viscosity detector ideal for analyzing the changes that asphalt-rubber samples undergo during the curing process.

Comparison of Asphalt Type

The interaction of the rubber and the base asphalt was very much dependent upon the asphalt composition. Initially, Asphalt #3, produced by combining a highly asphaltenic, 40,000 poise asphalt with a highly aromatic, 5.5 poise recycling agent, interacted with the rubber much better than the other asphalts studied (Figure 2-20). Similarly, the initial increase in the 60 °C (140 °F) complex viscosity (Figure 2-15), and initial increase in the temperature susceptibility (Figure 2-16), were much greater for Asphalt #3. This interaction is most certainly explained by the presence of the highly aromatic recycling agent, which could have just as easily been called a rubber extending oil since such highly aromatic oils are used in the rubber processing industry because of their rubber compatibility. In fact, the miscibility with rubber of the oils used in the rubber processing industry diminishes in the order aromatic > naphthenic > paraffinic (Blackley, 1983). Apparently, the light aromatic oils are able to diffuse into and thus, interact with the rubber particles at a much faster rate than the heavier asphalts.

Comparing the rate of rubber dissolution, the slope of Figure 2-20, shows that with curing time, the aromatic oils did not enhance the rubber dissolving ability of Asphalt #3 after 10 hours of curing relative to the other asphalts since the slopes in Figure 2-20 after 10 hours were approximately the same for all of the asphalts that were studied. Similarly, the rate of increase in complex viscosity with curing time was approximately the same for all the asphalts that were studied (Figure 2-15). Furthermore, the temperature susceptibility of Asphalt #3 did not improve with curing time as fast as the other asphalts (Figure 2-16). However, this was more than offset by the larger initial improvement in the temperature susceptibility with the 10/90, RM #1 - 10/Asphalt #3 blend.

The low-temperature performance of Asphalt #3, which had a creep stiffness of 377 MPa, was much worse than either Asphalt #1, 208 MPa, or Asphalt #2, 101 MPa. Apparently, not enough of the light aromatics are present to offset the effect of the large amount of heavy polar aromatics present in Asphalt #3. However, with the addition of rubber, the low-temperature properties of Asphalt #3 improved more than the other asphalts (Figure 2-14). The light aromatics apparently help accelerate the enhancement of the cold-temperature creep stiffness by the elastic rubber particles. Once again, the other asphalts improve with curing time at a faster rate than Asphalt #3 (Figure 2-14). This, however, is more than offset by the larger initial decrease in the creep stiffness of the Asphalt #3 blends.

At the other end of the temperature scale, the high-temperature viscosity was also very dependent on both asphalt type and curing time. The high-temperature viscosity of Asphalt #1 blends was the most dependent on curing time (Figure 2-17). This phenomenon is very desirable since the binder will now be compactable. Interestingly, Asphalt #2 and Asphalt #1 dissolved about the same amount of rubber (Figure 2-20) and both had approximately same high-temperature viscosity after 48 hours of curing (Figure 2-15), but the path for arriving at the 48 hour, high-temperature viscosity value was very different (Figure 2-15).

Figure 2-22 is an interesting comparison of 10 percent RM #2 -40 in Asphalt #2 and Asphalt #3 after 24 hours of curing. It looks as if depolymerization occurred much less in Asphalt #3. Asphalt #2 is a typical AC-5 but Asphalt #3, a blend of heavy resin and a very light aromatic material, is low in asphaltenes but high in heavy polar aromatics and very light naphthene aromatics. The rapid initial rate of rubber dissolution in Asphalt #3 can be explained by rapid diffusion of the light aromatics, but it is difficult to explain the subsequent lack of depolymerization unless asphaltenes are involved in this reaction.

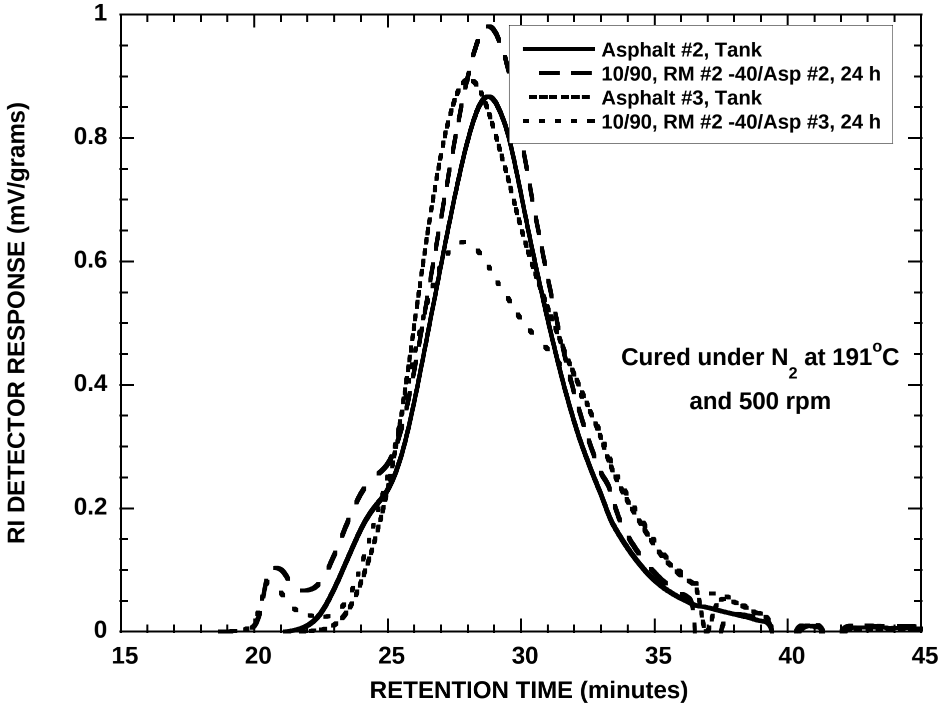

Figure 2-22. GPC Data for RM #2 -10 Blends of Asphalts #2 and #3.

Comparison of RM #1 and RM #2 Rubber

Ground rubber from two sources was used in this curing study. RM #2 rubber was better at lowering the creep stiffness (Figure 2-14) and increasing the 60 °C (140 °F) complex viscosity (Figure 2-15) of Asphalt #1. The advantage of the RM #2 rubber is most likely caused by an increased interaction between the asphalt and the rubber. Sieve analysis showed that for a given mesh size, the size gradation of RM #2 rubber was finer than RM #1 rubber and thus, with more surface area per unit mass, they were better able to dissolve the rubber (Figure 2-20). Interestingly, the RM #2 -10 mesh particles initially were actually dissolving faster than the RM #1 -40 mesh particles. At high temperatures the RM #2 rubber particles were less detrimental to the viscosity of Asphalt #1 than the RM #1 rubber particles (Figure 2-17). Initially, the RM #2 -10 mesh blend had a lower high-temperature viscosity than even the RM #1 -40 blend (Figure 2-17).

The relative performance of RM #1 and RM #2 rubber was somewhat asphalt dependent. Like Asphalt #1, Asphalt #2 was better able to dissolve and interact with the RM #2 rubber (Figure 2-20). As expected, the creep stiffness (Figure 2-14) and the temperature susceptibility were better for the RM #2 blends. On the other hand, however, the RM #2 rubber was not better for the high-temperature viscosity, and the RM #1 blends actually have a higher 60 °C (140 °F) complex viscosity than the RM #2 blends (Figure 2-15). This oddity can most likely be explained by the interaction between the asphalt composition and the rubber composition, with one of the crumb rubbers possibly containing more natural than synthetic rubber and therefore be better able to interact with an asphalt with a certain composition.

Experimental Plan #2

Utilizing a higher rate of mixing significantly increased the interaction of the rubber and the asphalt. Figure 2-23 shows that as much crumb rubber dissolved in 2.0-3.0 hours utilizing a mixing speed of 1550 rpm as dissolved in 48 hours utilizing a mixing speed of 500 rpm. Figure 2-24 shows that not only was more rubber going into solution at the higher mixing speed, but also that the molecular weight of the dissolved material was being reduced. This strongly indicates that the devulcanization and depolymerization of crumb rubber during the curing process is a mass transfer limited process, with the increased dispersion of the higher mixing speed allowing improved swelling of the rubber and therefore, increased interaction between the asphalt and rubber. As with previous results, the flux of rubber into the asphalt phase improved the low-, intermediate-, and high-temperature rheological properties of a binder. Figure 2-25 shows the much more rapid decrease in creep stiffness for the higher mixing speed of 1550 rpm. Thus, curing at a higher shear rate for a shorter period of time produced similar binder properties as curing the same binder at lower shear for a much longer period of time. In fact, corresponding roughly to the power input, it is estimated that increasing the mixing speed threefold decreases the required curing time ninefold.

Experimental Plan #3

Increasing the curing temperature significantly increased the interaction between the crumb rubber and the asphalt. Figure 2-26 shows that the higher the curing temperature the higher the amount of rubber dissolving. Some of the increased interaction can be explained by the lower asphalt viscosity at the higher temperatures causing increased mass transfer between the asphalt and rubber. However, the majority of the increased interaction is probably due to the rubber-asphalt reaction, like any chemical reaction, being very dependent upon temperature. The rubber-asphalt reaction is one of devulcanization and depolymerization in which breaking of the cross-linking network and shortening of the main chains takes place (Franta, 1989). As before, all rheological properties improved with increased rubber dissolution. Figure 2-27 shows that the higher the curing temperature, the higher the complex viscosity at a given curing time.

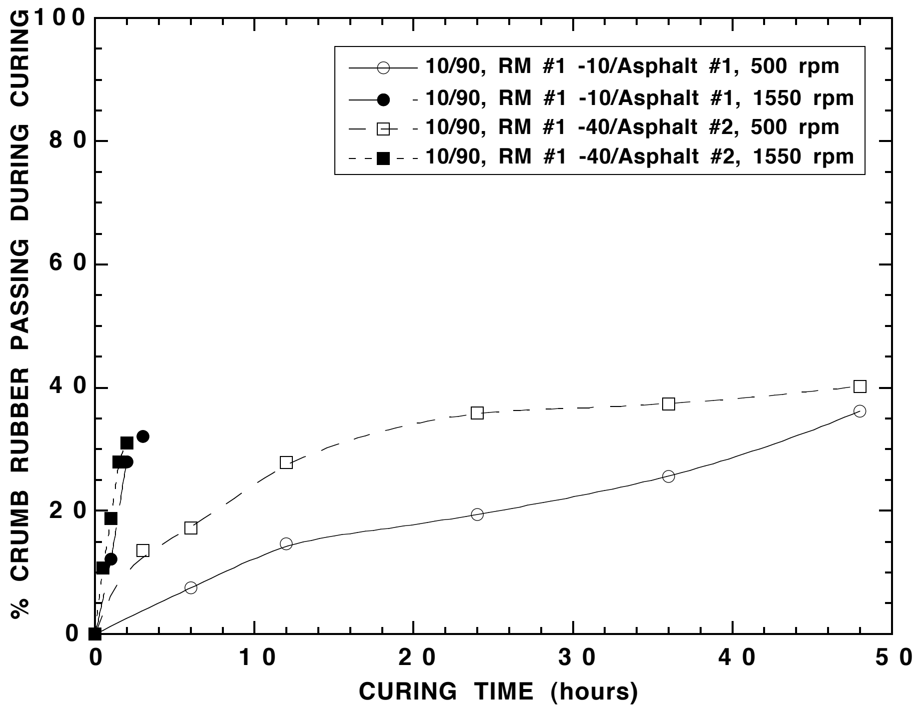

Figure 2-23. Rubber Passing Data Comparing 500- and 1550-rpm Blends.

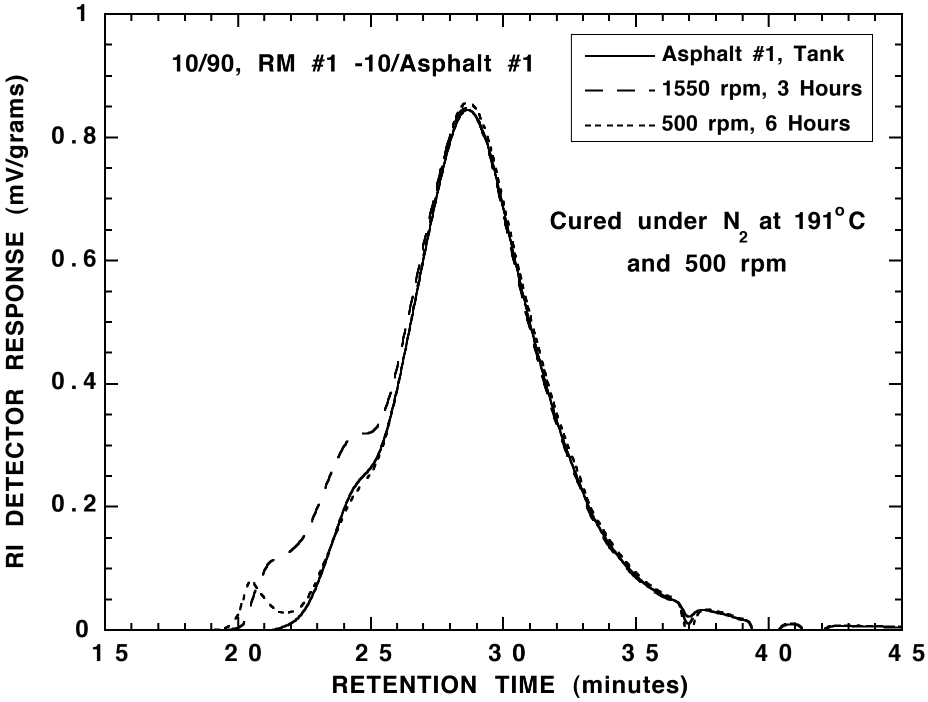

Figure 2-24. GPC Data Comparing 500- and 1550-rpm Blends.

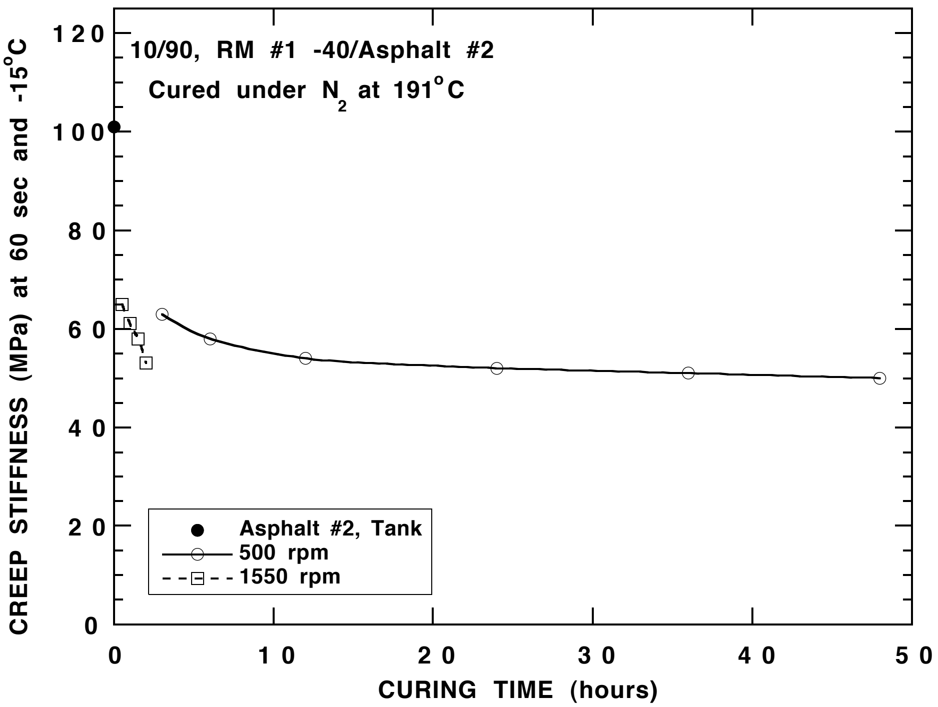

Figure 2-25. Creep Stiffness Data Comparing the Effect of Mixer Speed.

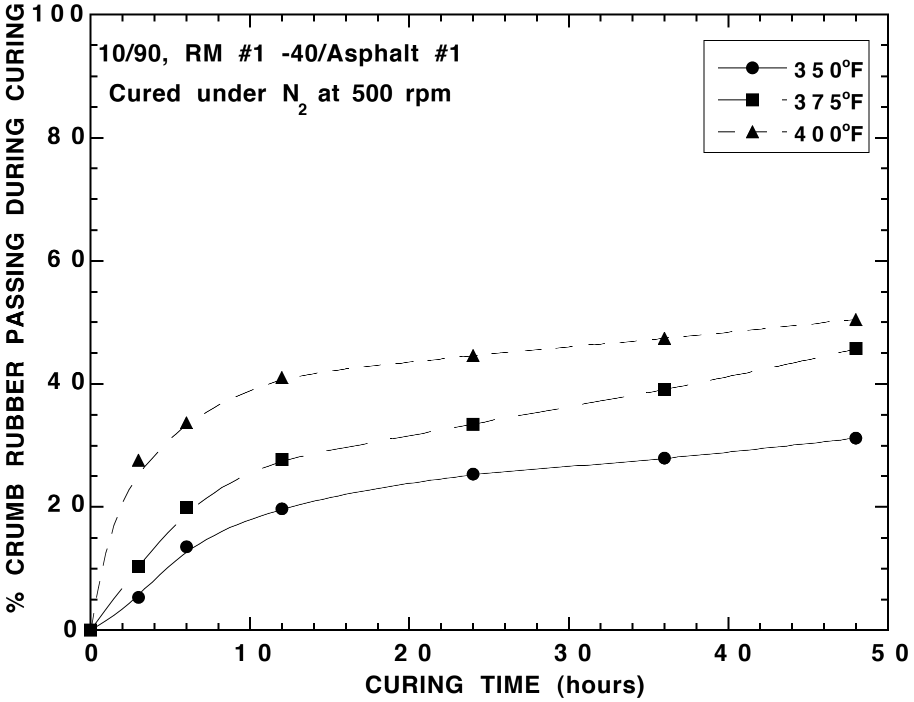

Figure 2-26. Rubber Passing Data Comparing the Effect of Curing Temperature.

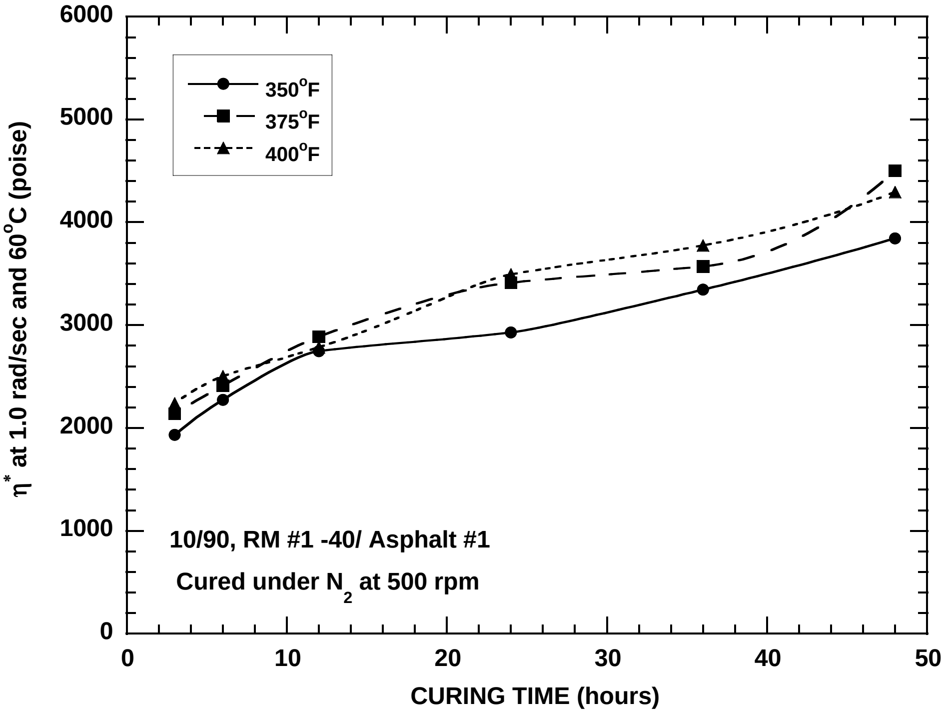

Figure 2-27. Complex Viscosity Data Comparing the Effect of Curing Temperature.

Conclusions

These results are a powerful indicator that the 1.0 hour curing time at 177 °C (350 °F) and relatively low shear, used in the field, are not optimal. On the other hand, the extended curing times utilized in this study would not be agreeable with field personnel. However, the results of this study strongly imply that increasing curing temperature and shear rate can reduce the required curing time to an acceptable level. In fact, by utilizing high temperature and high shear, along with extended curing time, the rubber particles can be devulcanized and depolymerized into the asphalt to produce an asphalt-rubber binder that is both homogeneous and truly elastic. This can be done with no trade-off in binder properties, in fact binder performance may be enhanced.

PRODUCTION OF ASPHALT-RUBBER BINDERS BY HIGH-CURE CONDITIONS

(Pages 2-39 through 2-53 reprinted with permission from T. C. Billiter, R. R. Davison, C. J. Glover, and J. A. Bullin. Production of Asphalt-Rubber Binders by High-Cure Conditions. In *Transportation Research Record 1586*. Transportation Research Board, National Research Council, Washington, D.C., 1997, pp. 50-56)

Abstract

A curing study was undertaken to determine the effect of asphalt composition, rubber content, rubber mesh size, curing time, curing temperature, and the rate of mixing on asphalt-rubber properties. Curing temperatures of 232 or 260 °C (450 or 500 °F) and a high-shear laboratory mixer were used to produce the asphalt-rubber blends. The properties studied were rubber dissolution, rubber settling, molecular weight distribution, and low-, intermediate-, and high-temperature rheological properties. Increasing the curing temperature from 232 to 260 °C (450 to 500 °F) drastically increased the rate of devulcanization and depolymerization of the rubber, while increasing the rate of mixing from 4000 rpm to 8000 rpm drastically decreased the settling rate of rubber in a binder. Lower molecular weight asphalts were better at devulcanizing the rubber, while higher molecular weight asphalts were better at depolymerizing the rubber. These high-cure binders are homogeneous in appearance, slow to phase separate on standing, and have acceptable compaction viscosities at hot-mix temperatures, higher $G^*/\sin\delta$ at rutting temperatures and lower stiffness (S) at cold temperatures than the base asphalt.

Introduction

Currently, the standard industry wet process to produce asphalt-rubber binder uses a curing time of about one hour at about 177 °C (350 °F) in a low-shear rate environment (Takallou and Takallou, 1991). Billiter et al. (1997a) showed that at these curing conditions, adding rubber to asphalt improved the low-temperature creep stiffness, the temperature susceptibility in the 0-90 °C (32-194 °F) temperature region, increased G^* and η^*, and decreased δ at 60 °C (140 °F) and 1.0 rad/sec. On the other hand, they also showed that the addition of rubber greatly increased the viscosity in the compaction temperature region of 149-194 °C (300-380 °F), which can cause compaction problems (Allison, 1967).

Later, Billiter et al. (1997b) showed that by extending the curing time and increasing the curing temperature and intensity of mixing, the high-temperature viscosity could be significantly reduced from the value obtained by curing at 177 °C (350 °F) and a low-shear rate for 1 hour. They also found that the low temperature rheological properties of a binder could also be improved by using longer curing times, higher temperatures, and higher mixing rates. This was explained by the (partial) devulcanization and depolymerization of the rubber during the curing process. Other authors, Franta (1989) and Zanzotto and Kennepohl (1996), have similarly discussed the devulcanization and depolymerization of rubber in the presence of asphalt and application of temperature and shear.

While the depolymerization and devulcanization 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 pavements. However, the extended curing times used by Billiter et al. (1997b), up to 60 hours, will not be acceptable to the paving industry. Obviously, the determination of the optimal curing environment 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 Table 2-6, were used in this study. Asphalts #2, #4, and #5 were produced in the laboratory, Asphalt #2 by blending Asphalt #1 with an AC-10 from the same refinery as Asphalt #1 in equal proportions, and Asphalt #4 by combining Asphalt #3 and a commercially available recycling agent in a 94/6 ratio. Asphalt #5 was produced in the laboratory by supercritically fractionating an AC-20. The asphalts produced in this study were compared to Asphalt-Rubber #1, a homogeneous, commercially available asphalt-rubber binder which uses rubber at the 10 percent level and reportedly uses Asphalt #3 as its base asphalt.

The compositions of these asphalts are listed in Table 2-7. The compositions of Asphalt #1, Asphalt #3, and Asphalt #5 were obtained by Corbett analysis. The composition of Asphalt #2 was obtained by performing a Corbett analysis on its constituent asphalts and then calculating the composition by a mass balance and assuming that the compositions are additive. The composition of Asphalt #4 was obtained by a mass balance using the Corbett analysis of Asphalt #3 and the advertised composition of the recycling agent.

Minus 10 and -40 mesh rubber were acquired from Granular Products, also known as Tire Gator (TG), located in Mexia, Texas. The TG -40 mesh rubber was made from tire buffings and is given the label of TG -40B throughout this work. The TG -10 mesh rubber was made from whole tires and is given the label of TG -10WT throughout this work.

Experimental Methods

To produce the asphalt-rubber binders, asphalts and rubbers were 'cured' or mixed at high temperatures, 232-260 °C (450-500 °F). During the curing process, the asphalt-rubber blend was mixed in a one gallon paint can under a nitrogen blanket by a Silverson L4RT high-shear mixer. The Silverson mixer can turn its 5.7 cm (2.25 inch) slotted disintegrating head at up to 10,000 rpm.

A supercritical fractionation unit was used to produce Asphalt #5 of this study. A detailed description of the operation of this unit can be found in Jemison et al. (1995).

Table 2-6. Specification of Asphalts Studied.

Asphalt Name	Source Refinery	Laboratory Modifications	Resultant η* (dPa·s (poise)) at 60°C & 1.0 rad/sec
Asphalt #1	A	None	238.6
Asphalt #2	A	Blended 50/50 with an AC-10 from Refinery A	507.9
Asphalt #3	B	None	952.0
Asphalt #4	B	Blended 94/6 with a commercially available recycling agent: [η*= 5.5 dPa·s (poise)]	561.0
Asphalt #5	C	Supercritical fractionation of an AC-20	369.0

Table 2-7. Compositions of the Asphalts Studied.

Asphalt	% Asphaltenes	% Polar Aromatics	% Naphthene Aromatics	% Saturates
Asphalt #1	3.00	38.18	49.65	9.19
Asphalt #2	8.73	34.15	46.50	10.64
Asphalt #3	12.68	26.60	48.41	12.31
Asphalt #4	11.93	25.81	49.76	12.50
Asphalt #5	2.97	35.74	52.58	8.70

The ASTM D4124 method (1994), sometimes referred to as the Corbett procedure, was used to obtain asphalt compositions.

Low-temperature properties of the asphalt-rubber binder were evaluated using a bending beam rheometer (BBR) as specified in AASHTO Designation TP1 (1993) with the exception that the BBR specimens were allowed to sit for 12 hours before removal from the molds. Furthermore, all material tested for this paper was unaged.

The intermediate-temperature rheological properties were tested with a Carri-Med CSL-500 dynamic shear rheometer configured for oscillatory operation in the parallel plate geometry. Controlled-strain testing was used to assure linear viscoelastic behavior. An acceptable value of the maximum shear strain (strain amplitude) was determined for each test temperature, based upon tests on a variety of asphalt-rubber materials. The strain amplitude must be small enough to produce linear viscoelastic behavior but large enough to produce stresses (torques) high enough to be reliably measured. This resulted in 50 percent shear strain at 60 °C (40 °F) and 0.5 percent at 0 °C (32 °F). Furthermore, the gap width was chosen such that the rheological properties taken at wider gap widths, were independent of the gap width. A more detailed description of the method used with the Carri-Med CSL-500 is given in Billiter et al. (1997a).

A Brookfield rotational viscometer Model RVF 7 was used to obtain the high-temperature (>121 °C [250 °F]) viscosities of the asphalt-rubber binders.

A Mattson 5020 Galaxy Series Fourier Transform Infrared (FTIR) Spectrometer was employed to determine if the asphalt was oxidizing during the curing process. The Attenuated Total Reflectance (ATR) method described by Jemison et al. (1992) was used.

Gel Permeation Chromatograph (GPC) analyses were performed using a Waters 712 sample processor and a Waters 600E multisolvent delivery system. A Waters 410 Differential Refractometer and a Viscotek H502 Viscometer were used to monitor sample elution. Columns with pore sizes of 1000 Å, 500 Å, and 50 Å were connected in series. The operating conditions of these units are given in Billiter et al. (1997a). Samples were prepared by dissolving 0.20 to 0.25 grams of binder, depending upon the rubber content, in 10 mL of THF and filtering through a PTFE syringe filter with a membrane pore size of 0.45 µm (0.45 micron).

The extent to which the rubber had dissolved or colloidally dispersed into the asphalt was determined using a gravimetric procedure. This procedure involved dissolving an asphalt-rubber sample in THF and then filtering it through a Whatman 42 slow-speed paper filter. A detailed description of this procedure is given in Billiter et al. (1997a).

The settling of rubber in asphalt-rubber was determined with a settling tester, a 15.24 cm (6 inch) section of 2.86 cm (1.125 inch) diameter pipe, capped at one end. Sealable sampling holes are located 0.64 cm (0.25 inch), 6.99 cm (2.75 inch), and 13.34 cm (5.25 inch) from the bottom of the capped pipe. The asphalt-rubber, which had been in an oven at 102 °C (215 °F) for 1.0 hour, was thoroughly mixed and then poured into the apparatus. The settling tester was immediately placed in an upright position in an oven at 102 °C (215 °F). After 24 hours, samples of approximately 5.0 grams were taken from each sampling hole, topmost first, then increasingly closer to the capped end. The extent of settling was determined by the 60 °C (140 °F) complex viscosity gradient.

Experimental Design

Table 2-8 shows the combinations of curing variables that were used to produce the 14 blends that were investigated in this study. 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 (>121 °C [>250 °F]), high-temperature settling (102 °C [215 °F]), intermediate-temperature rheological properties (0-90 °C [32-194 °F]), low-temperature creep stiffness (-24 °C [-11 °F]), rubber dissolution, molecular weight distribution, and FTIR.

Table 2-8. Experimental Design.

Blend	Asphalt	Weight Percent Rubber	Mesh Size	Silverson Mixer Speed (rpm)	Curing Temperature
Blend #1	Asphalt #1	10	-10WT	4000	232°C (450°F)
Blend #2		10	-10WT	4000	260°C (500°F)
Blend #3		10	-10WT	8000	260°C (500°F)
Blend #4		10	-40B	4000	260°C (500°F)
Blend #5		20	-10WT	4000	260°C (500°F)
Blend #6	Asphalt #2	10	-10WT	4000	260°C (500°F)
Blend #7	Asphalt #3	10	-10WT	4000	232°C (450°F)
Blend #8		10	-10WT	4000	260°C (500°F)
Blend #9		10	-10WT	8000	260°C (500°F)
Blend #10		10	-40B	4000	260°C (500°F)
Blend #11		20	-10WT	4000	260°C (500°F)
Blend #12	Asphalt #4	10	-10WT	4000	260°C (500°F)
Blend #13	Asphalt #5	10	-10WT	4000	232°C (450°F)
Blend #14		10	-10WT	4000	260°C (500°F)

Results and Discussion

As discussed in the introduction, previous results in the literature suggest the dissolution of rubber is desirable for binder properties. Consequently, the primary objective of this research was to study the variables of curing time, curing temperature, and mixer speed in hopes of assessing optimal curing conditions. The variables of asphalt composition, mesh size, and rubber content are also presented.

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. The rate of rubber dissolution into the asphalt was much faster at 260 °C (500 °F) than at 232 °C (450 °F) (Figure 2-28). This assumes that the amount of rubber dissolution is proportional to the amount of rubber passing a Whatman 42 paper filter. This is not perfectly true since rubber contains about 30 percent carbon black and thus, the high percentages passing the filter must include some of the carbon black. Higher temperatures, of course, resulted in more rapid mass transfer and chemical reaction rates. 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 the type of asphalt-rubber reaction can be seen by comparing Figures 2-29 and 2-30, which are GPC chromatograms as measured by an intrinsic viscosity detector. The rubber species represented by the data in Figures 2-29, 2-30, and 2-31 are smaller than the 0.45 µm (0.45 microns, 4500Å) filter pore size used before GPC injection and even smaller than 1000Å as the chromatographs showed no exclusion.

The blends represented in Figures 2-29 and 2-30 were produced using the same curing conditions except that the blend in Figure 2-29 was cured at 232 °C (450 °F), and the blend in Figure 2-30 was cured at 260 °C (500 °F). At 232 °C (450 °F) the rubber appears to be mostly devulcanizing, defined as the cleavage of the sulfur crosslink bonds, during the curing process. Some additional depolymerization, defined as the breaking of backbone of the main chain, also appears to 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 of 20 to 21.5 minutes. The molecular weight distribution in this region 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 2-30) which corresponds to a molecular weight distribution 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 260 °C (500 °F) the devulcanization reaction, and especially the depolymerization reaction, is occurring at a much faster rate (Figure 2-30). In Figure 2-30, the large peak between 20 to 21.5 minutes is the highest at 0.5 hours. This peak decreases with curing time as the devulcanized rubber is depolymerized

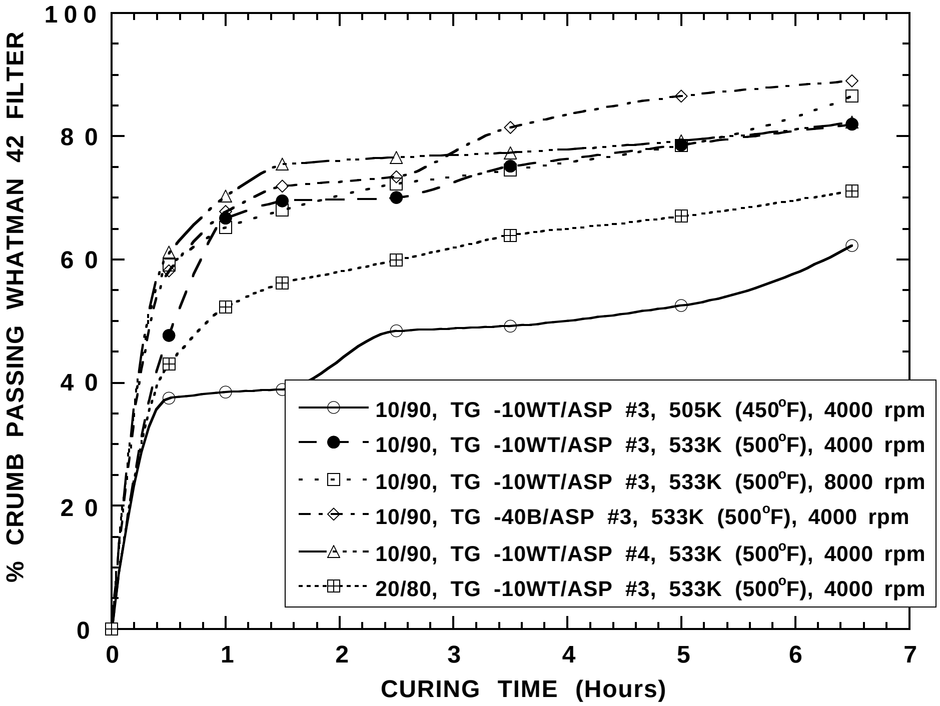

Figure 2-28. Rubber Percent Passing Data for Asphalt #3 Blends.

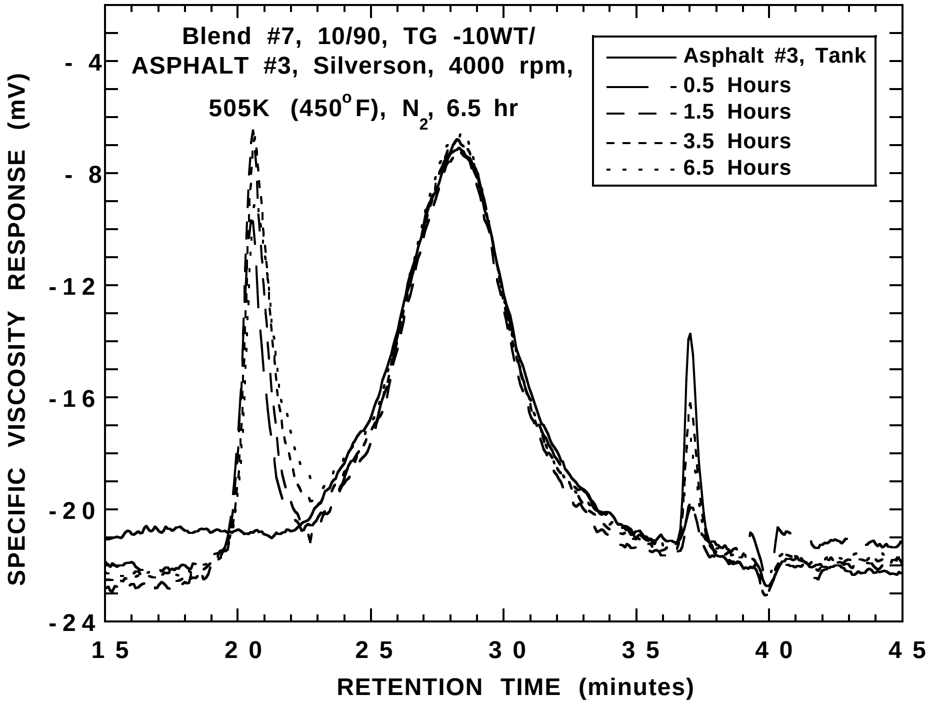

Figure 2-29. GPC Data for 10/90, TG-10WT/Asphalt #3, Cured at 232°C, 4000 rpm.

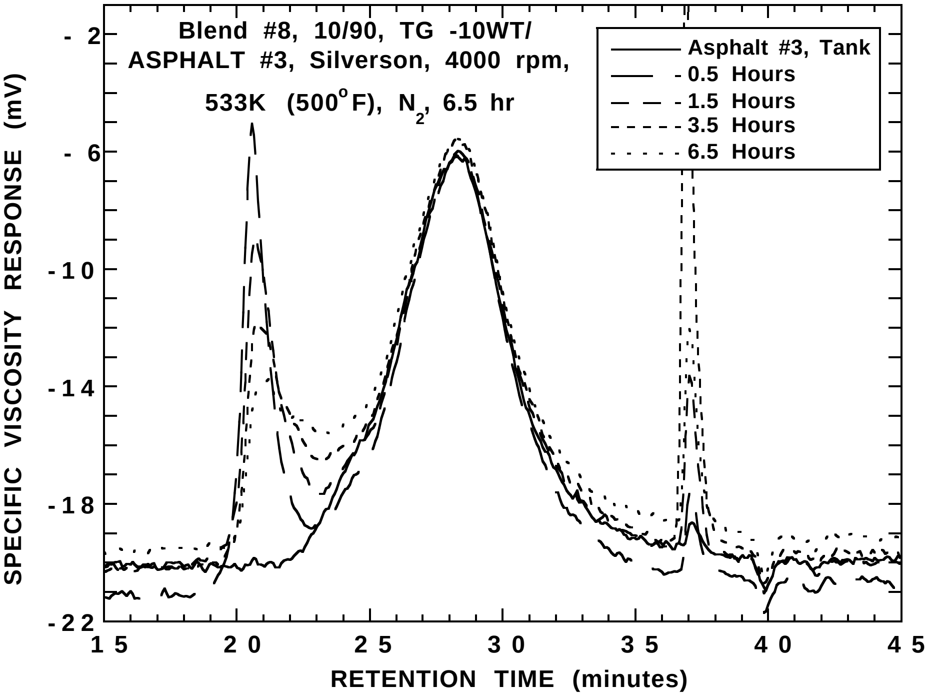

Figure 2-30. GPC Data for 10/90, TG-10WT/Asphalt #3, Cured at 260°C, 4000 rpm.

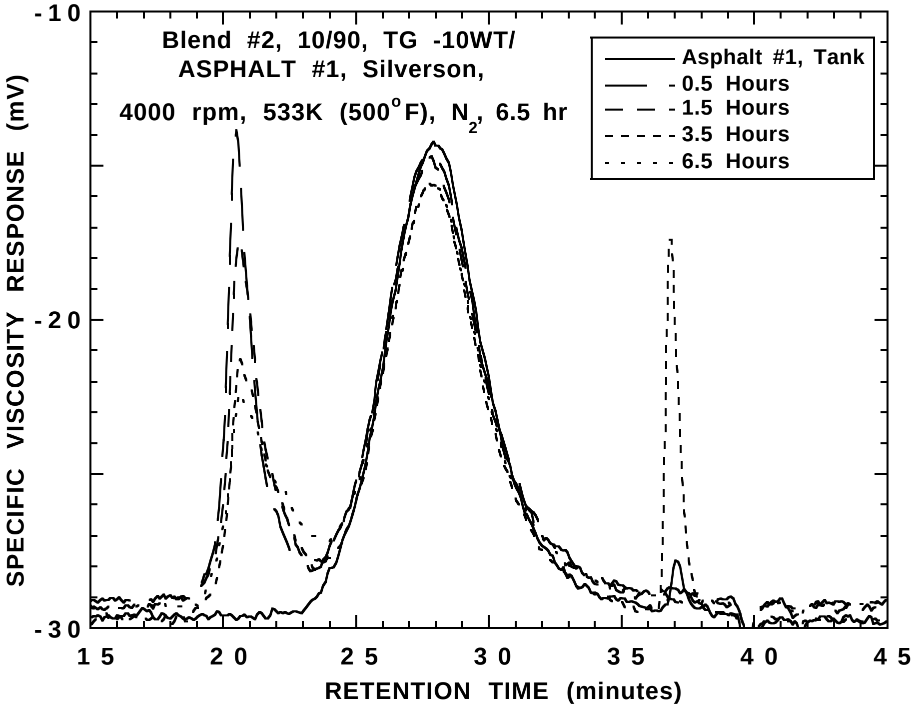

Figure 2-31. GPC Data for 10/90, TG-10WT/Asphalt #2, Cured at 232°C, 4000 rpm.

to produce smaller molecular weight material. Interestingly, the devulcanization of the rubber does not stop after 0.5 hours, but continues as proven by rubber dissolution analysis (Figure 2-28).

The settling properties of some of the blends are given in Table 2-9. The Asphalt-Rubber #1 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. For the samples in Table 2-9, the smaller the difference in settling ratio values from top to bottom, the more dissolution had occurred as measured by the Whatman 42 paper filter. Increasing the curing temperature from 232 °C (450 °F) to 260 °C (500 °F) greatly improved the settling properties of a blend.

The high-temperature viscosity was lower for the blends produced at 260 °C (500 °F), however even the viscosity of the blend produced at 232 °C (450 °F) is comparable to the base asphalt viscosity (Figure 2-32). 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: $\eta=\eta_s(1+2.5\varphi)$, 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). 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 as the particles are devulcanized and depolymerized into the asphalt phase of the solution.

For the majority of blends, their complex viscosity and phase angle at 60 °C (140 °F) and 1.0 rad/sec, and temperature susceptibility for the 0-90 °C (32-194 °F) region arrived at near constant values within a curing time of 6.5 hours. However, Figures 2-33 and 2-34 show that these values for the complex viscosity and phase angle were highly dependent on curing conditions. 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.

A blend cured at 260 °C (500 °F) had a lower phase angle and was therefore more elastic than a blend cured at 232 °C (450 °F) (Figure 2-33). The complex viscosity was lower for a binder cured at 260 °C (500 °F) than for a binder cured at 232 °C (450 °F) (Figure 2-32). Generally, the complex viscosity decreased with curing time until becoming nearly constant.

The low-temperature properties for the Asphalt #3 blends as measured at -24 °C (-11 °F) are presented in Figure 2-35. The creep stiffness of the Asphalt #3 blend cured at 232 °C (450 °F) decreased with curing time. However, the creep stiffness of the other Asphalt #3 blends, all cured at 260 °C (500 °F), increased with curing time. Nonetheless, the creep stiffness at 6.5 hours is still lower than the creep stiffness of the base, Asphalt #3.

Table 2-9. Viscosity and Delta Ratios.

Sample Details	Sample	At 60°C (140°F) & 1.0 rad/sec η* (dPa·s (poise))	δ (degrees)	η* Ratio	δ Ratio
Blend #7	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
Blend #8	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
Blend #10	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
Blend #9	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
Asphalt-Rubber #1	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
Blend #3	Tank	326.9	87.73		
	Top	315.8	87.78	0.966	1.00
	Middle	338.7	87.69	1.036	1.000
	Bottom	339.8	87.70	1.039	1.000

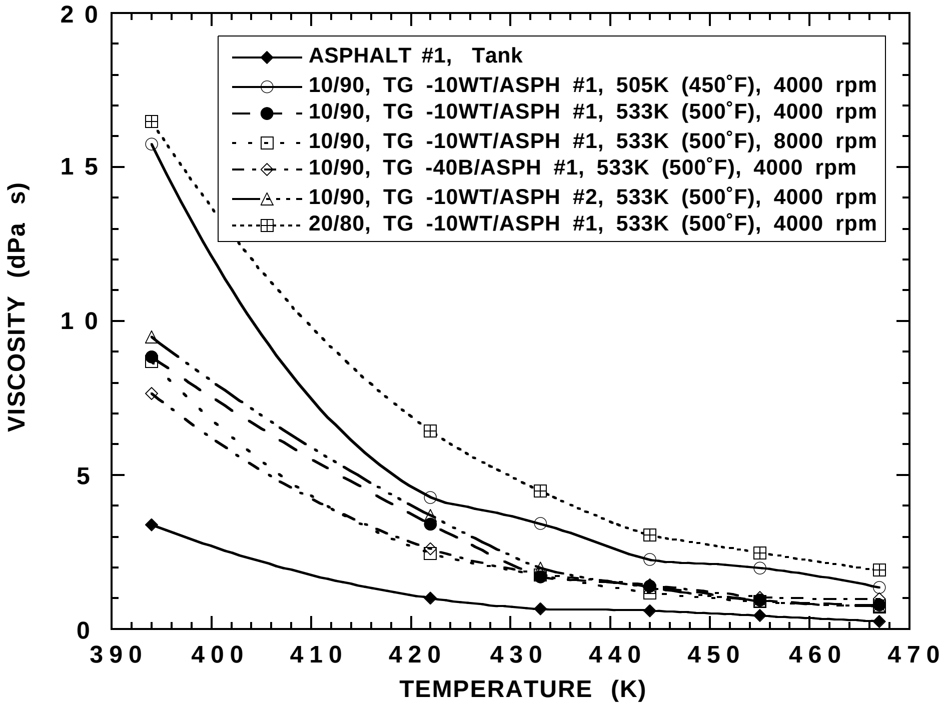

Figure 2-32. High-Temperature Viscosity for Asphalt #1 Blends.

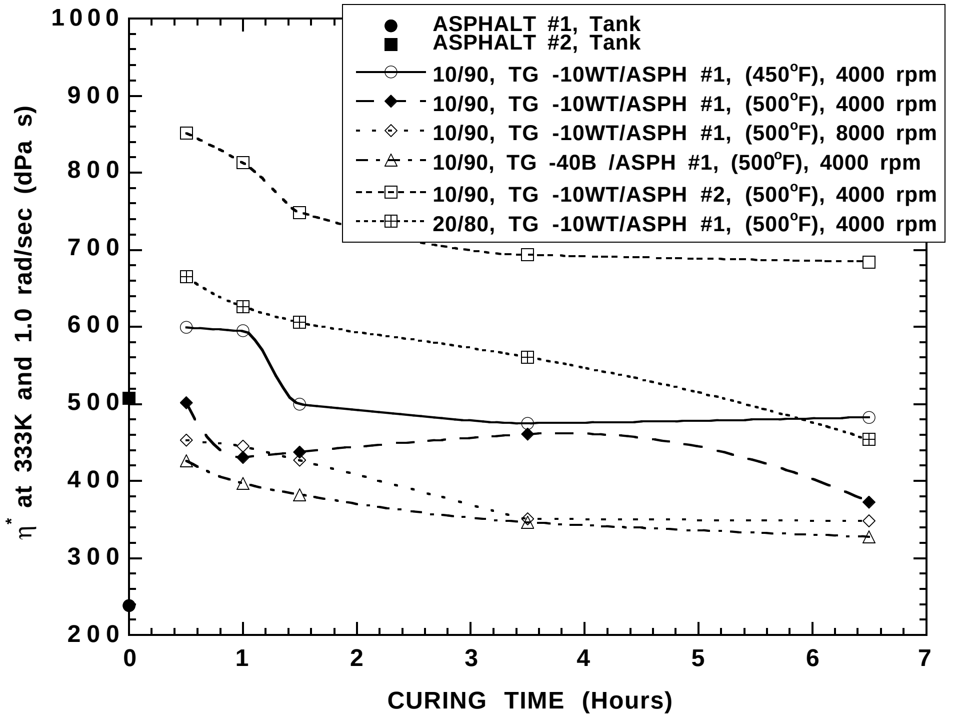

Figure 2-33. Complex Viscosity Data for Asphalt #1 Blends.

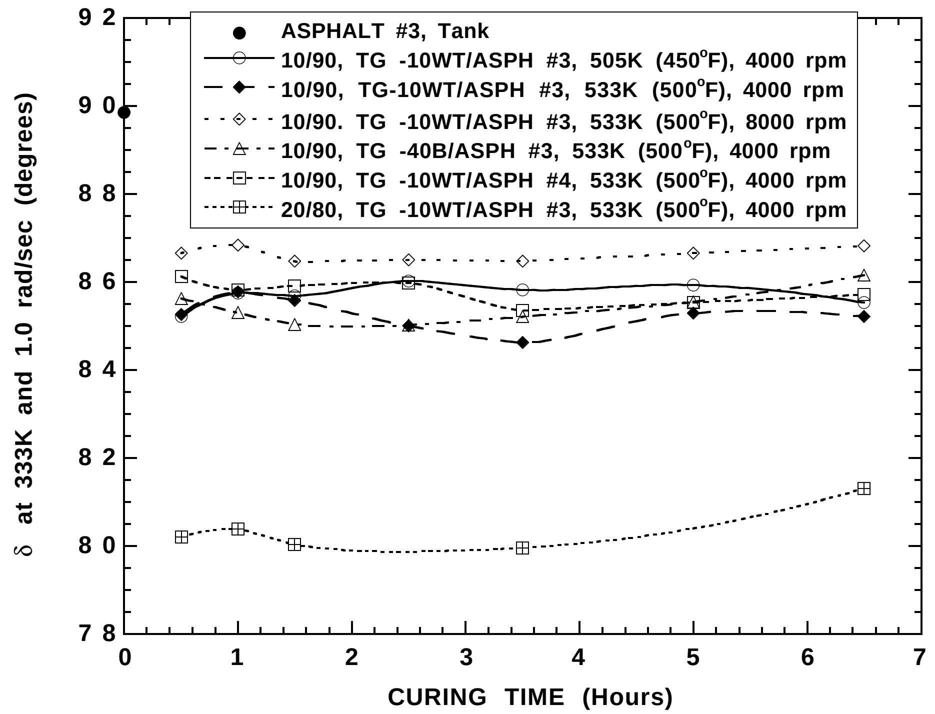

Figure 2-34. Phase Angle Data for Asphalt #3 Blends.

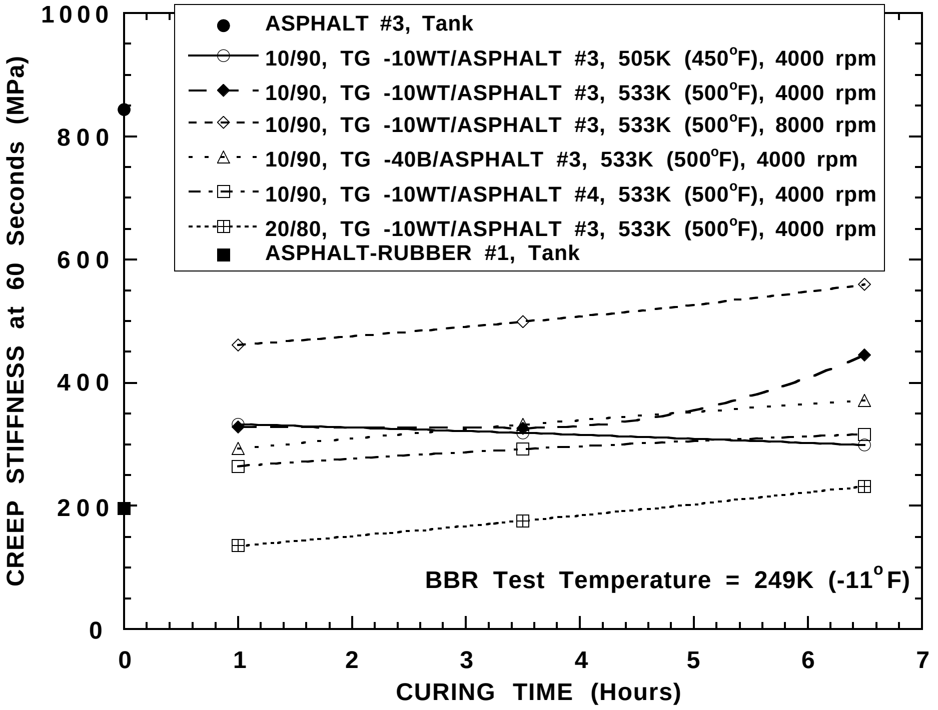

Figure 2-35. Creep Stiffness Data for Asphalt #3 Blends.

Mixer Speed

For Asphalt #1, increasing the mixer speed increased the rate of rubber dissolution into the asphalt. For Asphalt #3, the amount of rubber dissolution was not substantially affected by mixing speed (Figure 2-28), with the curing variable of rubber mesh size having a much larger effect.

The phase angle at 60 °C (140 °F) was higher and the complex viscosity at 60 °C (140 °F) was lower at the higher mixing speed of 8000 rpm, shown in Figures 2-34 and 2-33, respectively. Apparently, the more severe the curing environment, i.e., the higher the curing temperature and shear rate, the lower the complex viscosity (Table 2-10). Asphalt-Rubber #1 at 60 °C (140 °F) and 1.0 rad/sec had a complex viscosity and delta of 433.3 dPa·s (poise) and 88.72 °C (191 °F), respectively, and its reported base asphalt, Asphalt #3, had a complex viscosity and phase angle δ of 952.0 dPa·s (poise) and 90 °C (194 °F), respectively. Apparently, the process for producing Asphalt-Rubber #1 has digested the rubber to a point where the cured material is less viscous than the original asphalt. Even so, some of the rubber is apparently still in polymer form since the phase angle of Asphalt-Rubber #1 is lower than that of its base asphalt, Asphalt #3, and therefore, Asphalt-Rubber #1 is still more elastic than its base asphalt.

The blends produced at 8000 rpm and the blends produced at 4000 rpm had similar high-temperature viscosities (Figure 2-32). Furthermore, increasing the blending speed greatly improved the settling properties of a blend (Table 2-9). The settling properties of the binders produced at 8000 rpm and 260 °C (500 °F) improved with curing time. The blend produced at 8000 rpm had the worst low-temperature creep stiffness of the Asphalt #3 blends, but was still less stiff than the base asphalt (Figure 2-35). Asphalt-Rubber #1 had better low-temperature properties than any of the 10 percent, Asphalt #3 blends (Figure 2-35).

Asphalt Composition

For the asphalts studied, the extent and rate of rubber dissolution were asphalt dependent, as seen in Figure 2-28. The five asphalts ranked in the following order: Asphalt #1 > Asphalt #5 > Asphalt #2 > Asphalt #4 > Asphalt #3. Comparing these rankings with the Corbett compositions in Table 2-7, the lower the saturate and asphaltene content, the better an asphalt was at effecting dissolution of the rubber. This is reasonable as the extending oils used in the rubber processing industry are light, highly aromatic oils and their miscibility with rubber follows the order aromatic > naphthenic > paraffinic (Blackley, 1983). 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 it.

In Figures 2-30 and 2-31 it appears that Asphalt #3, which had the slowest devulcanization rate, has a much faster depolymerization rate than Asphalt #1 as indicated by the material in the retention time region of 21.5 to 24 minutes. Asphalt #3 has the largest percentage of asphaltenes, Table 2-7, and probably also has more heavy polar aromatics than the other

Table 2-10. Viscosity Increase Ratios.

Sample (See Table 2-3) (Silverson, N_2)		η* (dPa·s (poise)) at 60°C & 1.0 rad/sec		Viscosity Increase Ratio
		Base Asphalt, Tank	6.5 hrs of Curing	
Blend #1	Asphalt #1	238.6	482.9	2.024
Blend #2	Asphalt #1	238.6	372.8	1.562
Blend #3	Asphalt #1	238.6	348.3	1.460
Blend #4	Asphalt #1	238.6	327.9	1.374
Blend #5	Asphalt #1	238.6	454.0	1.903
Blend #6	Asphalt #2	507.9	684.5	1.348
Blend #7	Asphalt #3	952.0	1,694	1.779
Blend #8	Asphalt #3	952.0	1,414	1.485
Blend #9	Asphalt #3	952.0	1,276	1.340
Blend #10	Asphalt #3	952.0	1,212	1.273
Blend #11	Asphalt #3	952.0	1,807	1.898
Blend #12	Asphalt #4	561.0	906.0	1.615
Blend #13	Asphalt #5	369.0	1,374	3.724
Blend #14	Asphalt #5	369.0	1,223	3.314

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. Asphalt #5 had a slightly faster depolymerization rate than Asphalt #1. Although they have very similar Corbett compositions, Asphalt #5 is more viscous than Asphalt #1, indicating that it is comprised of higher molecular weight material. Similarly, the heavier components produced by combining Asphalt #1 and an AC-10 in a 50/50 ratio, improved the ability of Asphalt #2 to depolymerize the rubber relative to Asphalt #1.

The increase in complex viscosity that occurred with the addition of rubber and curing was very asphalt dependent (Table 2-10). The viscosity increase ratio is the complex viscosity at 60 °C (140 °F) after 6.5 hours of curing divided by the complex viscosity at 60 °C (140 °F) of the tank base asphalt. Interestingly, adding light molecular weight material to Asphalt #3 (to produce Asphalt #4) caused the viscosity increase ratio to increase to 1.615 from 1.485 (blend 8 versus blend 12), and adding the heavy molecular weight material to Asphalt #1 (to produce asphalt #2) caused the viscosity ratio to decrease from 1.562 to 1.348 (blend 2 versus blend 6).

Mesh Size

The amount of rubber dissolution relative to mesh size was asphalt dependent. For Asphalt #1 there was no real difference between the -40 mesh and -10 mesh particles at these high-cure conditions. This contrasts with Asphalt #3, where there was an appreciable difference between the -40 mesh and -10 mesh particles (Figure 2-28). This is most likely a diffusion phenomenon, where Asphalt #1, being of much lower molecular weight, can penetrate throughout the larger -10 mesh particles as thoroughly as it can the -40 mesh particles.

Figure 2-33 indicates that the complex viscosity of a -40 mesh blend produced at 4000 rpm and 260 °C (500 °F) was very comparable to a -10 mesh blend produced at 8000 rpm and 260 °C (500 °F). As measured by the viscosity increase ratio, the -40 mesh particles were not as effective as the -10 mesh particles in raising the complex viscosity (Table 2-10). The -40 mesh and -10 mesh blends had very similar high-temperature viscosities and phase angles (Figures 2-32 and 2-34). On the other hand, the -40 mesh blend had much better rubber settling properties than the -10 mesh blend (Table 2-9). At low temperature, the -40 mesh and -10 mesh blends had very similar creep stiffness values (Figure 2-35).

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.

Rubber Content

The percentage of rubber dissolution was lower at the 20 percent rubber level (Figure 2-28). Apparently, the increase in rubber level corresponded to an increase in viscosity which slowed the rate of mass transfer. Nonetheless, the rubber still dissolved faster for a 20 percent blend cured at 260 °C (500 °F) than for a 10 percent blend cured at 232 °C (450 °F). This is an indicator of the importance of curing temperature on the curing process.

The increased rubber content increased the complex viscosity and the high-temperature viscosity (Figures 2-33 and 2-32). The phase angle was lowered by the higher rubber content and generally increased with curing time (Figure 2-34). The combined effect of a higher viscosity and reduced phase angle results in an increased $G^*/\sin\delta$ at rutting temperatures. At low temperature, the creep stiffness was lowered by the higher rubber content (Figure 2-35). The higher value of high-temperature viscosity, coupled with a lower low-temperature creep stiffness, indicate a blend with a reduced temperature susceptibility.

Conclusions

The implications of these results are that nearly homogeneous, asphalt-rubber binders can be produced using high-shear and high-temperature curing conditions. These high-cure binders are slow to phase separate and have reasonable viscosities at hot-mix temperatures, while still having higher values of $G^*/\sin\delta$ at rutting temperatures and lower values of creep stiffness (S) at low temperatures than the base asphalt.

AN INVESTIGATION OF OXIDATIVE CURING ON THE PROPERTIES OF HIGH-CURE ASPHALT RUBBER

(Pages 2-54 through 2-70 reprinted with permission from S. E. Leicht, P. Juristyarini, R. R. Davison, and C. J. Glover. An Investigation of Oxidative Curing on the Properties of High Cure Asphalt Rubber. Paper 000971 presented at the Transportation Research Board Annual Meeting, Washington, D.C., January 2000)

Abstract

Air blowing is combined with high-temperature, high-shear mixing to produce a high-cure asphalt rubber that differs in several important ways from conventional asphalt rubber material. It has excellent grade-span, good settling properties and low high-temperature (135 °C [275 °F]) viscosity, important characteristics for easy use as a binder in dense-graded mixes. These properties are related to curing conditions, rubber mesh and asphalt composition. The grade span is very dependent on asphalt composition and the extent of hardening but relatively insensitive to other curing variables and to mesh size. Settling is dependent on the extent of oxidation, original mesh size and the degree of high-shear mixing.

Introduction

To most asphalt technologists the term asphalt rubber refers to a material consisting of a high content of ground tire rubber blended into asphalt for up to an hour at about 175-200 °C (347-392 °F) with a low shear stirrer. In fact, ASTM D8-97 method (1999) defines "asphalt rubber" as "a blend of asphalt cement, reclaimed tire rubber, and certain additives in which the rubber component is at least 15 percent by weight of the total blend and has reacted in the hot asphalt cement sufficiently to cause swelling of the rubber particles." The result is a material of significantly increased viscosity (certainly above the 3 Pa·s Superpave specification value at 135 °C [275 °F]) containing swollen particles which will settle on standing. To lay hot-mix with these materials usually requires a gap graded mix and/or increased binder content and continued circulation in storage. Though there have been many successful projects using this material there have also been numerous disasters and placement difficulties encountered by contractors and increased cost to the buyer so that resistance is frequently encountered when the use of asphalt rubber is suggested.

The material studied in this project should not be confused with the material described above. It is better to designate this material as highly cured asphalt rubber or HCAR. It has a considerably lower viscosity, particularly at high temperature, than the usual asphalt-rubber product. The particles are not swollen but are considerably smaller than the original particle size, and the material has a significantly lower settling rate. Also, we do not include a specific rubber content in the definition as we are open to optimizing performance return against cost. Our objective, ultimately, is to produce materials that will provide a reduced life-cycle cost.

There is published work (Billiter, et al., 1997b; Billiter et al., 1997c) demonstrating the advantages of using high-cure techniques (high-shear blenders, higher temperature, longer blending time) to produce HCAR. This produces a more stable material greatly reducing settling and viscosity which is an aid in mixing with the aggregate and the subsequent compaction. This makes it possible to use the material in dense graded mixes and at the usual binder level of about 5 percent. This coupled with the fact that much coarser mesh rubber can be used, greatly reduces binder cost when compared to conventional (low cure) asphalt-rubber mixes. This material also has a much slower hardening rate at road conditions than unmodified asphalt (Chipps et al., 1998), a property which should lead to significant increases in durability.

Recent work indicates that combining air blowing with curing speeds and enhances the blending process. Since air blowing alone can produce materials with a wide Superpave grade span and good aging characteristics (Davison et al., 1999) this seems a promising combination. Flanigan (1995) patented the process of producing a stable combination of tire rubber and asphalt by bombarding the blend with a high volume of air (1600-2800 ft^3/min.) under pressure (6-15 psi). Ground tire rubber in an amount ranging from 1 percent to 27 percent of the blend was loaded into a reactor equipped with an air sparger and a stirrer. The reaction started at an initial temperature of 148-190 °C (300-375 °F). The temperature was increased to 251 °C (485 °F) during the blending process, which lasted 2.0 to 6.0 hours. Duong and Boisvert (1993) developed a process for devulcanizing crumb rubber in asphalt binders by air-blowing the blend under pressure at temperatures from 220-260°C (428-500°F). Behling and Oelsner (1974) invented a procedure for air-blowing a blend of asphalt, flux oil, and a rubber derived from ethylene and propylene units. The procedure involved air blowing and stirring the blend for 8.0 to 20 hours at temperatures ranging from 148-260 °C (300-500 °F).

The study described here involves an investigation of how process variables affect the properties of HCAR produced by combining air blowing and blending. It should be viewed as preliminary as there are many variables to consider: type of blender, mixer rpm, quantity of air and how it is introduced, time and temperature of blending, percent rubber and rubber mesh and finally, asphalt composition.

The objective of this study is to explore at least some conditions that might be used to produce a superior HCAR using air and make comparisons with curing without air and without rubber. The effect of asphalt composition is also studied. Evaluation is made primarily with respect to Superpave grade (continuous grade is reported as this is more meaningful) and settling rate. Carbonyl areas were determined as a measure of oxidation. Viscosity at 135 °C (275 °F) is reported for some mixtures and Gel Permeation Chromatographs (GPC) are presented for several blends. While it is recognized that Superpave specifications were not designed for modified asphalts, they are being used and, as yet, there is no official alternative. Potential benefits from reduced pavement oxidation have been discussed previously (Chipps, et al., 1998).

Materials

Two asphaltic materials and two rubbers were used in this study. One asphalt was an AC-10 having a viscosity of 101 Pa·s (1011 poise) at 60 °C (140 °F). Its Corbett analysis is asphaltenes, 12.7 percent; polar aromatics, 26.6 percent; naphthene aromatics, 48.4 percent, and saturates, 12.3 percent. The other material was a resin from a supercritical unit with a viscosity of 28.1 Pa·s (281 poise) at 60 °C (140 °F) and a Corbett analysis of 3.0 percent asphaltenes, 38.2 percent polar aromatics; 49.7 percent naphthene aromatics and 9.2 percent saturates.

The rubbers used had mesh sizes of 10 and 80. The 80 mesh material (RS-80) is a black powder-like rubber which mainly consists of reprocessed tire tread and was obtained from Rouse Rubber Industries in Vicksburg, Mississippi. The 10 mesh rubber was acquired from Granular Products & Services in Mexia, Texas. This is a "whole tire" product which includes the white walls (primarily composed of nitrile rubber and ethylene propylene diene monomer rubber, EPDM); thus, the 10 mesh rubber (TG-10WT) has a salt and pepper appearance. Both materials are ambiently ground rubbers.

Experimental Methods

Asphalts and rubbers were mixed and cured at various temperatures, mixing speeds, and air-nitrogen ratios. The temperatures under study were 204 °C, 232 °C, and 260 °C (399 °F, 449 °F, and 500 °F). The mixing speed ranged from 1500 to 8000 rpm. A drill press modified with a mixing blade with a diameter of 6.4 cm was used to mix at a low speed of 1550 rpm (low-shear impellor, LSI). Another mixer, a Silverson L4RT high-shear laboratory mixer with a mixing blade diameter of 5.1 cm was used to obtain speeds of 1500, 4000, and 8000 rpm (high-shear disintegrator, HSD). The air-nitrogen ratios investigated were 0.0, 0.47, 0.73, and 1.6. During the curing process, seven samples were removed at various times in order to show the effect of the curing time on the properties of each binder produced.

The binders produced were then subjected to a performance test, oxidation analysis, and GPC analysis. The performance test followed the Superpave™ performance grades. A Cannon Thermoelectric Bending Beam Rheometer (BBR) was used to measure the low-temperature properties of asphalt-rubber binder after being Rolling Thin Film Oven Test- (RTFOT) and Pressure Aging Vessel- (PAV) aged. The evaluation was conducted according to AASHTO Designation TP1.

A Carri-Med CSL-500 Dynamic Shear Rheometer (DSR) in parallel plate configuration and "controlled strain" mode was used to measure the intermediate-temperature rheological properties. The gap size chosen was 1500 μm to assure a minimal effect of rubber particle size on the measurements. The "controlled strain" mode is actually controlled stress with a feedback loop that changes the peak stress to the level needed to achieve a desired level of peak strain. In accordance with Superpave protocol, this maximum peak strain was kept low enough to provide testing within the linear viscoelastic region (Billiter et al., 1997a). A more detailed description of the methods used with Carri-Med CSL-500 has been documented by Billiter et al. (1997a). A

Brookfield Rotational Viscometer, model RVF7, was used to measure the high-temperature viscosities at 135 °C (275 °F).

A Mattson 5020 Galaxy Series Fourier Transform Infrared spectrometer was used to determine the degree of oxidation as a function of the curing time and curing conditions.

A qualitative measure of the change in rubber size small enough to enter the GPC column as a function of curing time was analyzed using a gel permeation chromatograph with a Viscotek H502 Intrinsic Viscosity Detector. Three columns with pore sizes of 100 Å, 500 Å, and 50 Å were connected in series. The sample was prepared by dissolving 0.200 to 0.222 grams of the binder in 10 mL of tetrahydrofuran (THF). The solution was passed through a PTFE syringe filter with a membrane pore size of 0.4 μm.

A settling tester was used to determine the settling of rubber in asphalt-rubber binders. The binder sample was poured into a section of a pipe with the size of 16.5 cm long and 2.86 cm in diameter, capped at one end. The entire apparatus was placed in an upright position in an oven at 104 °C (219 °F) for 24 hours. Three to five gram samples were removed through three holes in the pipe wall, located 13.0 cm, 6.8 cm, and 0.64 cm from the bottom of the capped pipe. The extent of settling was determined by measuring dynamic complex viscosities (η^*) of the samples at 60 °C (140 °F) and a frequency of 1.0 s^{-1}.

Discussion of Results

Figure 2-36 shows how 60 °C (140 °F) viscosity changes as high-shear curing proceeds for the AC-10 asphalt and 10-mesh rubber. For the no-air run (run 27) the viscosity actually decreases at these high temperatures and high-shear conditions. This contrasts markedly with conventional curing during which the viscosity generally increases as curing proceeds. When air is included in the process, the material tends to harden as the asphalt oxidizes to produce asphaltenes. This is complicated, however, by the fact that oxidation tends to break up the rubber particles and devulcanize and depolymerize the rubber. As a result in the A/N 0.47 (air/nitrogen ratio) run 20 Table 2-11, the viscosity only increases a little and actually decreases for a period. The A/N, 0.73 run 22 is anomalous. Not only did it harden much faster than the pure air run 28, which may be partly the result of a higher total flow rate, but the big viscosity jump at the end is unexplained. It is suspected that local overheating occurred producing char particles as this material also exhibited very poor settling characteristics (discussed later in Table 2-13).

The results in Figure 2-36 are consistent with the GPCs of the same materials shown in Figure 2-37. Note that everything which appears in these chromatograms passed a 0.4 µm filter and that the prominent early peak in sample 27 is rubber material and that the large, later peak seen in all samples is composed of the base asphaltic components. For this system a retention time of 20.6 minutes corresponds to a molecular weight of 190,000 for a linear polyethylene standard. At 21.56 minutes, this reference molecular weight is 37,900 and at 24.4 minutes it is 5970. With the viscosity detector there is much greater sensitivity for higher molecular weight

Table 2-11. Summary of Curing Conditions of AC-10.

Sample ID	Asphalt Type	Rubber Type	Rubber Percent	Temperature (°C)	(°F)	Speed (rpm)	Total (mL/min)	A/N
5	AC-10	80	10	204	400	8000	17667	1.65
7	AC-10	80	10	204	400	4000	17667	1.65
8	AC-10	80	10	204	400	8000	13441	0.47
9	AC-10	80	10	204	400	4000	13441	0.47
10	Resin	80	10	204	400	8000	13441	0.47
11	Resin	80	10	204	400	4000	13441	0.47
12	Resin	80	10	204	400	4000	17767	1.62
13	Resin	80	10	204	400	8000	17767	1.62
14	AC-10	80	10	204	400	1500	13441	0.47
15	Resin	10	10	232	450	4000	13441	0.47
16	Resin	10	10	260	500	4000	13441	0.47
17	Resin	10	10	232	450	4000	13441	0.47
18	AC-10	80	10	204	400	4000	13441	0.47
19	AC-10	80	10	204	400	1550	13441	0.47
20	AC-10	10	10	204	400	8000	13441	0.47
21	AC-10	10	10	204	400	1550	13441	0.47
22	AC-10	10	10	204	400	8000	15799	0.73
23	AC-10	10	10	204	400	1550	15799	0.73
25	AC-10	--	0	204	400	8000	15799	0.73
26	AC-10	10	10	204[a]	400[a]	8000	15799	0.73
27	AC-10	10	10	204	400	8000	4310	0.00
28	AC-10	10	10	204	400	8000	6681	∞
29	Resin	--	0	260	500	4000	13441	0.47
30	AC-10	10	10	232	450	8000	15799	0.73
31	AC-10	10	15	204	400	8000	6681	∞

[a] This temperature was maintained for 3.5 hours and then increased to 232°C (450°F).

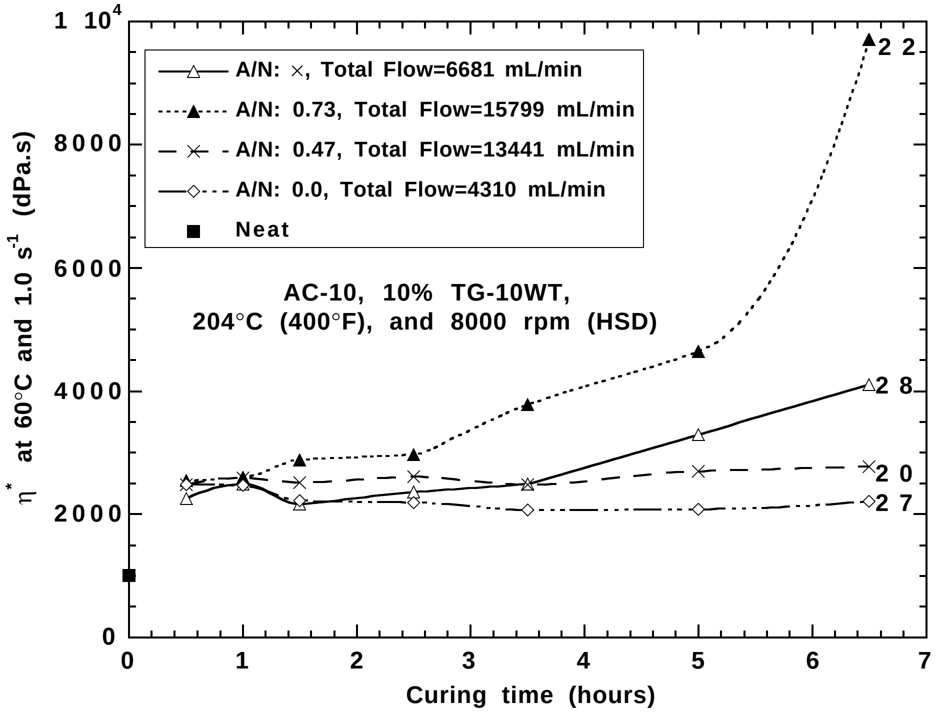

Figure 2-36. Complex Viscosity Data for AC-10 Blends (10% TG-10WT) with Varying A/N Ratios.

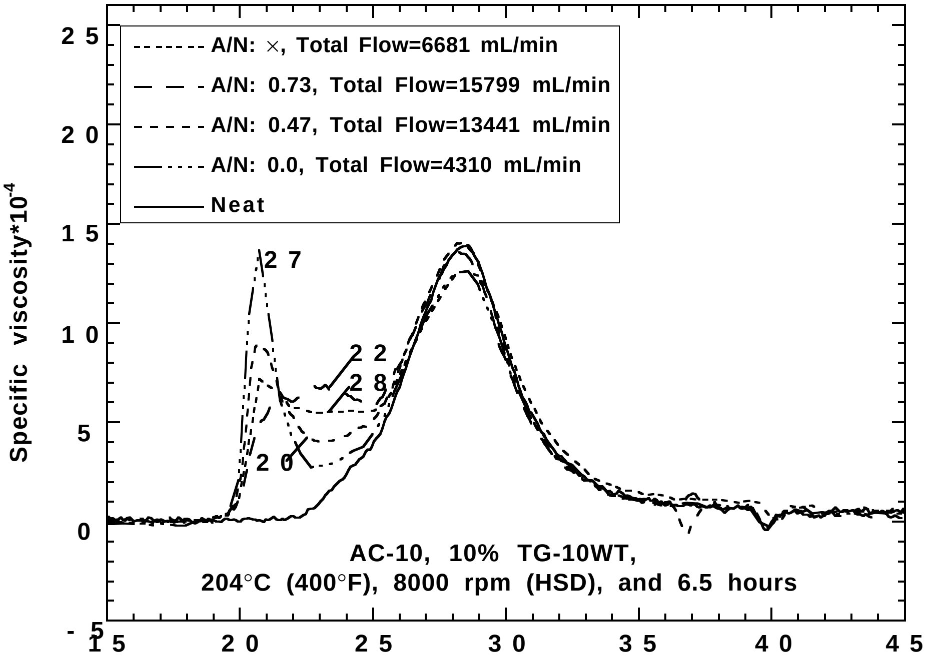

Figure 2-37. Comparison of GPC Data for AC-10 Blends with Varying A/N Ratios.

materials than for lower molecular weight materials so that the relative mass of the materials detected at longer times is much greater than indicated. What we see is that materials in Figure 2-36 showing larger viscosity gains, corresponding to greater oxidation, also show less material in the higher molecular weight peak and more material centering around about 23 minutes. Clearly the larger molecular weight material is being cut up by oxidation.

Figures 2-38 and 2-39 show hardening and oxidation (carbonyl area growth, Figure 2-39) rates of the resin with 80 mesh rubber. The strange behavior of the viscosity is even more apparent in these runs. Though the 8000 rpm, A/N, 1.6 (run 13) shows by far the highest rate of oxidation (carbonyl increase), until 4.0 hours it has one of the lowest viscosities. The 8000 RPM, A/N, 0.47 (run 10) actually decreases in viscosity after three hours though the carbonyl increases smoothly.

Figure 2-40 is a GPC of runs 11 and 12, shown also in Figures 2-38 and 2-39. The striking point here is the difference between these chromatographs and those in Figure 2-37. It seems that while the rubber is disintegrating sufficiently to pass the 0.4 µm filter, there is subsequently no further depolymerization such as occurs extensively in the AC-10 asphalt.

There are not many direct comparisons between 4000 and 8000 RPM and there is no discernable pattern in the data (Table 2-12, runs 8 versus 9, 10 versus 11, and 12 versus 13). On the other hand, the LSI at 1550 RPM (Table 2-12, runs 19, 21, and 23) gives much larger growth in carbonyl and in viscosity. This is entirely an artifact of the sparger geometry which has a diameter larger than the HSD so that most of the air escapes being sucked through this device. Thus the LSI actually produced a better air dispersion, though with a much lower shearing and disintegrating effect on the rubber.

Table 2-12 gives some 135 °C (275 °F) viscosities. It was not possible to correlate these with other parameters. As would be expected the LSI values with 10 mesh rubber were generally higher, but all the runs' viscosities at 135 °C (275 °F) were well below the 3.0 Pa·s (30 poise, = 30 dPa·s) Superpave specification for pumpability near hot mix temperatures.

The Effect of Air Curing on Superpave Grade Span

In Table 2-12 it is not shown whether the top grade is limited by $G^*/\sin\delta$ before or after RTFOT, neither is it shown whether the low grade is S or m limited. This was necessary to reduce complexity in the table where there are already too many variables. These parameters will be discussed later. However, Figure 2-41 shows a remarkable correlation between grade span and top grade for all the AC-10 results and that the top grade and total grade span can be increased by air blowing and/or by adding rubber. Note the neat asphalt near the left bottom of the figure. There is no significant difference between 10 and 80 mesh. Run 30, cured at 232 °C (450 °F) (all the others are at 204 °C [400 °F]) is very near the line. There is no significant difference between the LSI runs and the 4000 and 8000 RPM HSD runs as far as grade is concerned. The one run with 15 percent -10 mesh rubber, run 31, is only about 2 °C (35 °F) above the line. Even 4 °C (39 °F) below the line. In other words a big increase in grade span

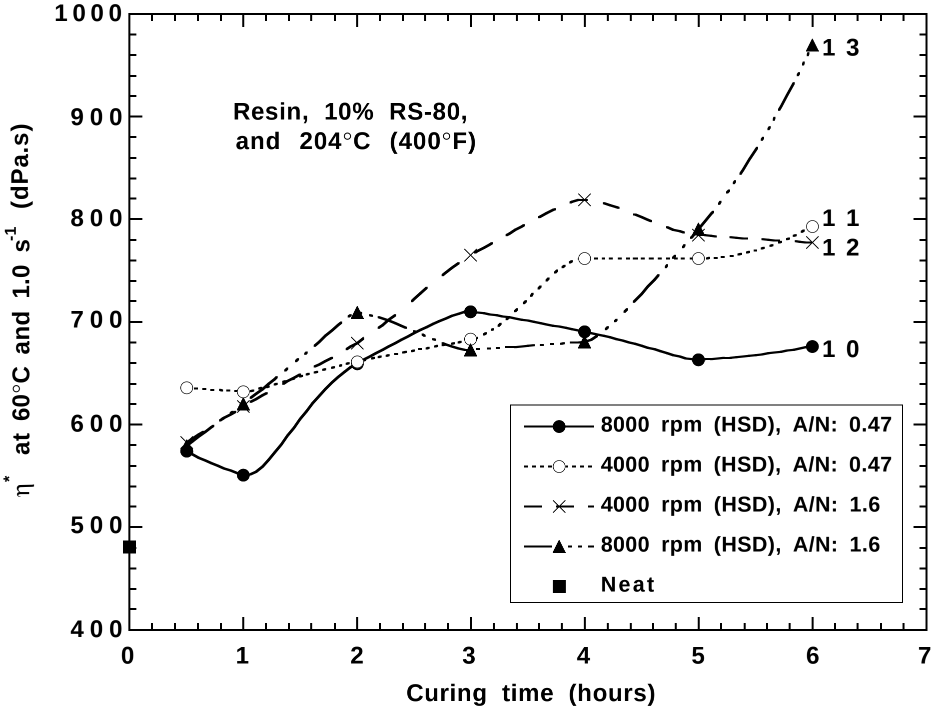

Figure 2-38. Complex Viscosity Data for Resin Blends (10% RS-80) with Varying A/N Ratios.

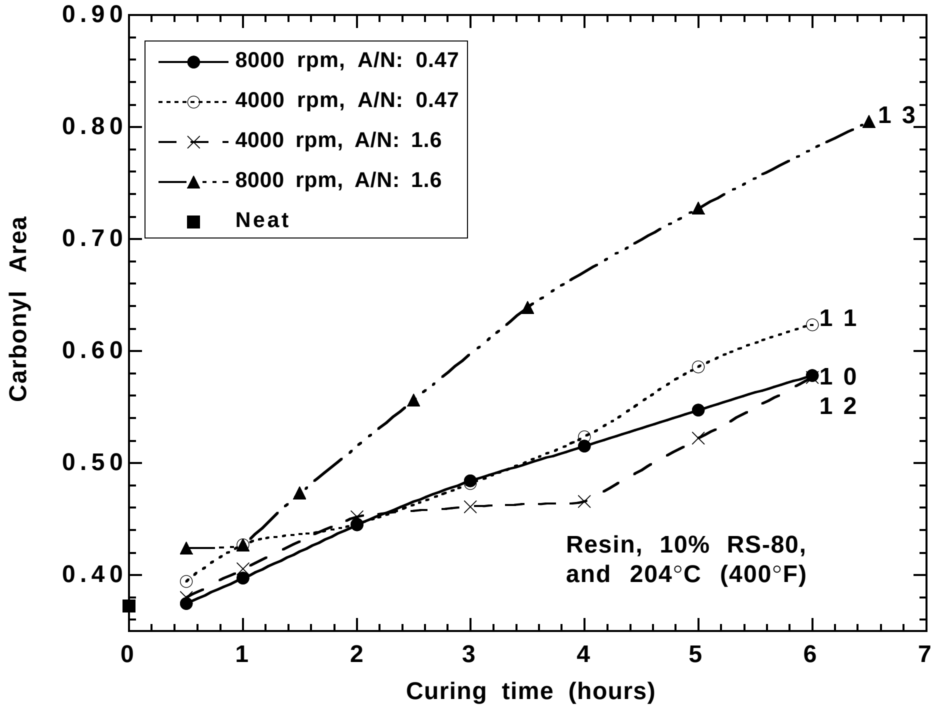

Figure 2-39. Carbonyl Areas of Resin Blends (10% RS-80) with Varying A/N Ratios.

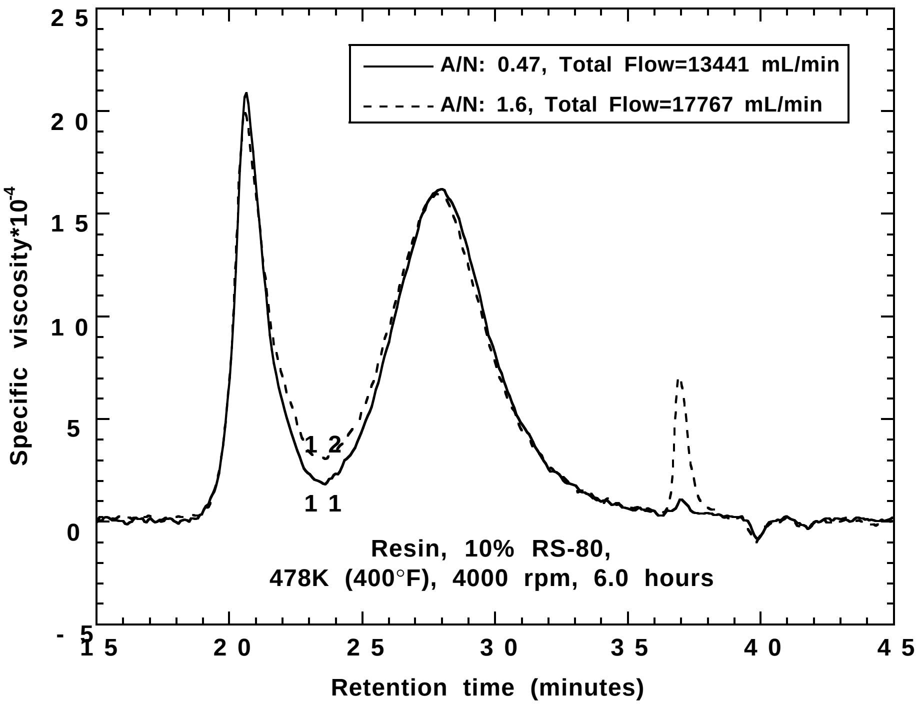

Figure 2-40. Comparison of GPC Data for Resin Blends with Varying A/N Ratios.

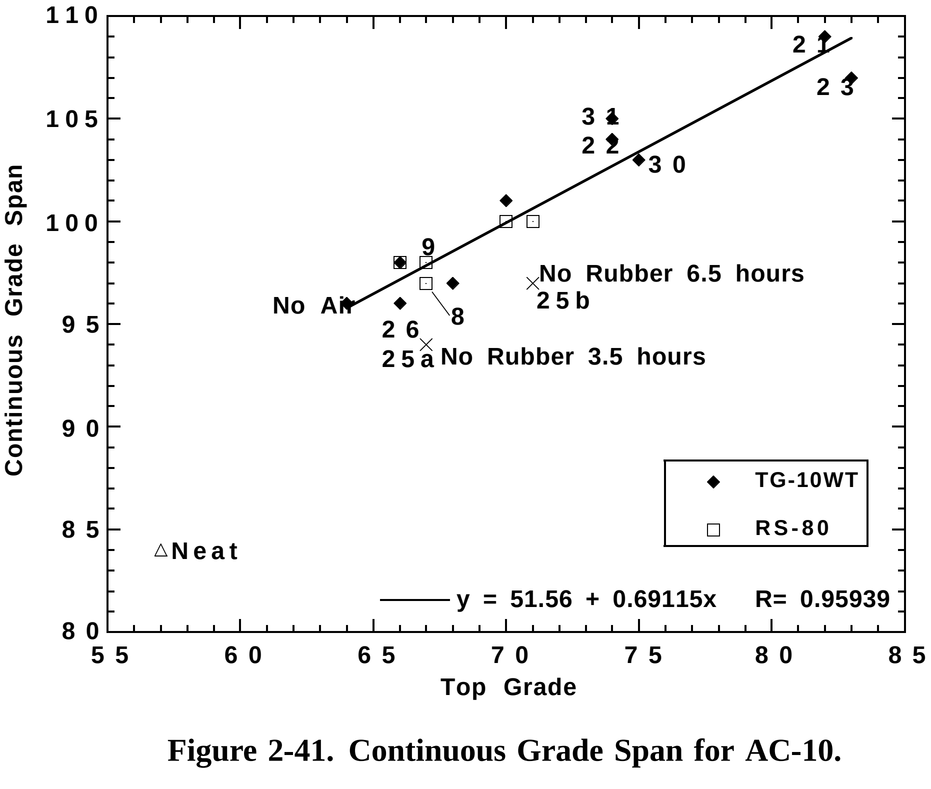

Figure 2-41. Continuous Grade Span for AC-10.

Table 2-12. Viscosities, Carbonyl Areas, and Continuous Performance Grades of AC-10 and Resin.

Sample ID	Asphalt Type	Time (hours)	$\eta^*_{60^\circ C}$ (dPa·s) e)	$\eta_{135^\circ C}$ (dPa·s)	Carbonyl Area	Continuous Grade	Span
5	AC-10	6.0	6429.0	2.26	0.80	70-30	100
7	AC-10	6.0	3921.0	2.31	0.56	67-30	97
8	AC-10	6.0	3532.0	1.00	0.62	67-30	97
9	AC-10	6.0	3458.0	1.12	0.51	67-31	98
10	Resin	6.0	676.4	--	0.58	51-29	80
11	Resin	6.0	793.2	--	0.63	52-30	82
12	Resin	6.0	777.4	--	0.58	53-29	82
13	Resin	6.0	969.4	--	0.80	55-29	84
14	AC-10	6.0	3183.0	1.25	0.51	66-32	98
15	Resin	6.5	703.8	--	0.62	54-28	82
16	Resin	6.5	1354.0	--	0.77	61-23	84
17	Resin	6.5	643.5	--	0.58	53-31	84
18	AC-10	6.5	3966.0	2.88	0.56	67-30	97
19	AC-10	6.5	7452.0	1.99	0.80	71-29	100
20	AC-10	6.5	2773.0	1.72	0.52	70-31	101
21	AC-10	6.5	12740.0	2.98	0.82	82-27	109
22	AC-10	6.5	9713.0	2.80	0.93	74-30	104
23	AC-10	6.5	38300.0	4.69	0.96	83-24	107
25a	AC-10	3.5	2533.0	--	0.48	67-27	94
25b	AC-10	6.5	6529.0	0.49	0.58	71-26	97
26a	AC-10	5.0	3406.0	--	0.55	66-30	96
26b	AC-10	8.0	3439.0	1.74	0.59	66-30	96
27a	AC-10	1.5	2217.0	--	0.50	66-32	98
27b	AC-10	3.5	2068.0	--	0.52	66-32	98
27c	AC-10	6.5	2211.0	1.04	0.56	64-32	96
28a	AC-10	1.5	2165.0	--	0.54	66-32	98
28b	AC-10	3.5	2491.0	--	0.57	66-32	98
28c	AC-10	6.5	4109.0	1.32	0.72	68-29	97
29	Resin	6.5	1802.0	--	0.63	63-23	86
30	AC-10	6.5	8727.0	1.97	0.70	75-28	103
31	AC-10	6.5	8205.0	2.19	0.74	74-31	105

-- Data unavailable

can be achieved by air blowing alone or by rubber alone, while the combination might add still another grade.

The increase in span with air blowing, which increases asphaltenes, is consistent with the findings of Domke et al. (1999a) in which asphaltenes and saturates were added to aromatics in incremental quantities followed by grading of the blends. It was found that increasing asphaltenes raised the top grade considerably more than the bottom grade so that the span increased.

The primary contribution of the rubber in the blends produced by air curing is to hold the bottom grade. If in Figure 2-41 one passes a line through the neat asphalt and the air blown samples with no rubber, it is approximately parallel to the other line and about 4 °C (39 °F) lower. This difference, depending on the actual continuous low-temperature grade, may provide enough improvement to gain one grade.

The results with the resin (Figure 2-42) are much less definitive. Again, note the neat resin in the lower left corner. There are fewer data and much more scatter. The lower grade span overall is typical of highly aromatic material. It is not immediately obvious that rubber is helping these materials, though air blowing certainly is. However, if runs 29 and 16, both blown at 260 °C (500 °F) could be ignored, a fairly good straight line fit of the remaining data, including the neat resin, can be obtained having a slope not too dissimilar to that in Figure 2-40. Comparing runs 10 through 13 we see that as the top grade ranges from 51 to 55, the bottom is stable near -29.

The Effect of Curing on Settling Rate

In Figure 2-43, the settling ratio is plotted versus the carbonyl measurement. The ratio is the ratio of the bottom-sample viscosity in Table 2-13 divided by the top-sample viscosity. The carbonyl (which is given in arbitrary units) is a good measure of total oxidation and is a better correlator than viscosity with settling ratio as it is less affected by other variables such as original viscosity or rubber content and mesh size.

In general a higher level of curing, as indicated by settling ratio, is enhanced by higher temperature, higher shear, higher oxidation level, greater cure time, and finer initial rubber mesh. These trends are supported in Figures 2-43 and 2-44. In Figure 2-43, the AC-10, -10 mesh HSD data (solid diamonds) fall on a straight line with the exception of run 26 which is somewhat below the line. The materials represented by these points were all cured at 8000 RPM. Four points were cured at 204 °C (400 °F) and one at 232 °C (450 °F), all for 6.5 hours. A sixth point, run 26 was cured for 3.5 hours at 205 °C (400 °F) and then at 232 °C (450 °F) for a total of eight hours cure, accounting for it falling below the line. The 10-mesh blends cured in the LSI (open diamonds in Figure 2-43) are totally different with very poor settling ratios at high levels of oxidation. Figure 2-44 compares the GPC chromatograms of two, 10-mesh materials, both cured at 205 °C (400 °F) for 6.5 hours but with different shear. Note that the GPC shows only the

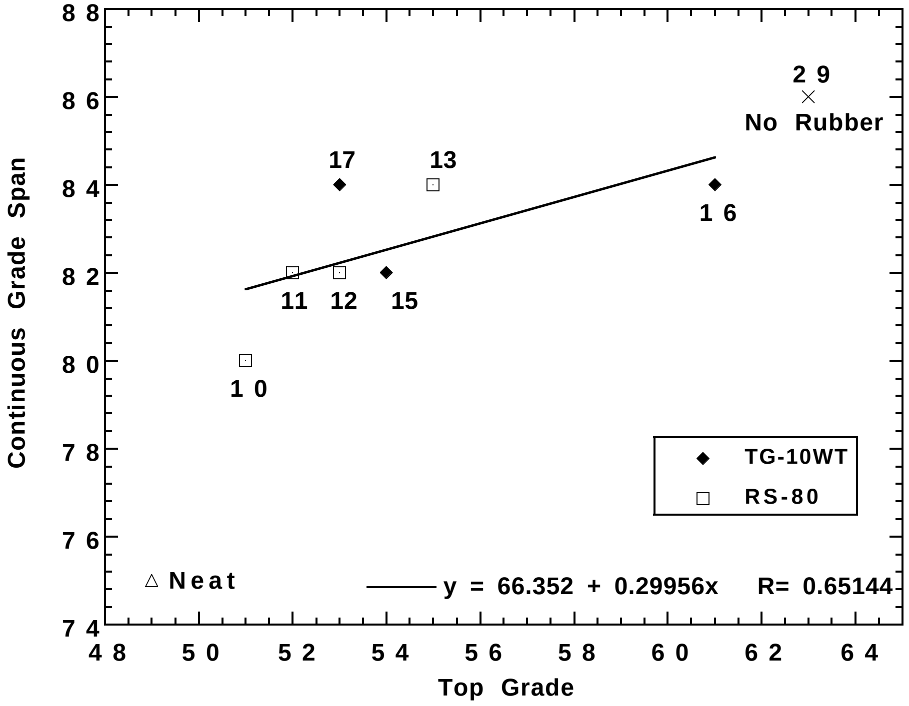

Figure 2-42. Continuous Grade Span for Resin-Based Materials.

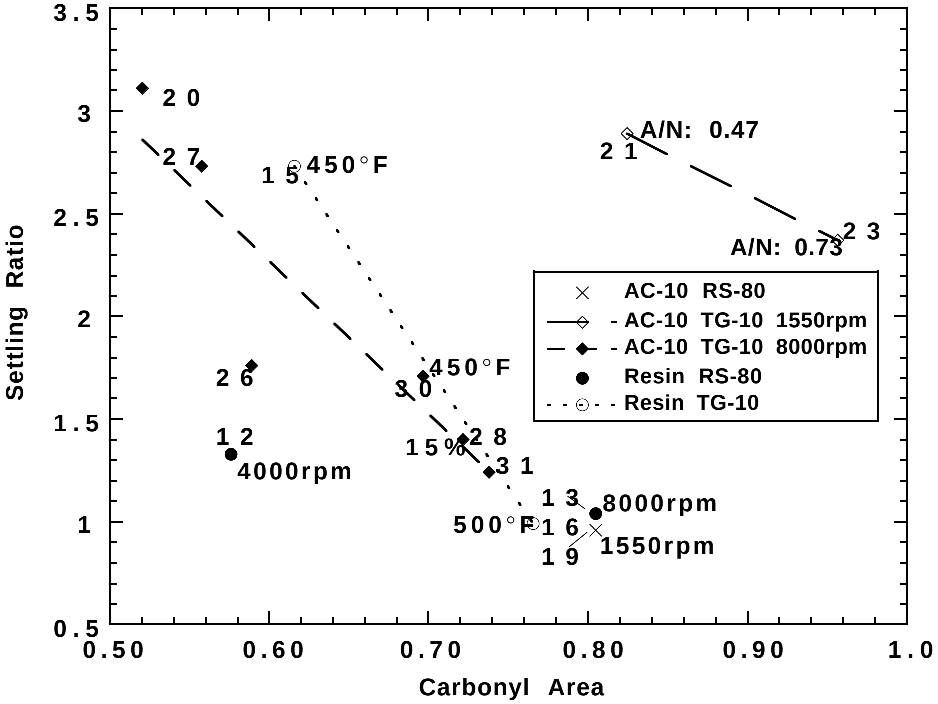

Figure 2-43. Settling Ratio versus Carbonyl Area for AC-10 and Resin.

Table 2-13. Settling Test Data for AC-10.

Sample	Sample Location	η* (dPa s)	η* Ratio
12	Top	722	
	Middle	800	1.33
	Bottom	968	
13	Top	961	
	Middle	996	1.04
	Bottom	994	
15	Top	729	
	Middle	702	2.73
	Bottom	2002	
16	Top	1532	
	Middle	1558	0.99
	Bottom	1516	
19	Top	8734	
	Middle	8697	0.96
	Bottom	8340	
20	Top	2604	
	Middle	2925	3.11
	Bottom	8089	
21	Top	13490	
	Middle	18950	2.89
	Bottom	39010	
22	Top	5851	
	Middle	6354	2.85
	Bottom	16600	
23	Top	31800	
	Middle	39300	2.37
	Bottom	75450	
26	Top	2344	
	Middle	2682	1.76
	Bottom	4125	
27	Top	1787	
	Middle	2040	2.73
	Bottom	4890	
28	Top	3778	
	Middle	4034	1.40
	Bottom	5290	
30	Top	8037	
	Middle	8837	1.71
	Bottom	13710	
31	Top	6741.0	
	Middle	7156.0	1.24
	Bottom	8387.0	

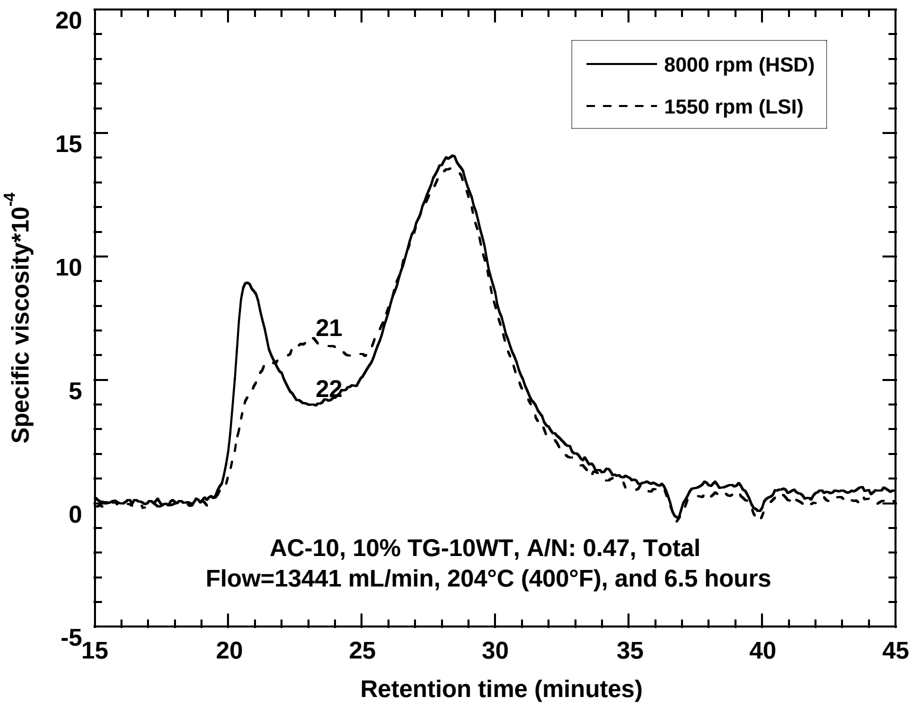

Figure 2-44. Comparison of GPC Data for AC-10 Blends (A/N Ratio of 0.47) with Varying Mixing Speeds.

material that passes the 0.4 filter; hence, rubber particles larger than this are not represented in the chromatogram. Both cured materials have poor settling ratios. This figure and Table 2-13 indicate that the high-oxidation rate in the LSI is further digesting the dissolved rubber while doing little for the settling ratio, as unlike the HSD it cannot disintegrate the larger particles which are only slowly attacked by oxygen.

This is not a problem with 80-mesh rubber. The 80-mesh material cured in the LSI (run 19) shows a superb settling ratio at a carbonyl value slightly lower than the 10-mesh LSI points and slightly above the intercept of the 10-mesh HSD line (Figure 2-43). With the resin, the -80 mesh material performs fairly well even at a low level of oxidation. At 8000 RPM and at high carbonyl, an excellent settling ratio was obtained (run 13). There are also two points for the resin and 10-mesh-rubber at 4000 RPM (runs 15 and 16) for which settling data were obtained. These data fall near the 10-mesh 8000 RPM data for the AC-10 asphalt. The higher temperatures, 232 °C (450 °F) and 260 °C (500 °F), likely compensate for the lower RPM. In fact the 10-mesh material cured at 260 °C (500 °F) (run 16) exhibits a superb settling ratio. Even though asphalt-rubber cured with -80 mesh rubber more readily produces material with low settling ratios, excellent results can also be obtained with 10-mesh rubber.

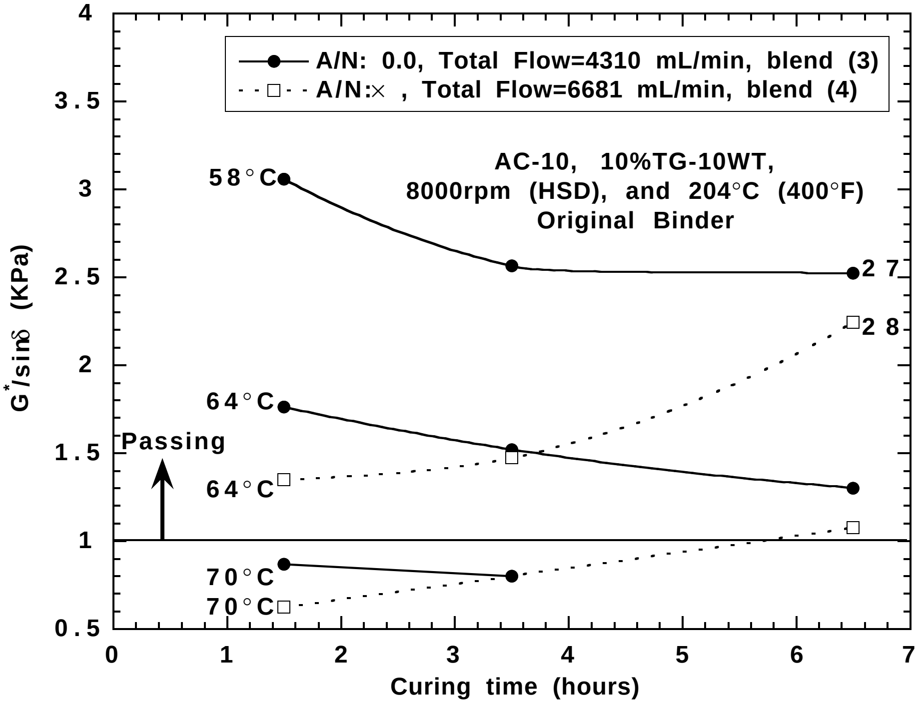

Figure 2-45. G*/sin delta versus Curing Time for Original AC-10 (10/90 TG-10WT) Binder with Varying A/N Ratios.

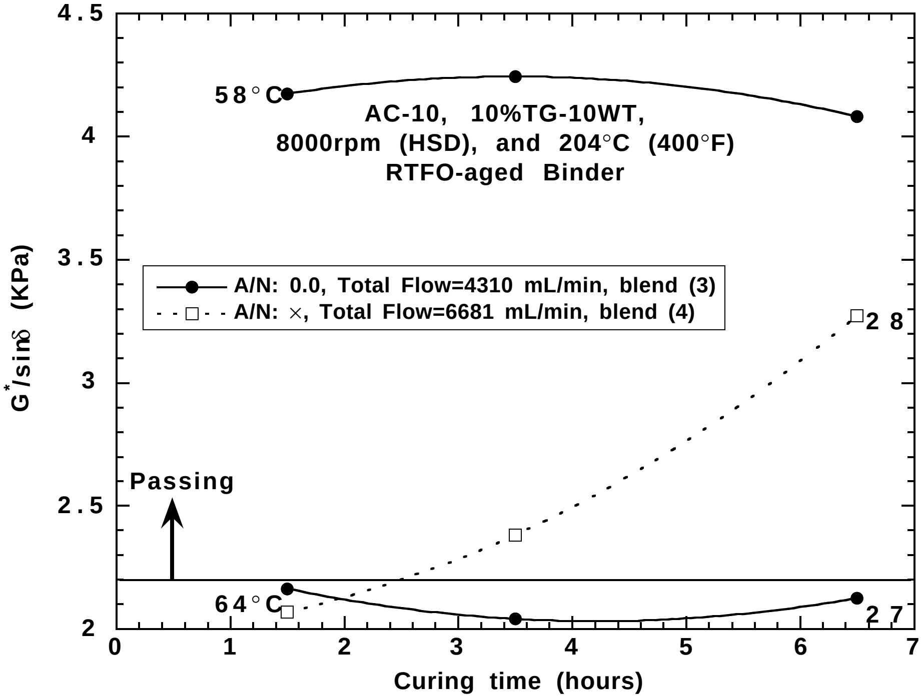

Figure 2-46. G*/sin delta versus Curing Time for RTFO-Aged AC-10 (10/90 TG-10WT) Binder with Varying A/N Ratios.

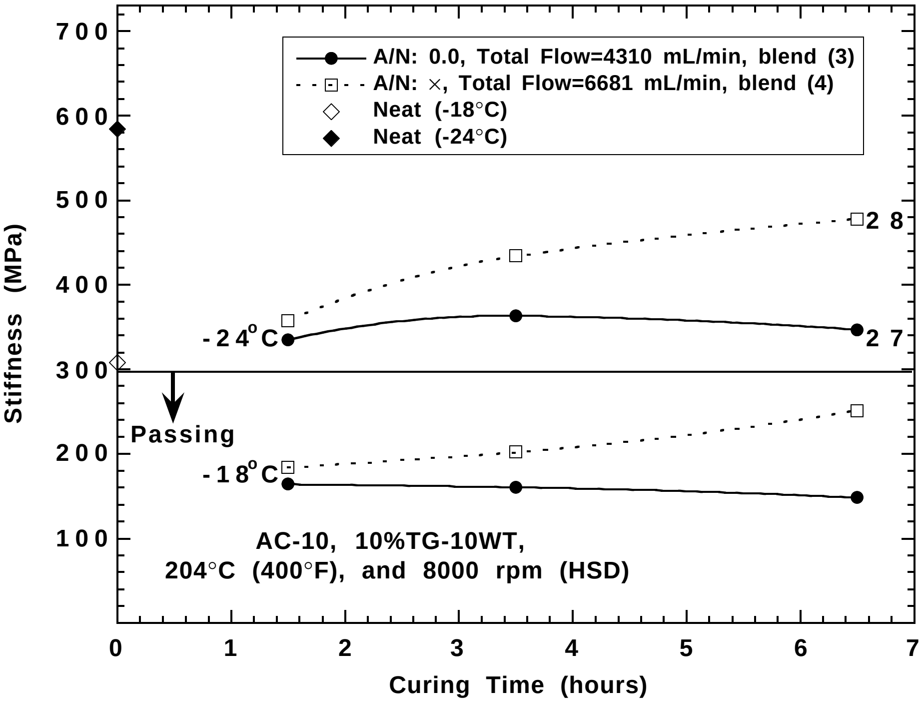

Figure 2-47. Stiffness versus Curing Time for AC-10 (10TG-10WT) Blends with Varying A/N Ratios.

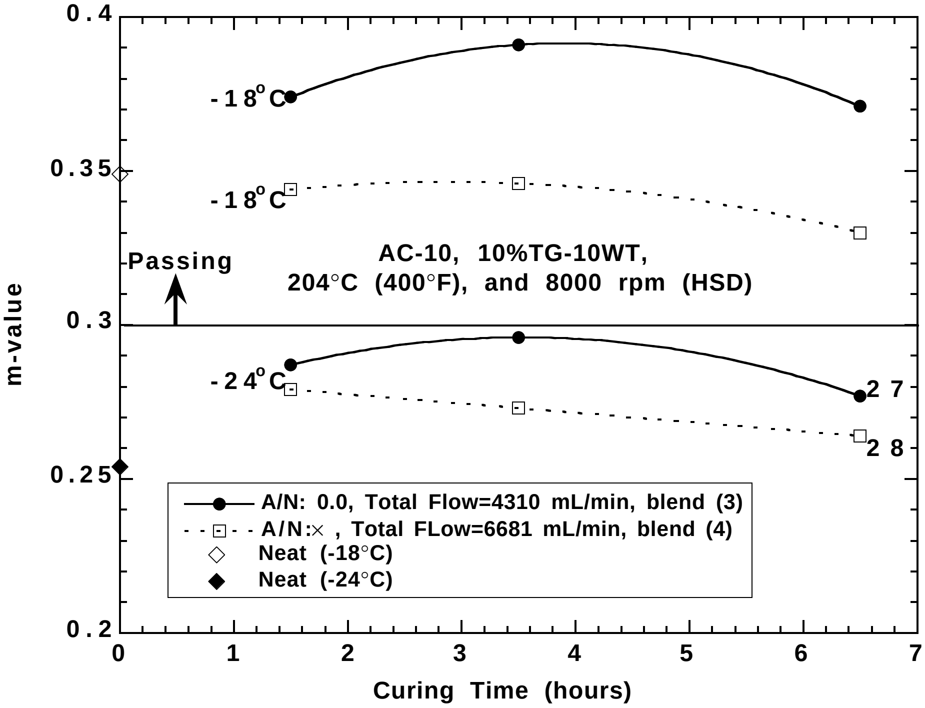

Figure 2-48. Creep Rate (m-value) versus Curing Time for AC-10 (10/90 TG-10WT) Blends with Varying A/N Ratios.

The Effect of High-Curing on Superpave Parameters

Figures 2-45 through 2-48 show how Superpave parameters change during curing for an AC-10, 10-mesh blend with and without air. Without oxidation, $G^*/\sin\delta$ decreases or remains constant as curing progresses, whether curing occurs with the original binder (Figure 2-45) or after RTFO aging (Figure 2-46). With air, the oxidation increases $G^*/\sin\delta$. Figures 2-47 and 2-48 compare the same two runs with respect to low-temperature parameters. Without air, curing time has little effect on the low-temperature parameters while air curing causes a slight deterioration in both S and m which is small when compared to the increase in $G^*/\sin\delta$. There is actually not much difference in the grade span of these two materials (cured without air versus cured with air). The chief advantage of air curing as far as grade is concerned is to raise the top end and thus the overall span.

Conclusions

Excellent grade material can be made by combining high-shear, high-temperature curing with air to produce HCAR. Very high grade span can be obtained with the main benefit of rubber being to perhaps add a grade at the bottom. Combining air oxidation and high shear is particularly effective in producing a material with excellent settling properties that also has a low high-temperature viscosity which aids compaction. Though more data are needed, there is evidence that curing temperatures at 260 °C (500 °F) would give excellent settling properties without harming the grade span. Recent studies also indicate that this material will possess improved long-term hardening characteristics relative to neat asphalts.

SUMMARY OF CHAPTER 2

A high-cure asphalt rubber binder suitable for use in dense graded mixes can be produced through a combination of high temperature and high shear. Temperatures close to 260 °C (500 °F), together with high shear in a colloid mill having a gap of 254 µm (0.010 inch) generally are capable of producing sufficient digestion of the rubber particles. The time required, however, varies with the composition of the asphalt and the starting mesh size of the rubber. Temperatures below 232 °C (450 °F) are significantly less efficient at curing the rubber. Milder conditions of shear and temperature, without the narrow-gap high-shear disintegrating head, may do little more than swell the rubber particles as they absorb compounds from the asphalt.

Production in the presence of oxygen can enhance the breakdown of rubber and the curing process. As with curing in the absence of oxygen, higher temperature, higher shear, and finer initial mesh rubber all decrease the time to achieve a high cure. With the addition of oxygen to the curing, however, there is an added effect of oxidizing the asphalt to a higher SuperPave performance grade, without seriously degrading the low-temperature grade. Typically, for every 10 degree increase in upper grade there is a five degree or less loss of low-temperature grade. Thus, combining oxidation with curing enhances both the rate of rubber cure and the PG grade span. Spans of over 100 degrees are readily obtained. As with any oxidation process using an organic material, safety precautions must be observed and temperatures and air flow should not exceed a safe level.

By either curing method (with or without oxidation) a material with excellent settling stability and a high-temperature (135 °C, 275 °F) viscosity that meets the SuperPave specification of less than 3 Pa·s (30 poise) can be obtained.

CHAPTER 3. ISSUES RELATED TO PERFORMANCE PROPERTIES OF CRUMB-RUBBER MODIFIED ASPHALT

In recent years Superpave PG specifications have been introduced for rating asphalt binders. These specifications address both high- and low-temperature performance (representing high and low extremes of pavement service temperatures). The high-temperature rating deals with the binder viscosity and is intended to address rutting as a failure mechanism while the low-temperature rating addresses thermal cracking. An intermediate-temperature parameter is designed to address fatigue cracking but is widely recognized to be deficient in this objective. All of these specification properties are measured after a designated aging period (20 hours) at elevated temperature and pressure as a means of taking into account binder in-service durability, but it is recognized that this process is fundamentally flawed and therefore is only a very approximate indication of acceptability with respect to aging and performance.

It should be noted that the Superpave PG system is designed for asphalt binders and has not been extended to modified binders, including asphalt-rubber materials. Nevertheless, an investigation of the PG properties of the high-cure asphalt-rubber materials of this project was performed as a necessary benchmark of the binder's performance relative to other materials.

This chapter details a laboratory investigation of the Superpave properties of crumb-rubber modified materials and other issues related to performance. Of particular interest is the effect of curing on the PG properties and how low-, intermediate-, and high-cure materials compare at both the high and low ends of the PG spectrum.

A second study continues PG evaluation but focuses more on settling stability as well. From a handling viewpoint, the better the rubber is cured, the less the tendency to settle and the easier the material handles with respect to hot-mix processing, storage stability, and pavement compaction. However, curing too far can result in a loss of the PG property enhancements imparted by the rubber.

Third, not all asphalts interact with ground tire rubber in the same way or to the same degree. Some binders experience considerably more PG improvement by the rubber than others, and curing differences are observed as well. A study of asphalt composition, in the sense of Corbett analyses, was undertaken to assess some of these differences.

A fourth study involved understanding how the high-temperature viscosity, relevant to hot-mix processing, is related to the extent of cure and rubber composition. More extensive curing can bring down this viscosity, but too much can adversely impact PG improvement. As part of this study, a method for tracking the curing has been developed which can be applied industrially as a QC/QA method for producing the properly cured material.

Finally, example data on the effect of incorporating high-cure ground tire rubber in asphalt on the low-temperature direct tension properties are presented.

THE EFFECT OF ASPHALT-RUBBER BINDER CURING ON PERFORMANCE GRADE PROPERTIES

Abstract

A number of blending strategies for producing CRMA, or asphalt rubber, were compared using Strategic Highway Research Program (SHRP) PG tests for asphalt binders. Process parameters that were studied were asphalt composition, rubber type and content, rubber mesh size, curing time and temperature, and the rate or shear of mixing on PG properties.

Curing at relatively low temperatures, around those of the hot-mix process, and low-shear rates, conditions typical of current industrial practices, leads to mineral interaction of the rubber material with the binder. The blended material has an increased viscosity due to the presence of the rubber particles. Low-temperature stiffness is improved, high pavement temperature G*/sin δ is increased significantly, and overall, the PG span is considerably widened; however, many low-cure materials do not meet the optional maximum high-temperature viscosity criterion of 3 Pa·s (30 poise) at 135 °C (275 °F) and settling of the swollen rubber particles can be a concern for storage.

Curing with higher shear mixing and higher temperature further breaks down the rubber particles and digests the long polymer chains and crosslink structures. The blend viscosity decreases with additional curing, but remains elevated above that of the base asphalt material. A particle phase continues to coexist with the binder, but its size distribution rapidly declines as shortened polymer chains are integrated into the binder phase. This yields a polymer-reinforced binder phase coupled with a lower particle fraction. Resulting viscosities at hot-mix installation and at rutting conditions are reduced compared to the lower shear preparations and can be lowered to the point of meeting the high-temperature viscosity criterion. However, it certainly is possible to cure too far. Materials produced at the highest level of curing indicate severe polymer degradation. These materials widen the PG span only incrementally when using a continuous grading, or single degree increment basis, but do not always yield improvement on a specification basis.

Concept of Superpave

Asphalt has traditionally been defined as the bottoms product of vacuum distillation of crude oil. As such, it is a hard viscoelastic liquid at room temperature which is ideal for a long-term adhesive. But road implementation is not limited to a single temperature, and many extremes, with respective stresses, can affect the performance. On hot days, the binder can liquefy and allow the pavement to permanently shift under load, a condition known as rutting; and on cold days, the binder may relax stresses too slowly leading to failure. In addition, asphalt is a reactive material. Embrittlement over time eventually erodes its ability to relax under stress, leading to failure. Many methods have been employed to characterize and predict the material’s ability to perform. The Superpave binder specifications are a combination of modern methods of evaluating and predicting the performance of asphalt binders (Asphalt Institute, 1995). Under this system, the ideal binder is capable of withstanding the possible temperature extremes expected to occur during the normal service life. It must withstand rutting at high temperatures maintaining a sufficient viscosity, while maintaining the capability to relax when low-temperature stresses are present. It must age without excessive hardening.

Tire Rubber Modifiers and Superpave

The addition of ground tire rubber to asphalt provides a resilient component to improve elastic properties. This is accomplished by employing a material that is far less sensitive to temperature changes than asphalt. But the presence of the solid also affects the viscosity. This influence on viscosity is a very important consideration, as the level of crumb rubber incorporation can be controlled. The Einstein equation (3-1) for a dilute solution of solid spheres may be considered a crude lower bound for analysis (Rosen, 1993).

$$\eta = \eta_s (1 + 2.5\varphi) \tag{3-1}$$

Another approximation, the Pal-Rhodes model (3-2), is more adjustable, and may therefore be more useful for lower cure blends (Pal and Rhodes, 1989).

$$\eta = \eta_s (1 - Kx)^{-\nu} \tag{3-2}$$

But these models become more difficult to employ as rubber begins to shift into the carrier phase. The decreasing solids fraction; x or φ, greatly offsets increasing liquid phase viscosity, η_s, as curing progresses. Utilizing more intensive blending conditions leads to a less heterogeneous matrix, lowering the bulk viscosity, especially in the compaction range. The resultant high-cure viscosity is considerably lower than previous lower cure blends and aging, and other properties are favorably affected (Billiter et al., 1997c). This work is a study of CRMA materials to determine and improve their performance properties.

Materials

Several asphalt materials were employed in this study including materials from the SHRP materials reference library (MRL). In addition to SHRP ABL-2 and SHRP ABM-1, one low-viscosity resin, two AC-5, two AC-10, and one AC-20 materials were obtained from Texas refineries. These binders are described in Tables 3-1 and 3-2. Table 3-1 identifies the asphalts by viscosity, while Table 3-2 indicates the compositional analyses of selected asphalts.

Further, several additional binders were produced in the laboratory to attain selected viscosity or compositional qualities. “ABM-F” and “SC (supercritical) Asphalt #1” were

Table 3-1. Description of Asphalts Studied. [a]

Asphalt Name	η* (dPa·s (poise)) 60 °C and 1.0 rad/sec	Source Refinery	Laboratory Modifications
SHRP ABL-2[b]	1,097	MRL	None
SHRP ABM-1[b]	2,409	MRL	None
Resin #1[c]	238.6	A	None
AC-5 #1	548.4	B	None
AC-5 #2	636.3	C	None
AC-10 #1	944.0	A	None
AC-10 #2[c]	952.0	C	None
AC-20 #1	2,029	D	None
ABM-F	201.8	MRL	Supercritical Fraction of SHRP ABM-1
House #1	507.9	A	1:1 Resin #1 and AC-10 #1
House #2	561.0	C	AC-10 #2 was blended 47:3 with a commercial recycling agent: η*= 5.5
SC Asphalt #1	634.6	E	SC Fraction of an AC-20 #3 (Refinery F)
Flux #1	70	F	Air-Blown to Viscosity or PG Grade - (Air Blowing Target)
F1AB-15	1,400	F	AC-15 - (AC-20)
F1AB-20	2,005	F	“A Mix” - AC-20 (AC-20)
F1AB-65	3,071	F	PG 65 - (PG 64)
F1AB-67	4,233	F	PG 67 - (PG 70)
F1AB-68	4,073	F	“B Mix” - PG 70 (PG 68)

[a] Portions after Billiter et al. (1997c).
[b] Jones (1993).
[c] Blending Study Materials

Table 3-2. Compositions of Selected Asphalts.

Asphalt	% Asphaltenes	% Polar Aromatics	% Naphthene Aromatics	% Saturates
SHRP AAA-1[a]	16.2	37.3	31.8	10.6
SHRP ABL-2[a]	17.0	47.6	24.9	8.6
SHRP ABM-1[a]	7.1	52.4	29.6	9.0
Resin #1[b]	3.0	38.2	49.6	9.2
AC-5 #1[c]	8.0	74.4[e]		17.6 [c]
AC-5 #2[d]	10.8	31.1	45.5	12.6
AC-10 #1[b]	14.5	30.1	43.4	12.1
AC-10 #2[b]	12.7	26.6	48.4	12.3
AC-20 #1	21.7	30.5	36.1	11.7
House #1[b]	8.7	34.2	46.5	10.6
House #2[b]	11.9	25.8	49.8	12.5
SC Asphalt #1	2.7	35.7	52.6	8.7

[a] Jones (1993).
[c] Chaffin (1996) and saturates by difference.
[b] Billiter (1997c).
[d] Bullin et al. (1996).
[e] Polar and naphthene aromatic fractions combined

produced by fractionating their respective source from materials fractionated in supercritical n-pentane by a modified Residual Oil Supercritical Extraction (ROSE) process, described by Jemison et al. (1992) and Stegeman et al. (1992). Asphalts "House #1" and "House #2" were created to study the effect of compositional differences on blend and aging properties (Corbett, 1970; Peterson, 1993).

A study by Domke et al. (1999b) removed pentane and hexane asphaltenes from a selection of SHRP asphalts and replaced them with heptane asphaltenes. By doing this a quasi-asphaltene fraction was removed from the materials, and the aging properties were examined. The Domke study suggests that these quasi-asphaltenes are prone to rapid aging and are affected by aging pressure. The industrial use of selective asphaltene removal by Corbett solvent extraction may be impractical. Instead the use of very light materials that do not initially contain the pentane and hexane asphaltenes was substituted. Flux #1 was selected to study a technique of removing rapid aging by pre-aging - i.e. mildly air blowing - a softer binder to the desired viscosity. Several batches of Flux #1 were air blown to the viscosity or grades listed in Table 3-1. The house air supply was found to fluctuate and timed air blowing was not feasible. To alleviate this problem, F1AB-20 and F1AB-68 were produced by air blowing several repetitions and mixing the resulting materials together. This allowed for further studies of an identical material, experiments not related to this study. F1AB-20, also called "A Mix," was produced by combining three air-blowing runs, while F1AB-68, "B Mix" was the result of seven runs.

Three types of ground tire rubber were obtained from two sources. RS- 40 was a -40 mesh material obtained from Rouse Rubber, located in Vicksburg, Mississippi. TG-10, a -10 mesh whole tire derivative, and TG-40, a -40 mesh material, were both obtained from Granular Products in Mexia, Texas. Blends produced ranged from 5 percent to 20 percent rubber by mass. (The Mexia, Texas, company is no longer in business.)

The majority of CRMA binders examined in this study were produced by Billiter et al. (1997a, 1997b, 1997c). All materials were prepared on a mass basis. Curing matrices were developed from the materials described above and represent a progression of curing degree. "Low-cure" blends (Billiter et al. 1997a), Table 3-3, were a comparison of up to three rubber materials blended at compositions of 5, 10, 15, and either 18 or 20 percent. All blending was performed at 177 °C (350 °F) and 500 rpm for one hour, using a motor-driven impeller. This material represents the state of the industrial practice in some Texas districts. SHRP ABL-2, ABM-1, ABM-F, and AC-5 #1 blends were produced by Billiter. In order to study this curing method further and compare it with other curing methods, blends of Resin #1 and AC-10 #2 were produced.

"Intermediate-cure" blending (Billiter et al. 1997b) of Resin #1, AC-5 #2, AC-10 #1, and AC-10 #2 was performed at 191 °C (375 °F) and either 500 rpm for 12 hours ("Long-Term") or 1550 rpm for six hours ("High-Shear"). Long-term blends, Blends #20x and #21x in Table 3-4, examined TG-40 and RS-40 at lower rubber content, 5 and 10 percent, while high-shear blending employed only TG-40 at 10 and 20 percent rubber content (Blends #22x).

Finally, Billiter et al. (1997c) studied "high-cure" blends of Resin #1 and AC-10 #2. Prior to high-cure blending, Billiter also performed some laboratory modification to these materials to study the effect of slight compositional differences (1997c), Table 3-1. Resin #1 was blended with AC- 10 #1, obtained from the same refinery, to produce House #1, with a higher viscosity than Resin #1, while AC-10 #2 was blended with a commercial recycling agent to produce House #2. High-cure blending was performed for 6.5 hours. Both Resin #1 and AC-10 #2, containing 10 percent TG-10, were produced at 4000 rpm and 260 °C (500 °F), which should be considered the "base high-cure" conditions. Then, one material or method parameter was allowed to vary to one of the following materials: 20 percent TG-10, 10 percent TG-40, or House #1 or #2; and methods: 8000 rpm, or 232 °C (450 °F), as shown in Table 3-5. The goal of substituting House #1 for Resin #1 (and of House #2 for AC-10 #2) was to study the effect on the blending process of a slightly varied asphalt composition. All of these materials were of relatively low viscosity.

Table 3-3. Low-Cure Blend Matrix. [a]

Asphalts	SHRP ABL-2	SHRP ABM-1	SHRP AAA-1 Fraction	SHRP ABM-1 Fraction	Weight Percent Rubber	Rubber Type / Mesh
Blend Designation	#101	#113	---	#128	5	TG-10
	#102	#114	#125	#129		TG-40
	#103	#115	---	---		RS-40
	#104	#116	---	#130	10	TG-10
	#105	#117	#126	#131		TG-40
	#106	#118	---	---		RS-40
	#107	#119	---	#132	15	TG-10
	#108	#120	#127	#133		TG-40
	#109	#121	---	---		RS-40
	#110	#122	---	---	18	TG-10
	#111	#123	---	---		TG-40
	#112	#124	---	---		RS-40
	---	---	---	#134	20	TG-10
	---	---	---	#135		TG-40

Asphalts	AC-5 #1	Resin #1	AC-10 #2	Weight Percent Rubber	Rubber Type / Mesh
Blend Designation	#141	---	---	5	TG-10
	#142	---	#153		TG-40
	#143	---	---	10	TG-10
	#144	#151	#154		TG-40
	#145	---	---	15	TG-10
	#146	---	#155		TG-40
	#147	---	---	20	TG-10
	#148	#152	#156		TG-40

[a] Curing Temperature: 177 °C (350 °F)
Mixer Conditions: 500 rpm impeller for 1 hour

Table 3-4. Intermediate-Cure Blend Matrix.

Asphalt	Resin #1	AC-5 #2	AC-10 #1	AC-10 #2	Weight Percent Rubber	Rubber Type / Mesh
Blend Designation[a]	---	#201	#205	#209	5	TG-40
	---	#202	#206	#210		RS-40
	---	#203	#207	#211	10	TG-40
	---	#204	#208	#212		RS-40
Blend Designation[b]	#221	#223	#225	#227	10	TG-40
	#222	#224	#226	#228	20	

[a b] Curing Temperature: 191 °C (375 °F)

[a] Mixer Conditions: 500 rpm impeller for 12 hours - (Long-Term)

[b] Mixer Conditions: 1550 rpm impeller for 6 hours - (High-Shear)

Table 3-5. High-Cure Blend Matrix. [a]

Modifier Blend #	Resin #1	AC-10 #2	SC Asphalt	Weight Percent Rubber	Rubber Type / Mesh	Silverson Mixer Speed (rpm)	Curing Temperature
	#301	#307	#313	10	TG-10	4000	260 °C (500 °F)
	#302	#308	#314				232 °C (450 °F)
	#303	#309	---			8000	260 °C (500 °F)
	#304	#310	---		TG-40	4000	
	#305	#311	---	20	TG-10		
House #1	#306	---	---	10			
House #2	---	#312	---				
AC-20 #1			#321	15	RS-80	8000	246 °C (475 °F)
			#322	10			

[a] Mixer Conditions: Slotted disintegrating head for 6.5 hours

To further study the effect of the high-cure process on materials with high viscosity and to facilitate test section projects, subsequent high-cure blends of AC-20 #1 were prepared as described in Table 3-5, and by a commercial colloid mill technique. Flux #1 was air blown to the desired asphalt concrete (AC) or PG grade and was cured as listed in Table 3-6. Blend designations #332 through #341 represent only four actual high-cure blends, with sampling at the indicated intervals. All high-cure blends were produced using a Silverson L4RT laboratory mixer with a slotted disintegrating head.

Experimental Methods

A large selection of the materials produced for Billiter et al. (1997b, 1997c) were evaluated using the Asphalt Institute PG testing methods, American Association of State Highway and Transportation Officials (AASHTO) designation MP1-93.1B (1996), with some modification of specifications as detailed below (Asphalt Institute, 1995). The RTFOT was employed for high-shear and high-cure blends in accordance with AASHTO T240-97 (1997). Materials produced by lower temperature and lower shear means were aged by the thin film oven test (TFOT), AASHTO T179-97 (1997). Long-term aging was simulated by the PAV, AASHTO PP1-93.1B (1996). Testing of aged and unaged materials was performed over three temperature ranges. High-temperature viscosity (HTV) was obtained using both a Brookfield Model RVF-7 rotational viscometer and a Brookfield DV-III rotational viscometer. The dynamic shear rheometer was used to evaluate intermediate-temperature properties, following AASHTO TP5-93.1B (1996). Low-temperature properties were measured using a Canon Thermoelectric BBR, following AASHTO TP1-93.1A (1993), and an Instron BTI-3 Direct Tension Test Machine, following AASHTO TP3-93.1B (1996). Preparation of the asphalt beams for the low-temperature tests was facilitated by a relaxation of the pouring temperature requirement, described below.

In reporting the final PG results, two methods were employed. The standard method employs incremental grading on a 6 °C increment basis. This value is the Superpave grade and is always reported as required by AASHTO MP1-93.1B (1996). In order to enhance comparisons of similar materials, a "continuous" PG grade was also determined. The material was evaluated over several Superpave test temperatures for any given test. The results are processed using an exponential fit to determine the temperature at which the specification was met. A comparison of unaged and (R)TFOT aged quadratic fits, for the high-grade value, produced a constraining minimum temperature, where both requirements are satisfied. This value is truncated to the unit's place and reported as the "continuous" grade. Similarly, the low-temperature BBR stiffness and m-value fits combined to determine a continuous lower bound. Comparisons of batches of material, blending matrices, etc. are readily made and communicated with this tool.

Of the materials available for this study, 49 low-cure, 20 intermediate-cure, and 26 high-cure blends, not all blends could be evaluated, due to lack of material. The nature of the RTFOT causes it to yield only 20 to 25 grams of aged material. Therefore, a minimum of three RTFOT bottles are required to fill the first PAV pan; 105 grams of material are needed to perform a

Table 3-6. Exploratory High-Cure Blends Using Flux #1.

Designation	Modification - Air Blow to:		Cure Time (hr)	Cure Technique
	Target	Result		
Blend #331	AC-20	AC-15	6.5	Silverson slotted disintegrating head mixer 12% GF-20 8000 rpm 260 °C (500 °F)
#332	F1AB-20		1.5	
#333	AC-20 “A Mix”	AC-20	3.0	
#334			4.5	
#335	F1AB-67		1.5	
#336	PG 64	PG 65	3.0	
#337			4.5	
#338	F1AB-67		1.5	
#339	PG 70	PG 67	3.0	
#340			4.5	
#341	F1AB-68		0.0	
#342			0.5	
#343	PG 70 “B Mix”	PG 68	1.0	
#344			1.5	
#345			2.0	
#346			3.5	

50-gram PAV test. Low- and intermediate-cure blends were produced in quart cans; and, previous testing had depleted many samples below the requirement. This challenge was eased by another problem that facilitated the use of the smaller sample sizes. Many of the low-cure blends, especially those with higher rubber content, failed to wet the bottles during the RTFOT. This created concerns that the RTFOT would not satisfactorily simulate short-term aging. In order to achieve the necessary hot-mix aging, the TFOT was substituted for the RTFOT. Once this necessity was realized, the substitution was made for the remainder of the low- and intermediate-cure modified blends. The respective neat asphalts were run by RTFOT. Therefore, a larger selection of blends could be evaluated by easing the material requirement to a multiple of the 50 gram TFOT/ PAV pans. About half of the high-cure blends were actually evaluated first, Blends #301 to #314, and no wetting problems were observed. Therefore, RTFOT aging results are presented for all high-cure blends.

Results

High-Temperature Viscosity

The failure of some low-cure blends to fully wet the RTFOT bottle is very indicative of the nature of the material. Tables 3-7 and 3-8 list HTV for a selection of curing conditions; Table 3-7 viscosities were measured using a Brookfield RVF-7 viscometer and Table 3-8 viscosities with the Brookfield DV-III. The HTV of several low-cure blends exceeds the optional 30 poise specification, in some cases by a great deal. This explains the inability to coat the RTFOT bottles. But because the objective of this work is a comparison of the materials and methods employed by Billiter et al. (1997b, 1997c), we report the PG results even if the material failed the HTV requirement. The high viscosities created problems in sample preparation for the BBR and the direct tension test (DT). The specification pour temperature is between 135 °C (275 °F) and 163 °C (325 °F), the same range at which HTV values were as high as hundreds of poise. A relaxation of this requirement was necessitated for some lower cure blends, which were prepared in the 200 °C range. Without this relaxation, the poured beams contained unacceptable air voids. The air voids were the result of the elevated viscosities and the increase in viscosity, due to cooling, as the specimens were poured. Samples with air voids were not tested.

Other interesting observations from the HTVs presented are the effects of cure level, rubber content, and rubber particle size. All blends show an increase in HTV as tire rubber is added, but the low-cure blends, Blends #1xx, show a rapid increase in viscosity above 10 percent content. In contrast the high-cure blends, Blends #3xx, show a modest increase at 20 percent content, Blends #305 and #311. With regard to particle size, the low-cure material HTV jumps incredibly high for Blend #111, the sample with the smaller particle size. This seems contrary to common sense, but the material possesses a much greater surface to volume ratio than the larger mesh rubber. Both increased rubber content and increased particle surface area raises the HTV, while higher curing temperature and shear reduced the HTV. This distinction indicates a greatly different interaction mechanism at the varied cure levels.

Upper Grade Performance

Of all the PG properties of the binder, the employment of CRMA has the most beneficial effect on high-temperature performance, an effect which diminishes with increased cure. The high-temperature portion of the PG span is indicative of the material’s rutting resistance. Tables 3-9 through 3-11 list both PG and the continuous grade of low-, intermediate-, and high-cure blends, respectively. The unfavorable high-temperature viscosity results, discussed above, suggest that significant improvement in the upper PG value can be made with the addition of tire rubber. This is especially the case for the low-cure blends, Table 3-9. A 10 percent rubber content increases the upper continuous grade by five degrees or more, easily resulting in an incremental PG jump, for most materials. The addition of more rubber continues to improve the upper grade, with some dependence upon the mesh size used.

Table 3-7. High-Temperature Viscosities of Selected Blends - Brookfield RVF-7 Viscometer.

Material Designation	Description	HTV [a]	Material Designation	Description	HTV [a]
SHRP ABL-2		3.2	AC-10 #1		3.4
Blend #104	10% TG-10	10.2	Blend #205	5% TG-40	4.6
Blend #105	10% TG-40	9.8	Blend #207	10% TG-40	11.6
Blend #110	18% TG-10	100	Resin #1		1.8
Blend #111	18% TG-40	407	Blend #303	8000 rpm	4.3
SHRP ABM-1		3.7	Blend #305	20% TG-10	10.0
Blend #116	10% TG-10	19.9	AC-10 #2		4.2
Blend #122	18% TG-10	143	Blend #307	Base Cure	7.6
AC-5 #1		3.0	Blend #308	450 °F Cure	9.1
Blend #146	15% TG-40	61.6	Blend #309	8000 rpm	6.3
Blend #147	20% TG-10	33.2	Blend #310	10% TG-40	7.7
			Blend #311	20% TG-10	21.7

[a] High Temp. Viscosity at 135 °C (275 °F)

Table 3-8. High-Temperature Viscosities of Selected Materials - Brookfield DV-III Viscometer.

Material Designation	Description	HTV [a]	Material Designation	Description	HTV [a]
Resin #1		1.6	SHRP ABL-2		3.8
Blend #151	10% TG-40	4.0	AC-20 #1		5.6
Blend #152	20% TG-40	37.2	Blend #321		14.6
AC-10 #1		2.9	Blend #322		33.3
Blend #153	5% TG-40	4.5			20.2
Blend #154	10% TG-40	8.8			38.0
Blend #155	15% TG-40	23	Flux #1 PG 67		4.4
Blend #156	20% TG-40	76	Blend #338	1.5 hr	9.8
			Blend #339	3.0 hr	9.25
Flux #1 AC-20		3.4	Blend #340	4.5 hr	9.0
Blend #332	1.5 hr	7.1	Flux #1 PG 68		---
Blend #333	3.0 hr	6.3	Blend #341	0.0 hr	46
Blend #334	4.5 hr	6.3	Blend #342	0.5 hr	11.3
Flux #1 PG 65		3.8	Blend #343	1.0 hr	10.7
Blend #335	1.5 hr	9.3	Blend #344	1.5 hr	10.1
Blend #336	3.0 hr	7.6	Blend #345	2.0 hr	9.3
Blend #337	4.5 hr	6.8	Blend #346	3.5 hr	8.0

[a] High Temp. Viscosity at 135 °C (275 °F)

Table 3-9. Performance Grade of Low-Cure Blends by TFOT Aging. [a]

Rubber Content	**Asphalt** Rubber Type / Mesh		
	SHRP ABL-2 - (Neat = **64-28** [b] / *65-31* [c] *)* [d]		
	TG-10	TG-40	RS-40
5 %	**70-28** / *71-33*	**64-** / *69-*	[e]
10 %	**70-28** / *70-28* [d]	**70-28** / *70-31* [d]	**70-28** / *74-33*
15 %	**88-28** / *93-30*	**82-28** / *84-31* [d]	**82-34** / *83-36* [d]
18 %	**88-28** / *91-30*	**94-28** / *99-32*	**88-** / *90-*
	SHRP ABM-1 - (Neat = **64-10** / *65-14*) [d]		
	TG-10	TG-40	RS-40
5 %	**64-** / *67-*	**64-16** / *68-17*	**64-16** / *68-16*
10 %	**76-16** / *77-20*	**70-16** / *70-21*	**70-16** / *70-21*
15 %	**76-22** / *79-24*	[e]	**70-** / *70-*
18 %	**88-22** / *81-26*	**70-28** / *74-28*	[e]
	ABM-F		**Resin #1** (Neat = **46 -22** / *49-27*) [d]
	TG-10	TG-40	TG-40
5 %	**58-16** / *60-20*	**58-16** / *58-20*	---
10 %	**64-22** / *65-23*	**58-18** / *60-23*	**46-28** / *51-31* [d]
15 %	**64-22** / *68-26*	---	---
20 %	**70-28** / *70-29*	---	**52-34** / *56-36*
	AC-5 #1 (Neat = **52-28** / *55-29*) [d]		**AC-10 #2** (Neat = **58 -28** / *59-28*) [d]
	TG-10	TG-40	TG-40
5 %	**58-28** / *62-28*	**58-28** / *59-29* [d]	**58-28** / *62-30* [d]
10 %	**58-28** / *63-31* [d]	**58-28** / *59-30* [d]	**64-28** / *64-33* [d]
15 %	**70-34** / *70-34*	**58-28** / *62-33*	**64-34** / *68-35* [d]
15 %	---	---	**64-34** / *69-34*
20 %	[e]	**64-34** / *66-35*	**70-34** / *74-37*

[a] Curing Temperature: 177 °C (350 °F)
Mixer Conditions: 500 rpm impeller for 1 hour

[d] RTFOT Employed

[b] **Superpave Performance Grade**

[c] *Continuous Performance Grade*

[e] Insufficient Sample or Data

Table 3-10. Performance Grade of Intermediate-Cure Blends by TFOT Aging. [a]

Rubber Content	Asphalt Rubber Type / Mesh		
	Resin #1 - (Neat = **46-22** [b] / *49-27* [c]) [d]		
	TG-40 (LT)	RS-40 (LT)	TG-40 (HS)
10 %	---	---	**58-28** / *58-29*
20 %	---	---	**58-28** / *62-33*
	AC-5 #2 - (Neat = **52-** / *56-*)		
	TG-40 (LT)	RS-40 (LT)	TG-40 (HS)
5 %	[e]	[e]	---
10 %	[e]	**58-** / *62-*	**58-34** / *62-34*
20 %	---	---	**64-28** / *68-31*[d]
	AC-10 #1 - (Neat = **58-22** / 61-24)		
	TG-40 (LT)	RS-40 (LT)	TG-40 (HS)
5 %	**64-22** / *65-24*	**64-22** / *65-26*	---
10 %	**64-22** / *67-26*	**64-22** / *67-26*	**70-22** / *70-25*
20 %	---	---	**76-28** / *78-29*
	AC-10 #2 - (Neat = **58-28** /*59-28*)[d]		
	TG-40 (LT)	RS-40 (LT)	TG-40 (HS)
5 %	[e]	**64-28** / *69-29*	---
10 %	**64-28** / *69-30*	**64-28** / *69-31*	**64-28** / *66-31*
20 %	---	---	**70-34** / *74-36*

[a]		
Curing Temp: Mixer Cond:	LT - 191 °C (375 °F) 500 rpm for 12 hours	HS - 191 °C (375 °F) 1550 rpm 6 hrs

[b] **Superpave Performance Grade**

[c] *Continuous Performance Grade*

[d] RTFOT Employed

[e] Insufficient Sample or Data

Table 3-11. Performance Grade of High-Cure Blends. [a]

Designation	Description / Modification from Base Cure		Grade
Resin #1	Neat		**46-22** [b] / *49-27* [c]
Blend #301	Base - Resin #1 - 10% TG-10 - 260 °C (500 °F) - 4000 rpm		**46-28** / *47-30*
Blend #302	232 °C (450 °F) Cure		**46-22** / *50-24*
Blend #303	8000 rpm		**46-28** / *49-29*
Blend #304	10% TG-40		**46-28** / *46-30*
Blend #305	20% TG-10		**46-28** / *50-33*
Blend #306	1:1 of Resin #1 and AC-10 #1		**52-22** / *55-27*
AC-10 #2	Neat		**58-28** / *59-28*
Blend #307	Base - AC-10 #2 - 10% TG-10 - 260 °C (500 °F) - 4000 rpm		**58-28** / *61-30*
Blend #308	232 °C (450 °F) Cure		**58-28** / *63-31*
Blend #309	8000 rpm		**58-28** / *60-30*
Blend #310	10% TG-40		**58-28** / *60-30*
Blend #311	20% TG-10		**58-34** / *61-34*
Blend #312	6% Recycling Agent [5.5 Poise] and AC-10 #2		**52-28** / *57-33*
AC-20 #1	Neat		**64-28** / *65-30*
Blend #321	AC-20 #1 - 15% RS-80 -246 °C (475 °F) - 8000 rpm		**70-28** / *74-31*
---	F1AB-65	Neat	**64-28** / *65-32*
---	F1AB-67		**64-28** / *67-30*
Blend #331	F1AB-15	12% GF-20 8000 rpm 260 °C (500 °F)	**64-28** / *65-32*
Blend #332	F1AB-20 - 1.5 hours		**58-34** / *62-38*
Blend #333	F1AB-20 - 3.0 hours		**58-34** / *61-37*
Blend #334	F1AB-20 - 4.5 hours		**64-34** / *66-34*
Blend #336	F1AB-65 - 3.0 hours		**64-34** / *64-36*
Blend #337	F1AB-65 - 4.5 hours		**64-34** / *64-34*
Blend #339	F1AB-67 - 3.0 hours		**64-28** / *68-30*
Blend #340	F1AB-67 - 4.5 hours		**64-28** / *67-32*

[a] Slotted disintegrating head mixer for 6.5 hours, unless noted

[b] **Superpave Performance Grade**

[c] *Continuous Performance Grade*

SHRP ABL-2 benefits the most from increased rubber content, even accelerating in grade with the addition of rubber. ABM-1 and AC-5 #1 also increase in grade, but the increases are smaller. Both of these materials contain lower levels of asphaltenes than ABL-2, as seen in Table 3-2. Employing a smaller particle size yields less improvement overall, while varying the tire rubber source does not produce an appreciable grading difference. These materials gain significantly in performance, but the gain is arguably beyond the rutting requirement and at the risk of severe installation problems. For the intermediate-cure blends, Table 3-10, the type of rubber used, again, does not seem to affect the upper grade. Examining increasing tire rubber content does not show the accelerated effect of raising grade as SHRP ABL-2 did, and the materials employed are more similar to ABM-1 and AC-5 #1 in both grading results and Corbett compositional content. Still, improvement in grade with increasing rubber content is realized. Curing at a higher shear rate for a shorter time produces results similar to the long-term method.

The high-cure blends serve as a comparison of five variations in materials and methods, and Table 3-11 lists their results. Only by varying the asphalt's compositional content is the six degree upper grade affected, as shown by Blends #306 and #312. Blend #307, prepared at 232 °C (450 °F), increases the upper value the most, but still not enough to raise the grade. Improved performance is attained with Blend #321, with a nine degree upper grade increase, probably related to its higher asphaltene content, the highest of all the materials studied.

Low-Temperature Performance

The low-temperature portion of the PG span is indicative of the material's resistance to cracking, due to fatigue and thermal factors. Not only does CRMA easily pass the fatigue cracking requirement, it also decreases the low-temperature stiffness and increases the m-value. Only slight incremental improvement is seen at levels below 18 or 20 percent, and it is independent of rubber type, mesh, and even cure, Tables 3-9, 3-10, 3-11. The best improvement is observed for low-cure blends of SHRP ABM-1, which has the poorest low-temperature properties for the asphalts employed in the study; up to three grades were gained with this material, Table 3-9.

Conclusions

Both increased rubber content and increased particle surface area raised the HTV, while higher curing temperature and shear reduced the HTV. Once the HTV is reduced to reliable levels, the observed improvement in the rutting resistance grade is more dependent upon asphalt properties than blending variations and, for lower viscosity materials, is incremental improvement at best. For low-temperature properties where gains were modest, only the poorest of materials showed significant improvement at low temperature, while blending may not affect or perhaps reduce m-value performance of viscous feeds. These results suggest that an asphalt graded around AC-15, with fair low-temperature properties, or an AC-20 with good low-temperature performance, would best benefit from high-cure blending with ground tire rubber.

THE EFFECT OF SEVERAL HIGH-CURE SCENARIOS ON PERFORMANCE GRADE AND SETTLING STABILITY

This is a continuation of a study of curing conditions. Variables are curing temperature, time, and mixer rpm with percent rubber and asphalt type also considered, but most runs are made with an AC-10 and 10 percent 10-mesh rubber. A distinctive feature of this study is that after a settling period, a bottom portion is withdrawn, re-cured, and blended with the remaining material. In this way, only part of the material is subjected to the most extreme curing conditions, which cause some grade deterioration. The extent of cure and settling stability are measured by three tests: the ratio of the viscosity between top and bottom can in a settling test, the weight of rubber removed by filtration of a sample of the bottom cans, and the percent dissolved after a second cure.

Material and Experimental Design

The asphalt-rubber binders employed in this research were prepared from the following materials by using various experimental conditions. The main asphalt type used to create the blends was Exxon AC-10; however, “Resin D,” which is a material produced by supercritical extraction of a vacuum tower bottom, the Vacuum Tower Bottom (VTB) itself, and SHRP ABM-1 were chosen to produce some blends in order to study effects of asphalt type. Corbett analyses of these materials are shown in Table 3-12. Tire Gator “whole tire” -10 mesh was the only rubber used to produce asphalt-rubber blends. Typically, 10 percent by weight of rubber was added to 90 percent by weight of asphalt. But one blend was produced with 15 percent rubber by weight in order to investigate the effect of rubber content. Curing temperature, curing time, shear rate, air blowing, settling temperature, and settling time are variables in this study. Three curing temperatures 204 °C, 232 °C, and 260 °C (400 °F, 450 °F, and 500 °F), two curing times (3.5 and 6.0 hours), two shear rates (4000 and 8000 rpm), and with and without air blowing were chosen as curing conditions. Two temperatures 121 °C and 177 °C (250 °F and 350 °F) and two periods of time (8.0 and 12 hours) were used as settling conditions.

Table 3-12. Corbett Analyses of Asphalt Used in This Research.

Corbett Results	Exxon AC-10	Resin D	Vacuum Tower Bottom	SHRP ABM-1*
Asphaltenes	10.1%	3.5%	17.3%	7.1%
Saturates	11.6%	17.8%	20.2%	9.0%
Naphthene Aromatics	46.2%	54.8%	45.2%	29.6%
Polar Aromatics	30.7%	21.6%	18.4%	52.4%

* SHRP core asphalt from CA valley (AR-4000).

Each blend was produced and subjected to a series of tests. First, one gallon of asphalt-rubber blend was produced by a mixer which is called the first curing. Then, the blend was performance graded according to the Superpave specification. Next, the blend was settled in a settling pipe. After settling, the blend was drawn out at the bottom of the settling pipe and distributed equally into four quart cans: bottom, middle bottom, middle top, and top cans. The bottom can contained the asphalt-rubber blend drawn from the bottom level of the settling pipe. The middle bottom, middle top, and top cans contain asphalt-rubber blends taken from the next three upper layers, respectively. The complex viscosity of the material in each can was determined at 60 °C (140 °F) and 1.0 s^{-1}. A complex viscosity ratio, the complex viscosity for each can divided by the complex viscosity of the top can, was calculated. This value was used as a settling ratio. Material from each can was analyzed by GPC for a qualitative indicator of the amount and size of the dissolved fraction. Finally, the weight of rubber in the bottom can was found by a filter test.

Some rubber particles which were not dissolved into the blend after the first curing were settled to the bottom of the settling pipe; therefore, in order to achieve the objective of producing homogeneous blends, a secondary curing and the testing series were required. Only the bottom can material was re-cured by the secondary curing. After that, all four quart cans were re-mixed by hand stirring and were re-settled in the settling pipe. Before re-drawing the blend to four quart cans, either approximately 2.5 percent or 5 percent by weight of the blend was removed in order to remove the remaining undissolved rubber particles. This part of the blend is called a discarded fraction (D fraction) which was used only in a centrifuge experiment to determine the amount of the undissolved rubber in that fraction. The remaining fraction, which is called a PG fraction, was distributed equally into four quart cans. The complex viscosity at 60 °C (140 °F) and 1.0 s^{-1} of the material from each quart can was found in order to obtain the new settling ratio. The GPC was used again to determine the changes in the amount of rubber in each quart can after re-curing and re-settling. The filter test was completed to find the amount of rubber particles in the bottom can that remained on the filter paper after re-curing. After that, all materials in these four quart cans were re-blended without curing to obtain the PG of the blend. Finally, the percent dissolved rubber was determined by the centrifuge experiment. Figure 3-1 shows the two-step curing process.

In retrospect, the removal of the D fraction before testing was unfortunate as it made the effect of the second curing uncertain since both the settling ratio and grade were done on the PG fraction, and the filter test was run on the bottom fraction after removal of the D fraction. In practice it might be a good idea to remove a small amount of material from the bottom, but from an experimental standpoint, tests should have been made before and after removal of the D fractions. It did turn out that the calculation of “percent dissolved,” which included all the material, generally agreed with the other tests.

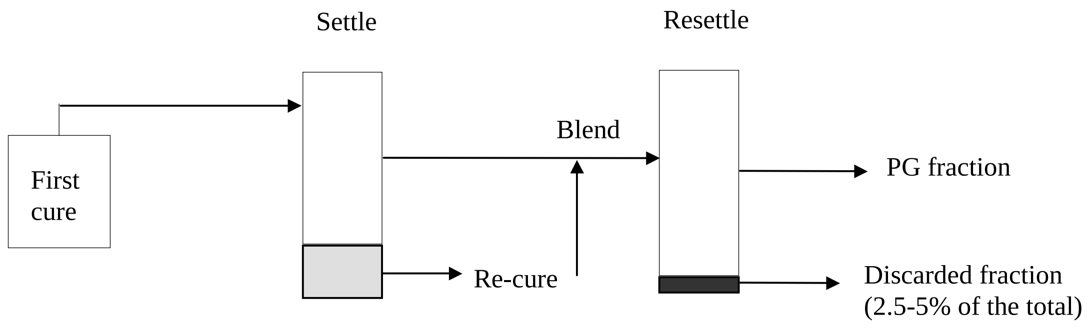

Figure 3-1. Schematic of the Two-Step Curing Process.

Filter Test

The filter test used in this research is modified from the method of Billiter et al. (1997b, 1997c). The purpose of this test is to determine the remaining rubber weight in asphalt-rubber blends as a function of curing conditions. This test is also used to confirm the percent dissolved rubber obtained from the centrifuge test.

The following is the filter testing procedure. Approximately one gram of asphalt-rubber binder was dissolved in 20 mL of THF overnight in order to ensure that all asphalt was dissolved and that only rubber remained. Then this solution was sonicated for about 30 minutes. The solution was vacuum filtered through the pre-weighed Whatman 42 filter paper. Additional THF was used to remove residual asphalt. The filter paper was then heated in an oven at 104 °C (220 °F) to evaporate the THF. The filter paper was removed from the oven after 1 hour and placed at ambient conditions for 24 hours to absorb humidity back into the paper. Finally, the paper was weighed and by difference the rubber weight was determined.

Centrifuge Experiment

An IEC MediSpin benchtop centrifuge was used to study the percent dissolved rubber in the asphalt blends. The centrifuge motor speed is 3100 rpm. The centrifuge has a six-place rotor which is symmetrically loaded with either two, three, four, or six tubes. The tubes must be of equal size and with contents of equal, to within one gram, weight. The translucent tube used in this test has a maximum volume of 14 mL.

The percent dissolved rubber is determined using the following centrifuge procedure. After re-settling the second-cure blend, either 2.5 percent or 5.0 percent, was taken from the bottom of the blend to remove the remaining undissolved material (see Figure 3-1). This part of the blend is called the discarded (D) fraction. Only the remaining material in the settling pipe was used to evaluate the performance of the binder; therefore, it is called the PG fraction. Consequently, each blend has two separated parts: D and PG fractions. Approximately 0.200, 0.500, and 1.000 grams of both D and PG fractions were put into the pre-weighed tubes. The samples were mixed with 14 mL of THF and sonicated for 30 minutes. After that, the solution was centrifuged for at least 30 minutes. The liquid solution was decanted, and the residual solid was left inside the tube. The tubes were placed in an oven at 104 °C (220 °F) for 24 hours in order to evaporate any THF remaining in the residual solid. After 24 hours, the tubes were removed from the oven and allowed to cool for five minutes before being weighed. The difference of the tare and dried weights of the tube is assumed to be the rubber weight.

However, any asphalt residue will result in error. In order to determine the error, neat Exxon AC-10 was put into five tubes: approximately 0.200 gram in two tubes, 0.500 gram in two tubes, and 1.000 gram in one tube. The centrifuge procedure followed the procedure mentioned above. The percent error was estimated from this step. Consequently, actual residual rubber weight can be found by subtracting the asphalt residue. Knowing the initial rubber content and the undissolved fraction in both PG and D fractions, the dissolved fraction could be calculated by a material balance, assuming the dissolved fraction to be the same in both PG and D fractions.

Experimental Results

The studies of this research can be classified into six categories. First, the effects of settling conditions were determined. Second, four blends produced at different curing conditions were re-cured at the same conditions in order to study the effect of the first curing conditions. Third, six blends were first produced at the same conditions, but the secondary curing conditions were varied in curing temperature, curing time, shear rate, and nitrogen or air blowing. The effects of the secondary curing conditions were evaluated from this experiment. Fourth, two rubber contents, 10 percent and 15 percent, were used to study the effect of rubber content. Fifth, different asphalt types were produced at the same conditions to investigate the effect of asphalt types. Finally, two air-blown asphalts were cured with rubber following a two-step curing process to determine the effects of air-blown asphalt. The principal effects studied in this research were the settling rate of rubber particles, the percent dissolved rubber, and the PG of the blends.

Settling Studies

Study I: Effects of Settling Conditions. To study the effects of settling conditions, four blends of Exxon AC-10 with 10 percent TG-10 rubber were produced at 204 °C (400 °F) and 8000 rpm for 3.5 hours under a nitrogen blanket. Then these blends were settled at different settling conditions as shown in Table 3-13. Except for the 121 °C (250 °F) and 8 hour test, there is little difference. Consequently, the settling conditions of 177 °C (350 °F) for 8 hours were used in further experiments.

Table 3-13. The Complex Viscosity and Settling Ratio After the First Curing and Settling of the Blends in Study I.

Blend/Can	Settling Temperature (°C)	Settling Time (hours)	η^* (poise)	η^* Ratio
09/02/97	121	8		
Top			1712	1.00
Middle Top			1596	0.93
Middle Bottom			1831	1.07
Bottom			2577	1.51
09/03/97	177	8		
Top			1568	1.00
Middle Top			1393	0.89
Middle Bottom			1818	1.16
Bottom			3231	2.06
09/09/97	121	12		
Top			1625	1.00
Middle Top			1941	1.19
Middle Bottom			2229	1.37
Bottom			3234	1.99
09/09/97	177	12		
Top			1500	1.00
Middle Top			1469	0.98
Middle Bottom			1552	1.03
Bottom			2932	1.95

It is quite probable that this settling time was marginal, particularly at higher viscosities, but as many runs were being made, it was a compromise, justified by the fact that relative values were of primary importance.

Settling Properties of Wright Asphalt. Wright asphalt is a binder of asphalt AC-10 with 10 percent rubber. It is believed to be a very homogeneous blend; therefore, the settling test was conducted to test the homogeneity of Wright asphalt. Due to the study of the settling conditions, Wright asphalt was settled at 177 °C (350 °F) for 8 hours. According to Table 3-14, it is obvious that the settling ratio of Wright asphalt in each quart can is almost equal to one. This verified that Wright asphalt is a very homogeneous binder. It is interesting to compare GPCs of Wright asphalt with asphalts produced in this study. The rubber that is able to be separated on the chromatographic column has passed a 0.4 µ filter and then separated on 1000 Å and smaller columns. It is safe to say that this material has been devulcanized and partly depolymerized. Figure 3-2 is the Wright asphalt, and Figure 3-3 is run 1/16/98(2) in Table 3-15. For the Wright asphalt, the large peak at about 20 minutes is completely gone. We assume that this peak is largely rubber that is devulcanized but not appreciably depolymerized. Yet there is still considerable material, though partly depolymerized, that has a higher molecular size than any asphalt components.

Though the settling properties of Wright asphalt are excellent, other desirable properties have been lost. In this work, we are attempting to produce material with good settling properties while retaining large rubber molecules and the properties they endow.

Table 3-14. The Complex Viscosity and Settling Ratio of Wright Asphalt.

Blend/Can	Settling Temperature (°C)	Settling Time (hours)	η^* (poise)	η^* Ratio
Before Settle	177	8	*577*	
Top			560	1.00
Middle Top			557	0.99
Middle Bottom			558	1.00
Bottom			553	0.99

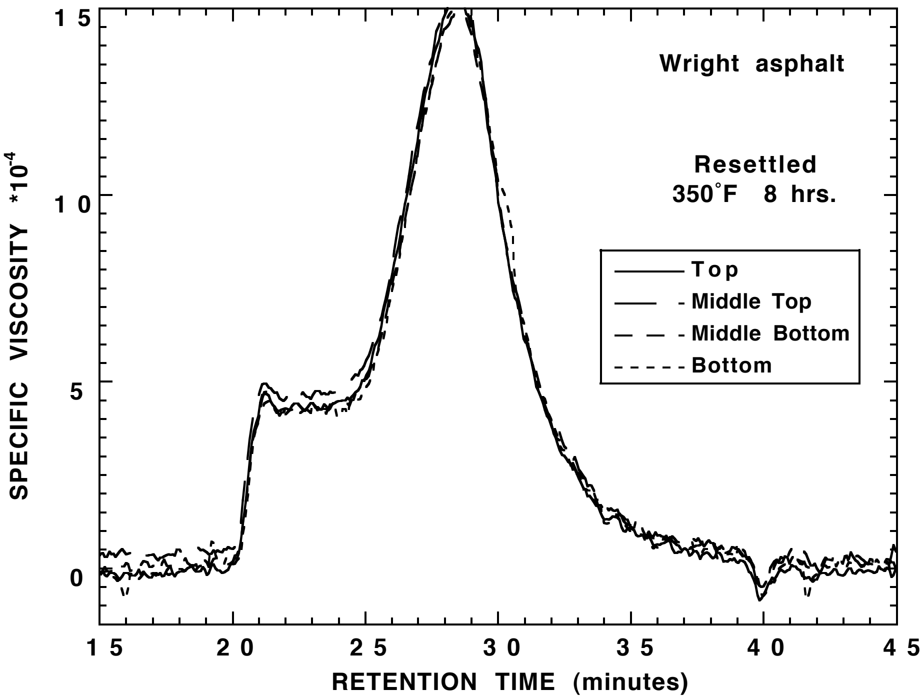

Figure 3-2. GPC Chromatogram of Wright Asphalt.

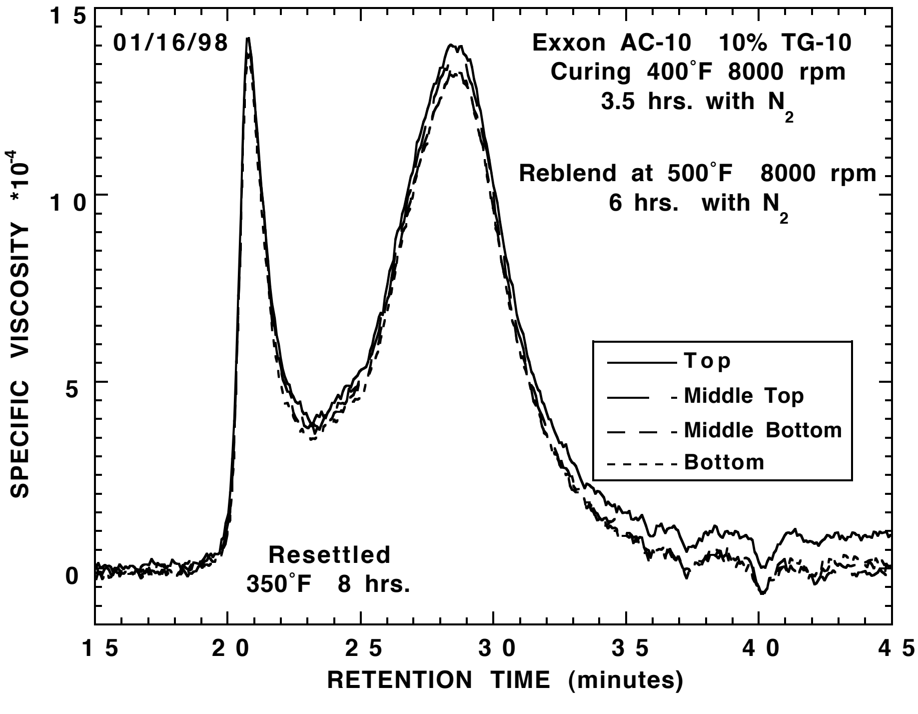

Figure 3-3. GPC Chromatogram of Blend 09/03/97 After Re-Curing.

Table 3-15. Studies of Curing Conditions and Asphalt Composition on Rubber Digestion.

Study	Asphalt Type	Rubber Amount (%)	Cure Conditions				η* Ratio	Filter Residue (g/g)	Centrifuge Test		
			Temp °C (°F)	Shear (RPM)	Time (hrs)	N_2 or Air			Undissolved		Dissolved
									PG Frac	D Frac	PG + D
Study II - Effect of First Cure Conditions											
First Cure:											
1-16-1998(1)	AC-10	10	400	8000	3.5	N_2	2.36	0.1842			
1-13-1998(1)	AC-10	10	450	8000	3.5	N_2	1.82	0.1064			
1-14-1998(1)	AC-10	10	400	8000	6	N_2	2.21	0.1323			
12-1-1997(1)	AC-10	10	450	8000	6	N_2	1.48	0.0974			
Second Cure:											
1-16-1998(2)	AC-10	10	500	8000	6	N_2	1.42	0.1183	4.09	0.53	5.37
1-13-1998(2)	AC-10	10	500	8000	6	N_2	1.31	0.0443	3.7	0.54	5.76
1-14-1998(2)	AC-10	10	500	8000	6	N_2	1.25	0.0668	2.71	0.64	6.64
12-1-1997(2)	AC-10	10	500	8000	6	N_2	1.16	0.0298	2.6	0.63	6.76
Study III - Effect of Secondary Cure Conditions											
First Cure:											
10-13-1997(1)	AC-10	10	400	8000	3.5	N_2	2.49	0.1868			
10-14-1997(1)	AC-10	10	400	8000	3.5	N_2	2.8	0.1381			
10-30-1997(1)	AC-10	10	400	8000	3.5	N_2	2.92	0.1596			
1-15-1998(1)	AC-10	10	400	8000	3.5	N_2	2.37	0.1496			
1-16-1998(1)	AC-10	10	400	8000	3.5	N_2	2.36	0.1842			
10-27-1997(1)	AC-10	10	400	8000	3.5	N_2	2.83	0.175			

Table 3-15. Studies of Curing Conditions and Asphalt Composition on Rubber Digestion. (Continued)

Study	Asphalt Type	Rubber Amount (%)	Cure Conditions				η* Ratio	Filter Residue (g/g)	Centrifuge Test		
			Temp °C (°F)	Shear (RPM)	Time (hrs)	N_2 or Air			Undissolved		Dissolved
									PG Frac	D Frac	PG + D
Study III (Continued)											
Second Cure:											
10-13-1997(2)	AC-10	10	400	4000	3.5	Air	1.81	0.1467	6.39	1.22	2.38
10-14-1997(2)	AC-10	10	400	4000	6	Air	1.39	0.0789	3.98	1.31	4.71
10-30-1997(2)	AC-10	10	450	8000	6	Air	1.23	0.0616	2.69	0.74	6.56
1-15-1998(2)	AC-10	10	450	8000	6	N_2	1.68	0.0895	4.27	0.55	5.17
1-16-1998(2)	AC-10	10	500	8000	6	N_2	1.42	0.1183	4.09	0.53	5.37
10-27-1997(2)	AC-10	10	500	4000	6	N_2	1.87	0.1242	3.33	1.48	5.18
Study IV - Effect of Rubber Content											
First Cure:											
12-1-1997(1)	AC-10	10	450	8000	6	N_2	1.48	0.0974			
3-2-1998(1)	AC-10	15	450	8000	6	N_2	1.87	0.1124			
Second Cure:											
12-1-1997(2)	AC-10	10	500	8000	6	N_2	1.16	0.0298	2.6	0.63	6.76
3-2-1998(2)	AC-10	15	500	8000	6	N_2	1.19	0.0529	5.28	0.41	9.31
									3.52[a]	0.27[a]	6.01[a]

[a] The value from the previous row, normalized to an initial rubber content of 10 wt percent.

Table 3-15. Studies of Curing Conditions and Asphalt Composition on Rubber Digestion. (Continued)

Study	Asphalt Type	Rubber Amount (%)	Cure Conditions Temp °C (°F)	Cure Conditions Shear (RPM)	Cure Conditions Time (hrs)	Cure Conditions N_2 or Air	η* Ratio	Filter Residue (g/g)	Centrifuge Test Undissolved PG Frac	Centrifuge Test Undissolved D Frac	Centrifuge Test Dissolved PG + D
Study V - Effect of Asphalt Type											
First Cure:											
12-1-1997(1)	AC-10	10	450	8000	6	N_2	1.48	0.0974			
3-4-1998(1)	VTB	10	450	8000	6	N_2	1.51	0.1197			
3-13-1998(1)	ABM-1	10	450	8000	6	N_2	1.67	0.1107			
Second Cure:											
12-1-1997(2)	AC-10	10	500	8000	6	N_2	1.16	0.0298	2.6	0.63	6.76
3-4-1998(2)	VTB	10	500	8000	6	N_2	1.17	0.0631	4.1	0.7	5.19
3-13-1998(2)	ABM-1	10	500	8000	6	N_2	1.19	0.0505	3.71	0.27	6.01
Study VI - Effect of Air Blowing											
First Cure:											
1-13-1998(1)	AC-10	10	450	8000	3.5	N_2	1.82	0.1064			
3-9-1998(1)	Air-blown AC-10	10	450	8000	3.5	N_2	1.57	0.1521			
2-27-1998(1)	Air-blown Resin D	10	450	8000	3.5	N_2	2.07	0.1811			
Second Cure:											
1-13-1998(2)	AC-10	10	500	8000	6	N_2	1.31	0.0443	3.7	0.54	5.76
3-9-1998(2)	Air-blown AC-10	10	500	8000	6	N_2	1.05	0.1019	4.38	0.55	5.07
2-27-1998(2)	Air-blown Resin D	10	500	8000	6	N_2	1.28	0.1388	4.94	0.59	4.46

Studies of Curing Conditions and Asphalt-Rubber Composition

The remaining five studies show the effect of curing parameters on settling and on PG. The settling data are given in Table 3-15. For the viscosity data, only the ratio is given as the only significant difference between the bottom can and the others, and only this ratio is discussed. The data for the re-curing of the bottom can follow the date and a (2) in parenthesis. The filter test data giving rubber recovered were obtained only on the bottom can after removal of the small D fraction. Following the filter test, the results of the centrifuge test are given showing the solids removed in the PG fraction as well as the D fraction. From this the dissolved or unprecipitated part of the rubber is calculated.

Table 3-16 shows the result of the PG. These data have been arranged so that it is easy to tell the effect of the curing condition on the top and bottom grade as well as the grade span.

Study II: The Effects of the First Curing Condition. In this study 10 percent rubber in AC-10 is subjected to four separate curing conditions. Following separation of the four fractions, the bottom fraction is subjected to a more severe curing. It would appear that raising the temperature from 204 to 232 °C (400 to 450 °F) on the final cure was more effective than increasing the time from 3.5 hours to 6.0 hours. The best filter test after the first cure was 12/01/97. However it was 1.0 to 4.0 °C lower in grade span than the others. Following the second cure, this sample was still best in viscosity ratio and filter test and also showed the highest percent dissolved. It also showed no further grade deterioration and was only 1.0 °C below the other samples in grade span. Except for the least cured sample, 1/16/98, there was little change in grade after the second cure. It is surprising the extent that the final cure was reflected in the second cure, but then it was only the bottom fraction that was re-cured.

After the second curing, the 1/13/98 run, at 232 °C (450 °F) for 3.5 hours, had lost its second place position relative to the viscosity ratio, and the percent dissolved to the 1/14/98 run at 204 °C (400 °F) for 6.0 hours initially, though the former was still second relative to the filter test.

Figures 3-4 to 3-7 show the general effect of curing on the Superpave parameters. The effect of rubber is to increase $G^*/\sin\delta$ before RTFOT but this deteriorates with respect to the severity of curing. In Study II the ranking of the cure conditions with respect to the increase in $G^*/\sin\delta$ relative to the tank asphalt is 204 °C (400 °F), 3.5 hours > 204 °C (400 °F), 6.0 hours > 232 °C (450 °F), 3.5 hours > 232 °C (450 °F), 6.0 hours. After RTFOT, the advantage of rubber in this respect is gone (Figure 3-7). Ironically, this is because the rubber reduces the tendency to harden on oxidation, which is a considerable long-term advantage. Both m and S are improved by rubber and only slightly affected by the curing intensity in this study (Figures 3-5 and 3-6).

Table 3-16. Studies of Curing Conditions and Asphalt Composition on Performance Grade.

Study	Asphalt		Rubber	Cure Conditions				Performance Grade	
	Type	Continuous Grade	Amount (%)	Temp °C (°F)	Shear (RPM)	Time (hrs)	N_2 or Air	Continuous Grade	Grade Span
Study II - Effect of First Cure Conditions									
First Cure:									
1-16-1998(1)	AC-10	60-29	10	400	8000	3.5	N_2	63-32	95
1-13-1998(1)	AC-10	60-29	10	450	8000	3.5	N_2	61-32	93
1-14-1998(1)	AC-10	60-29	10	400	8000	6	N_2	62-31	93
12-1-1997(1)	AC-10	60-29	10	450	8000	6	N_2	60-31	91
Second Cure:									
1-16-1998(2)	AC-10	60-29	10	500	8000	6	N_2	61-31	92
1-13-1998(2)	AC-10	60-29	10	500	8000	6	N_2	61-31	92
1-14-1998(2)	AC-10	60-29	10	500	8000	6	N_2	61-31	92
12-1-1997(2)	AC-10	60-29	10	500	8000	6	N_2	60-31	91
Study III - Effect of Secondary Cure Conditions									
First Cure:									
10-13-1997(1)	AC-10	60-29	10	400	8000	3.5	N_2	63-32	95
Second Cure:									
10-13-1997(2)	AC-10	60-29	10	400	4000	3.5	Air	63-31	94
10-14-1997(2)	AC-10	60-29	10	400	4000	6	Air	63-31	94
10-30-1997(2)	AC-10	60-29	10	450	8000	6	Air	64-29	93
1-15-1998(2)	AC-10	60-29	10	450	8000	6	N_2	62-31	93
1-16-1998(2)	AC-10	60-29	10	500	8000	6	N_2	61-31	92
10-27-1997(2)	AC-10	60-29	10	500	4000	6	N_2	61-31	92

Table 3-16. Studies of Curing Conditions and Asphalt Composition on Performance Grade. (Continued)

Study	Asphalt		Rubber	Cure Conditions				Performance Grade	
	Type	Continuous Grade	Amount (%)	Temp °C (°F)	Shear (RPM)	Time (hrs)	N_2 or Air	Continuous Grade	Grade Span
Study IV - Effect of Rubber Content									
First Cure:									
12-1-1997(1)	AC-10	60-29	10	450	8000	6	N_2	60-31	91
3-2-1998(1)	AC-10	60-29	15	450	8000	6	N_2	63-32	95
Second Cure:									
12-1-1997(2)	AC-10	60-29	10	500	8000	6	N_2	60-31	91
3-2-1998(2)	AC-10	60-29	15	500	8000	6	N_2	61-32	93
Study V - Effect of Asphalt Type									
First Cure:									
12-1-1997(1)	AC-10	60-29	10	450	8000	6	N_2	60-31	91
3-4-1998(1)	VTB	?	10	450	8000	6	N_2	72-26	98
3-13-1998(1)	ABM-1	?	10	450	8000	6	N_2	67-20	87
Second Cure:									
12-1-1997(2)	AC-10	60-29	10	500	8000	6	N_2	60-31	91
3-4-1998(2)	VTB	?	10	500	8000	6	N_2	74-22	96
3-13-1998(2)	ABM-1	?	10	500	8000	6	N_2	67-18	85

Table 3-16. Studies of Curing Conditions and Asphalt Composition on Performance Grade. (Continued)

Study	Asphalt		Rubber	Cure Conditions				Performance Grade	
	Type	Continuous Grade	Amount (%)	Temp °C (°F)	Shear (RPM)	Time (hrs)	N_2 or Air	Continuous Grade	Grade Span
Study VI - Effect of Air Blowing									
First Cure:									
1-13-1998(1)	AC-10	60-29	10	450	8000	3.5	N_2	61-32	93
3-9-1998(1)	Air-blown AC-10		10	450	8000	3.5	N_2	77-24	101
2-27-1998(1)	Air-blown Resin D		10	450	8000	3.5	N_2	84-16	100
Second Cure:									
1-13-1998(2)	AC-10	60-29	10	500	8000	6	N_2	61-32	92
3-9-1998(2)	Air-blown AC-10		10	500	8000	6	N_2	77-25	102
2-27-1998(2)	Air-blown Resin D		10	500	8000	6	N_2	85-16	101

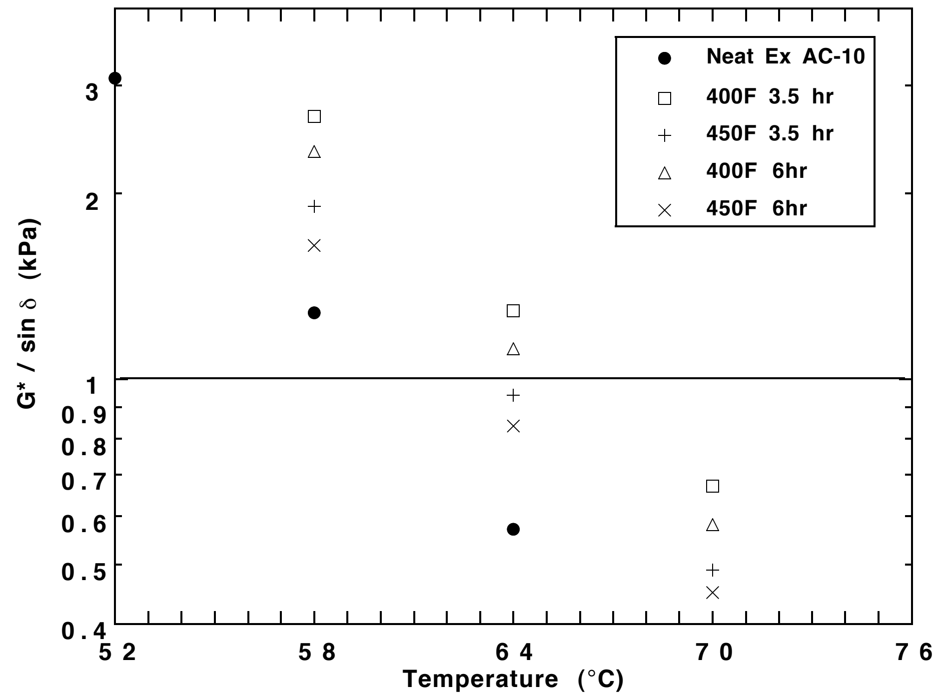

Figure 3-4. G*/sin(delta) of Original Binders After First Curing at Different Curing Conditions.

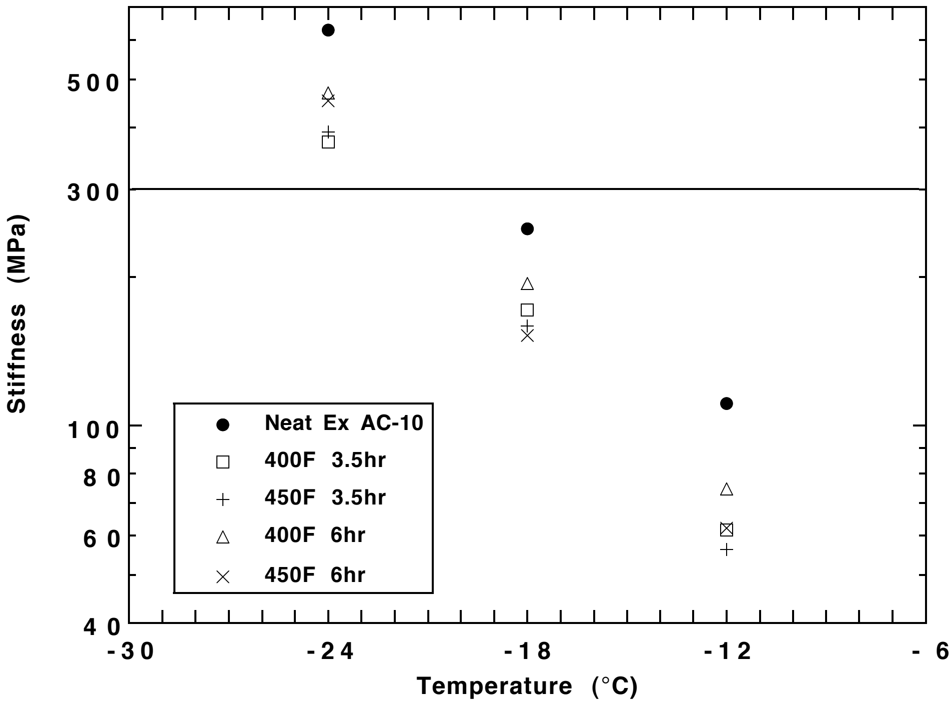

Figure 3-5. Stiffness of Binders After First Curing at Different Curing Conditions.

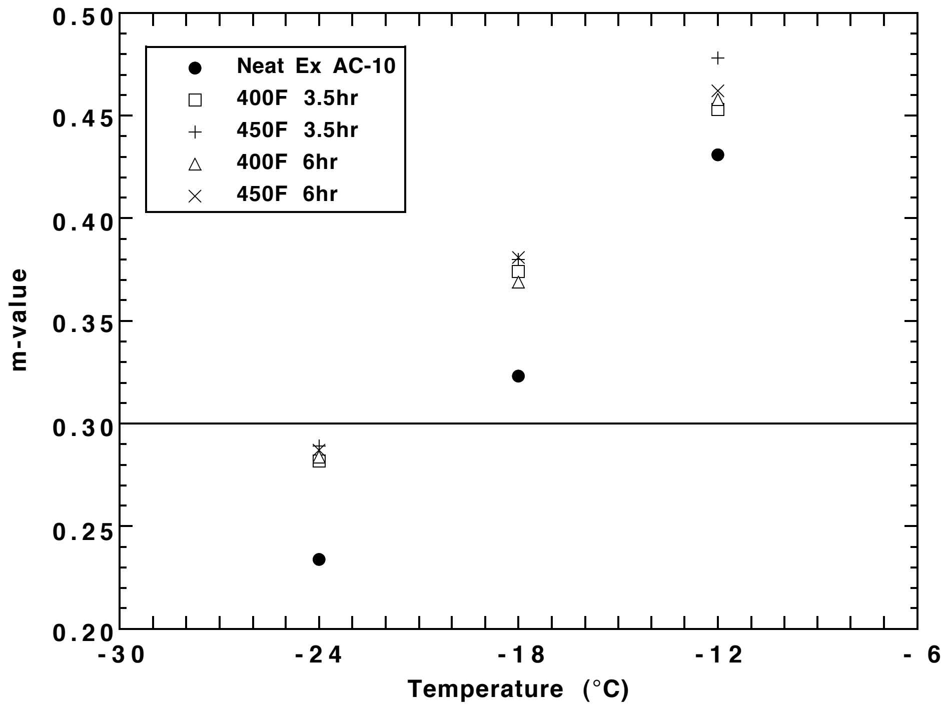

Figure 3-6. m-Value of Binders After First Curing at Different Curing Conditions.

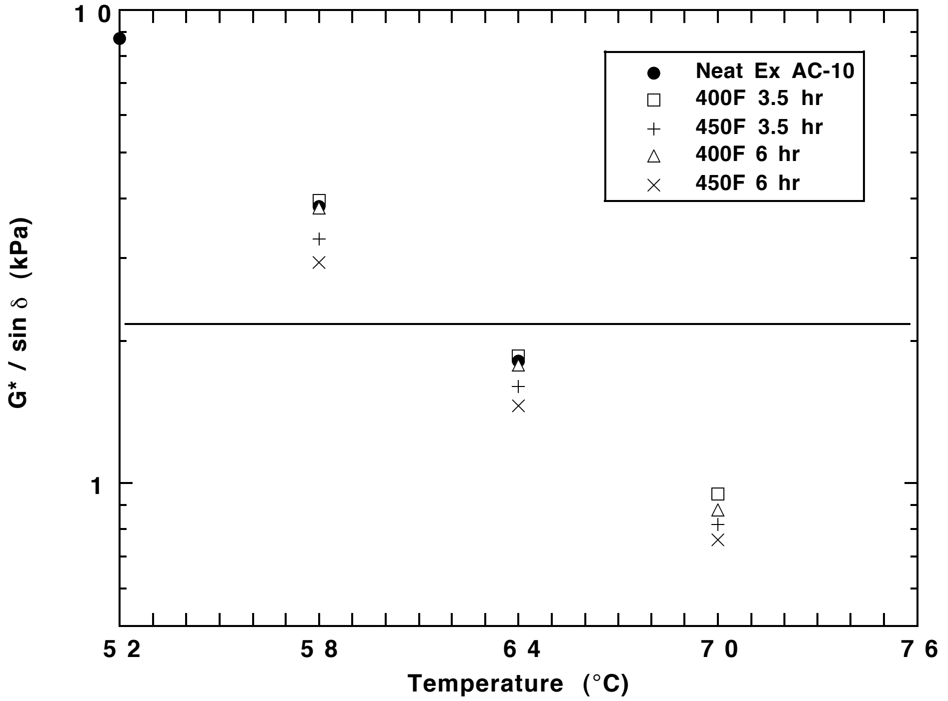

Figure 3-7. G*/sin(delta) of Binders After RTFO-Aged After First Curing at Different Curing Conditions.

Study III: Effects of Secondary Curing Conditions. In this study, six samples made from AC-10 with 10 percent rubber were cured first at 204 °C (400 °F) and 8000 rpm for 3.5 hours. This was followed by the second curing at different conditions including three using air. Curing the bottom fraction with air increases the intensity of curing but also raises the overall viscosity and increases the grade span slightly relative to those cured without air. However, the low temperature of 204 °C (400 °F) and 4000 rpm, sample 10/13/97, gave the poorest result in all settling criteria except viscosity ratio where it was next to last. Sample 10/30/97 cured at 232 °C (450 °F), 8000 rpm and for 6.0 hours with air, the severest condition, was best by all the settling criteria; best viscosity ratio, lowest weight on the filter test and highest percent dissolved in the centrifuge test. Sample 1/16/98, re-cured at 260 °C (500 °F), 8000 rpm and for 6.0 hours was second on the percent dissolved, on the viscosity ratio and on filter test. The rpm seems very important, at least some of the time, as the 260 °C (500 °F), 4000 rpm, 6 hour run, 10/27/97 did poorly on the settling ratio and filter test but better in the percent dissolved.

There were some real inconsistencies in this study. For instance 10/14/97 with air was second on the filter test and next to last on percent dissolved, but this was at 4000 rpm.

As far as grade is concerned, there was little difference. The effect of air on the second curing was in general to maintain the top grade at 63 or 64, 1.0 or 2.0 °C above the samples cured under nitrogen, while losing perhaps 1.0 °C on the bottom more than the N_2 cured samples.

Study IV: The Effects of Rubber Content. This study compared 15 percent rubber to 10 percent rubber in AC-10. The first curing was 232 °C (450 °F), 8000 rpm for 6 hours. Re-curing of the bottom fraction was at 260 °C (500 °F), 8000 rpm for 6.0 hours. These are severe conditions and both samples had good viscosity ratios, low weights on the filter test and high percent dissolved on the centrifuge test. The fraction of the total rubber present that was dissolved was 62 percent for the 15 percent sample versus 67.6 percent for the 10 percent sample. The 15 percent sample showed a 1.0 °C gain at both ends of the span relative to the 10 percent, PG 60-31 versus PG 61-32.

Study V: Effect of Asphalt Types. In this study AC-10 is compared to VTB and ABM-1. They were first cured at 232 °C (450 °F), 8000 rpm for 6.0 hours and then the bottom fourth of each was re-cured at 260 °C (500 °F), 8000 rpm for 6.0 hours. These are severe conditions and the same as in Study IV. The AC-10 gave the best viscosity ratio if one considers its lower viscosity relative to the VTB. It also gave the lowest filter residue and the highest percent dissolved. In general, the viscous VTB gave the poorest result. In fact, the degree of curing was in reverse ratio to the viscosity except for the viscosity ratio. Table 3-12 shows the Corbett analyses of these materials. It does not seem to be saturates or aphaltenes causing this trend. In fact, no Corbett parameter correlates with the curing rankings, only the viscosity, but of course this is a small sample.

The GPC chromatograms of these materials are interesting as shown in Figures 3-8 to 3-10 (12/01/97, 3/04/98, 3/13/98). It seems obvious that the VTB is not solubilizing the rubber

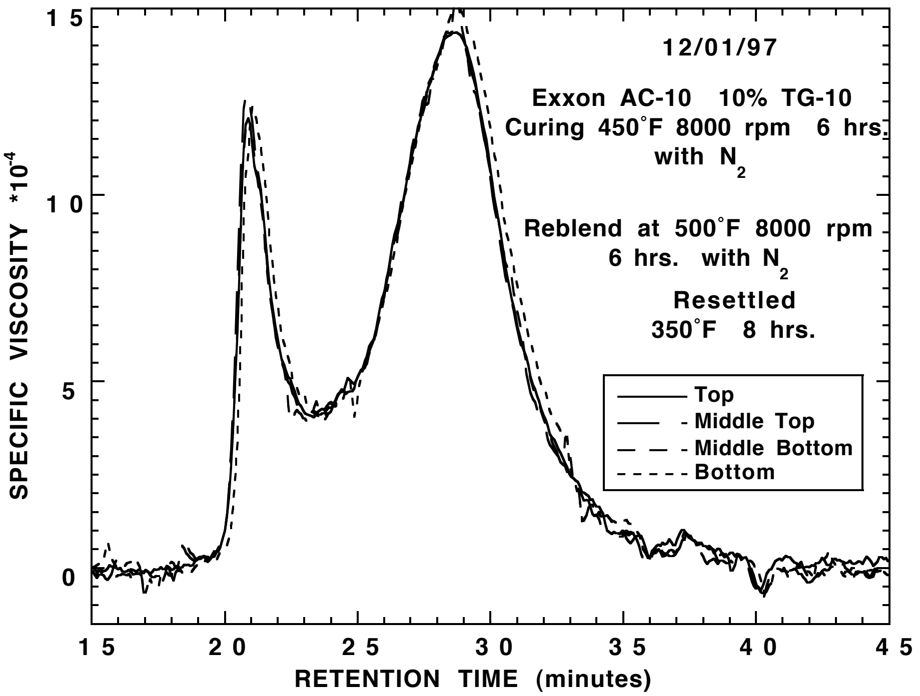

Figure 3-8. GPC Chromatogram of Blend 12/01/97 After Re-Curing.

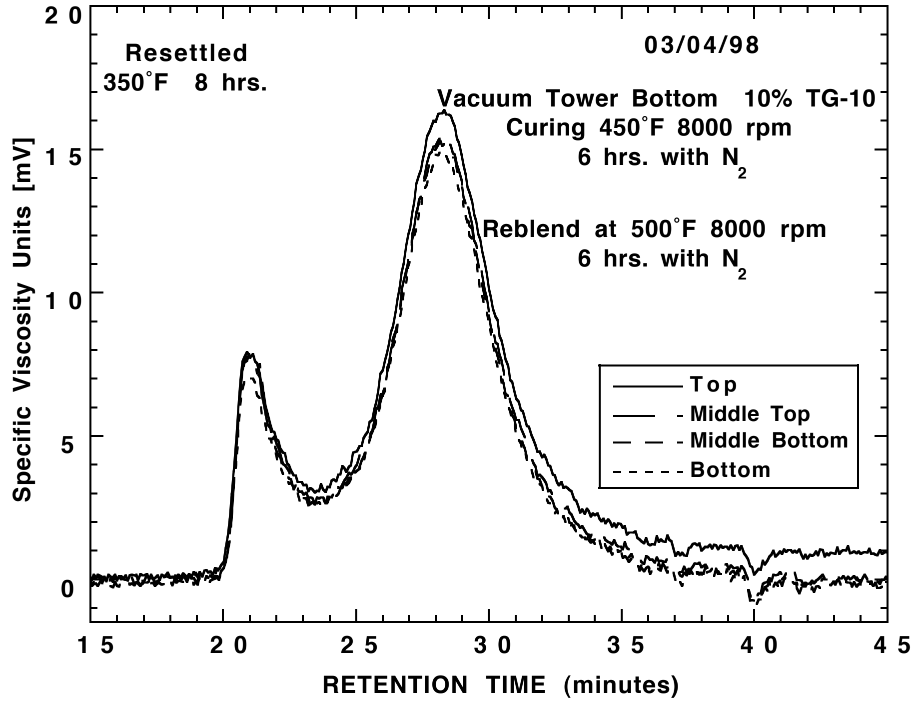

Figure 3-9. GPC Chromatogram of Blend 03/04/98 After Re-Curing.

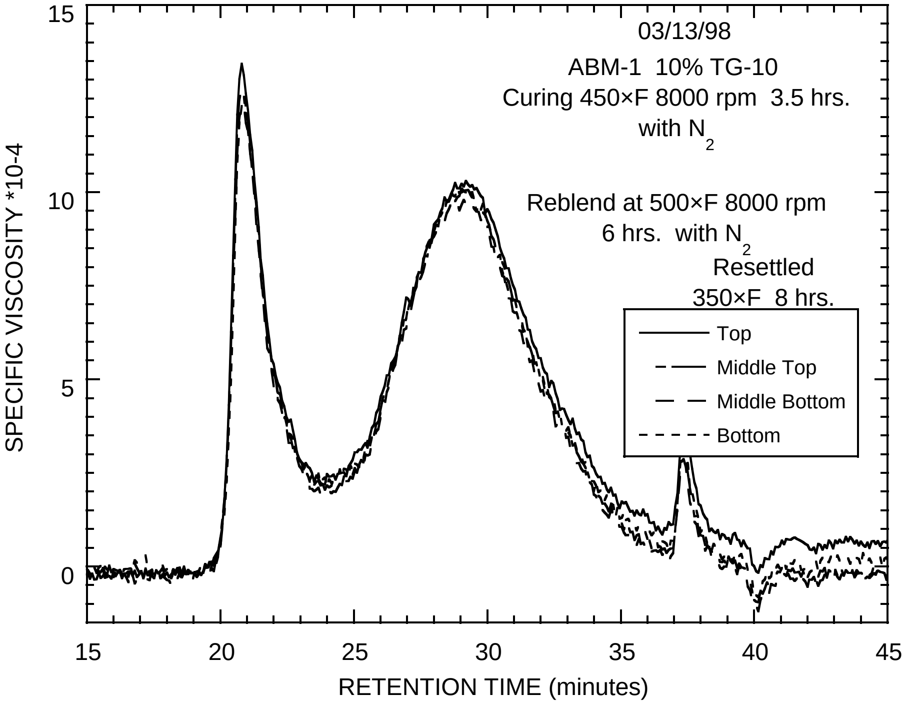

Figure 3-10. GPC Chromatogram of Blend 03/13/98 After Re-Curing.

to the same extent as AC-10 or ABM-1. However, the percent dissolved rubber for the VTB given in Table 3-15 is not as bad as the GPC would indicate.

The grade behavior is interesting. The behavior of the VTB was unusual in that after the second cure, the top grade temperature increased and the bottom decreased 4.0 °C. The ABM-1, which originally had a very poor grade span of 79, gained 6.0 °C overall while the poor curing VTB gained 10 °C, and the best curing AC-10 gained only 3.0 °C. Again, this is a small sample but the grade gain was inverse to the settling properties.

Study VI: Effects of Air-Blown Asphalts. Study VI investigates the effect of curing in air-blown asphalts. In this study, the AC-10 and Resin D were air blown at 232 °C (450 °F) for 3.0 hours. The blown AC-10 had a viscosity of 28,190 d Pa·s at 60 °C (140 °F), and the blown Resin D had a viscosity of 57,880. These materials along with the neat AC-10 were subject to an initial cure at 232 °C (450 °F), 8000 rpm for 3.5 hours, and a final cure of the bottom can at 260 °C (500 °F), 8000 rpm for 6.0 hours. Resin D, in spite of its high viscosity, had the highest viscosity ratio after the final cure. It also had the highest residue on the filter test. After the second cure, Resin D still had the highest filter residue. Both air-blown materials now had better viscosity ratios than AC-10, but only slightly so for Resin D in spite of its very high viscosity. Of significance is the considerable deterioration of the AC-10 by air blowing as indicated by the filter test residue, 0.102 versus 0.044. The fraction dissolved also followed AC-10 better than air-blown AC-10 which was better than air-blown Resin D. Again the results are consistent with the viscosity ranking, and thus may not be the result of the air blowing per se.

Comparison of Settling Measures

Three measures of settling were used in this study, the ratio of the viscosity between top and bottom can, the weight of rubber removed by filtration of a sample of the bottom cans, and the percent dissolved after the second cure. After the second cure both viscosity ratio and filter tests were made after the removal of the D fraction. Figure 3-11 shows the viscosity ratio minus 1.0, plotted against the filter test residues. As one might expect, the high viscosity air-blown samples give relatively low-viscosity ratios without a corresponding reduction in residue, placing them above the other data in this plot. With the viscosity already high, the effect of the rubber particles is relatively less, giving a smaller viscosity ratio. The VTB is also high and has a high viscosity. Apart from viscosity effects the scatter probably reflects error in measurement as neither test is highly precise.

The percent dissolved is an interesting measure which was not affected by removal of the D fraction, as the content of this fraction was included in the calculation. Note that values seem to have a ceiling below 70 percent, and this is consistent with tire rubber analysis. A typical tire rubber will contain about 30 percent carbon black plus some ash. Even though this material could never dissolve, the state of its dispersion could affect the settling viscosity ratio and the filter test residue. Actually, we have defined “dissolved” as the material that does not precipitate in the centrifuge, and we do not know its composition or the extent of its disintegration.

Figure 3-12 relates the results of the filter test to the percent dissolved as measured by the centrifuge test. Air-blown material and material cured at 260 °C (500 °F) appear to be high on the filter test. Considering that the filter test was conducted on the bottom can after removal of the D fraction, this agreement is about as good as could be expected. Furthermore, much more material is removed by the centrifuge than the filter, including perhaps some material from the top fractions, so the same particle distribution is not being measured.

Summary of Performance Grade Effects

Figure 3-13 contains the grade data for both cures in this work. Except for SHRP ABM-1 the top grade is a major factor in determining the grade span. Rubber alone appears to have added 2.0 to 6.0 °C to the span while air blowing has added that much more. On average it would appear that about a 2.0 °C increase in top grade results in a 1.0 °C loss of bottom grade. SHRP ABM-1 starts with a poor grade but is much improved by the rubber.

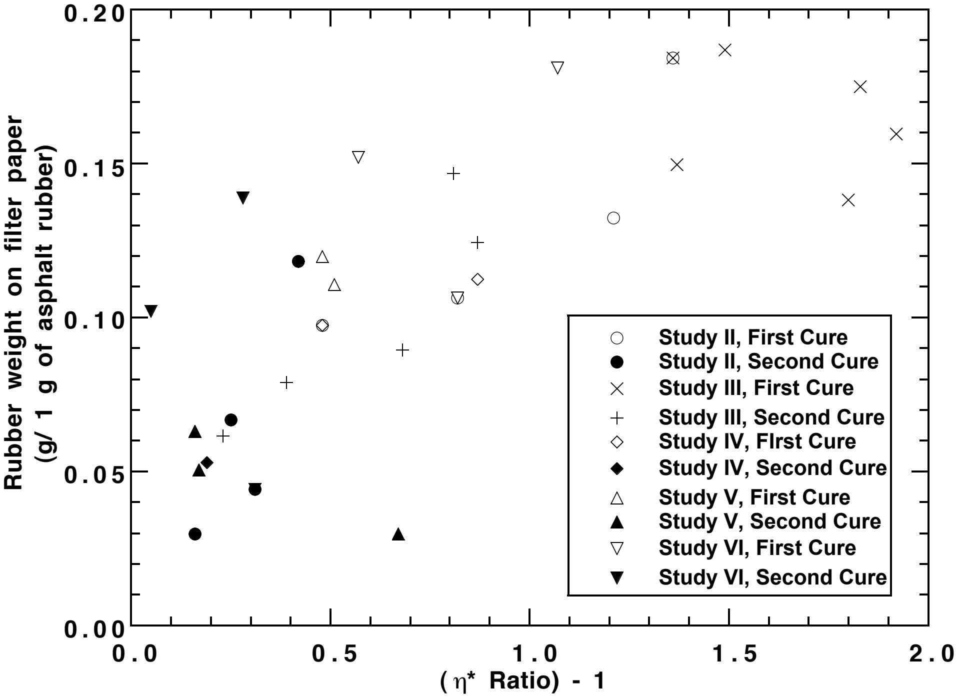

Figure 3-11. Settling Test After First and Second Curing.

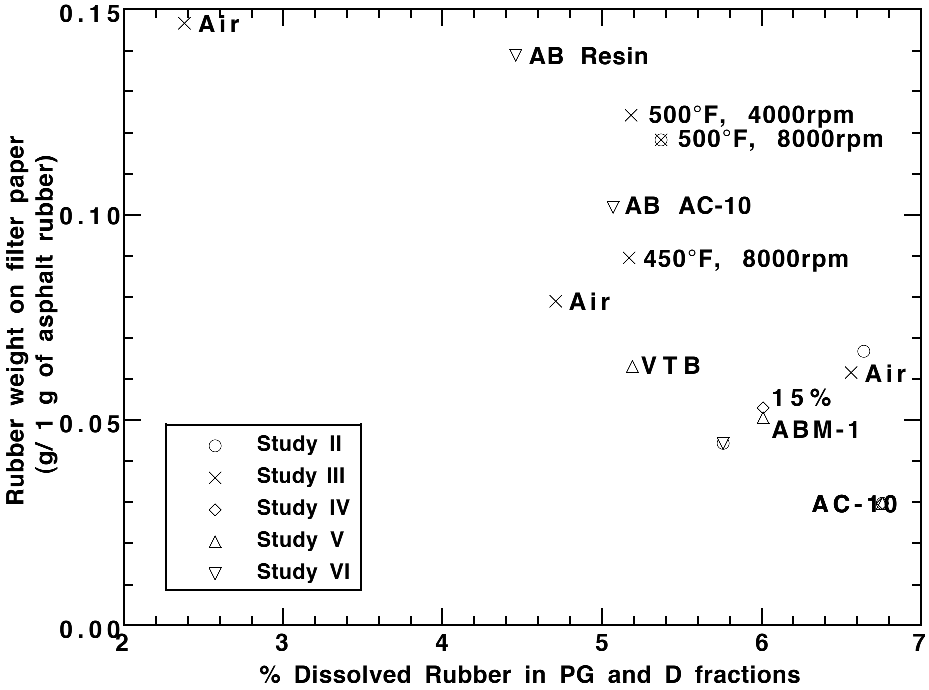

Figure 3-12. Rubber Weight and Dissolved Rubber in PG and D Fractions After Second Curing.

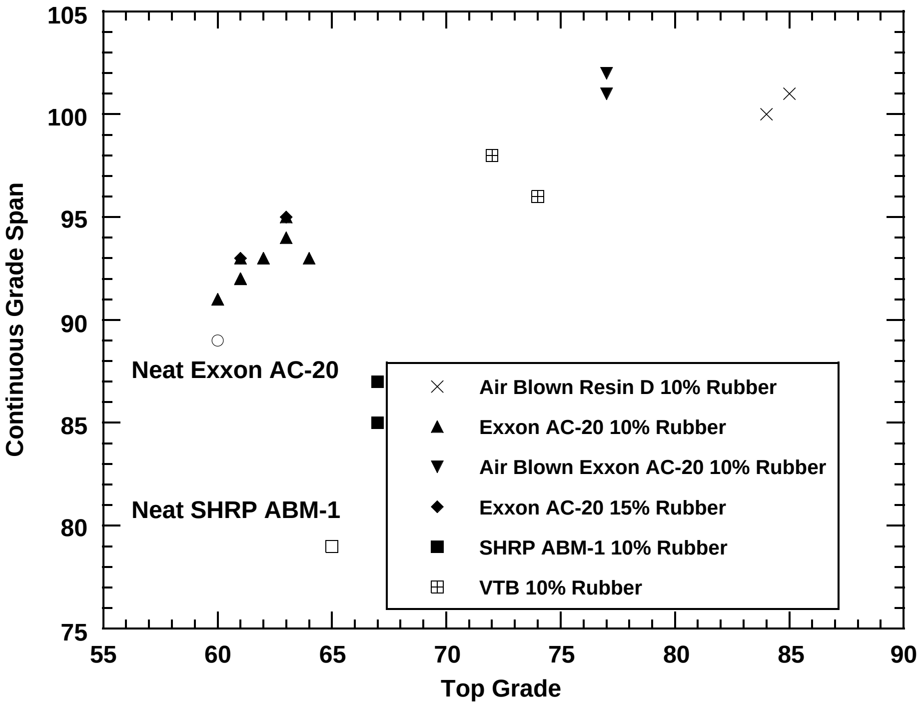

Figure 3-13. Continuous Grade Span of Neat Asphalt and Asphalt Rubber After First and Second Curing.

Conclusions

In spite of removal of the fraction D the three tests used to measure curing, i.e., viscosity ratio, and filter residue, which did not include fraction D and the percent dissolved which did, were in general agreement. To get good settling properties requires severe conditions of high temperature, such as 260 °C (500 °F), high shear, and perhaps air. Even air was not effective at 204 °C (400 °F). The consistently best cures from a settling standpoint are shown in Table 3-17. For the rather small number of asphalt compositions studied, the asphalt viscosity seemed to be the major asphalt property affecting the degree of curing.

As far as the effect of curing on grade, the span tends to decrease with increased cure, but the effect is small at the levels of curing studied here. It is primarily the top grade that declines. The use of air speeds curing and increases the grade span as the gain at the top is only partly offset by loss at the bottom.

It appears that settling and removal of a bottom fraction which is then severely re-cured might be a way to get good settling properties while minimizing grade loss. Another possibility would be curing in a relatively non-viscous fraction followed by addition of a high-viscosity component.

Table 3-17. Best Curing Conditions for Settling.

Run	First Cure Condition			Second Cure Condition		
	°C	rpm	time(hrs)	°C	rpm	time(hrs)
1/13/98	232	8000	3.5	260	8000	6.0
1/14/98	204	8000	3.5	260	8000	6.0
12/01/97	232	8000	6.0	260	8000	6.0
12/30/97	204	8000	3.5	232	8000	6.0/air
3/02/98	232	8000	6.0	260	8000	6.0
3/13/98	232	8000	6.0	260	8000	6.0

EFFECTS OF COMPOSITION ON HCAR PERFORMANCE GRADE AND SETTLING PROPERTIES

Abstract

To study the effect of Corbett fraction composition on rubber curing in asphalt, three refinery materials (asphalt solid, deasphalted oil [DAO], and resin) were blended in different proportions to obtain a total of six samples of varying composition. These blends were then cured with -20 mesh ground tire rubber using a single high-cure procedure. The effect of composition on curing was inferred from differences in the cured materials in PG properties and in rheological properties of samples obtained from the 48-hour Texas Settling test.

Concerning PG properties, resin lowered the grade span by increasing the bottom-grade temperature. DAO increased the grade span because of its higher saturate and naphthene aromatic content. Asphalt solid, comprised of asphaltenes and aromatics, helped improve the span primarily by raising the top grade. In terms of Corbett fraction compositions, a decrease in polar aromatics and increases in saturates lower the bottom-grade temperature, and increases in asphaltenes increase the top-grade temperature. The addition of asphaltenes and saturates results in a large grade span.

Concerning digestion of the rubber particles in the asphalt material, lowering the asphaltene and saturate contents, or, equivalently, increasing the polar material content, enhanced the dissolution of rubber.

Introduction

Among other benefits, asphalt is used primarily as a binder or adhesive component for pavement. It makes up 5 percent of road material. Asphalt is the continuous matrix and the only deformable component in the pavement. Its properties change with temperature. High temperature or prolonged loads induced by traffic result in rutting or permanent deformation. On the other hand, at low temperature or frequent-and-quick loads, asphalt behaves more like an elastic solid and if the temperature is too low, the asphalt cement becomes too stiff and prone to crack failure.

There have been tremendous efforts to improve the performance of asphalt pavements by blending asphalt with low-cost materials having desired properties. Rubber from scrap tires is one example. The blend of asphalt and rubber is commonly referred to as crumb-rubber modified asphalt. Tire rubber brings benefits to the asphalt binder as it neither melts during hot days nor fractures in cold climates. When mixed with asphalt, rubber also may reduce asphalt aging as a result of oxidation during service and may enhance the adhesion of asphalt to the aggregate.

Asphalt composition by itself varies among asphalts. This introduces a complication in the production of rubber modified asphalt binder in achieving the same PG for different neat asphalts.

Curing rubber in asphalt is a process of particle size reduction accompanied by devulcanization and depolymerization of the rubber (Zanzotto and Kennepohl, 1996). Hypothetically, the asphalt composition may have an effect on the curing process. Knowing the effects of each asphalt component will help optimize the use of rubber in asphalt.

The purpose of this study was to determine the effects of asphalt components on rubber curing. Materials of different composition were prepared under the same curing condition. The composition parameter studied was the Corbett fraction. This method of asphalt fractionation, developed by Corbett, yields four different asphalt fractions in order of decreasing molecular weight and/or polarity: asphaltenes, polar aromatics, naphthene aromatics, and saturates (ASTM [American Society for Testing and Materials] D4124, 1994; Corbett, 1969).

Materials

Commercially available asphalt solid, resin, and DAO, produced by a three stage supercritical extraction unit, were used in this study. The Corbett compositions (ASTM D4124, 1994) are given in Table 3-18. Viscosity at 60 °C (140 °F) of the resin and DAO are also given. The asphalt solid was too hard at this temperature to measure a viscosity. Minus 20 mesh ground tire rubber was supplied by a rubber manufacturer.

Table 3-18. Refinery Fraction Compositions, Corbett Compositions, and Viscosities of the Base Materials.

	Asphalt Solid	DAO	Resin	As	Sat	NA	PA	η* (60 °C, 0.1 rad/s) (Poise)
Asp Solid	100	-0-	-0-	47.92	1.97	17.47	32.64	--
DAO	-0-	100	-0-	0.09	20.25	53.44	26.22	47
Resin	-0-	-0-	100	2.00	10.30	47.50	40.20	232
Blend A Base	18.21	0.00	81.79	10.36	8.78	42.03	38.82	1790
Blend B Base	20.55	9.63	69.82	11.25	9.55	41.90	37.30	1717
Blend C Base	23.13	18.00	58.87	12.28	10.16	41.62	35.94	1724
Blend D Base	30.81	69.19	0.00	14.83	14.62	42.36	28.20	1044
Blend DX Base	30.81	69.19	0.00	14.83	14.62	42.36	28.20	1044
Blend E Base	27.52	41.89	30.59	13.84	12.18	41.72	32.26	1077
Blend F Base	9.32	0.00	90.68	6.28	9.52	44.70	39.50	734

[a] As = Asphaltenes; Sat = Saturates; NA= naphthene aromatics; PA = polar aromatics; -- = Data not available

Experimental Method

A total of six blends were produced for this study. Blends A, B, and C were made by curing -20 mesh rubber in pre-made AC-20 base, whereas Blends D, E, and F were made by curing -20 mesh rubber in a mixture of asphalt solid, DAO, and resin. The base for Blends A, B, and C were made by blending asphalt solid, DAO, and resin at varying compositions in a can wrapped by a heating tape and insulation. The temperature was maintained at 177 °C (350 °F), and to minimize oxidation the hot sample was blanketed from the atmosphere with a flow of nitrogen. The nitrogen flow was 11,175 mL/min. The mixing was conducted using a drill press and 2.54 inch diameter impeller at 1550 rpm for 1.0 hour. The target was to produce AC-20 grade materials. Each of these materials was then cured with 10 percent -20 mesh rubber in a Silverson mixer at 8000 rpm for 6.5 hours. The asphalt rubber was sampled periodically during curing at 0 hour, 15, 30, 45 minutes, 1.0, 1.25, 1.5, 2.5, 3.5, 5.0, and 6.5 hours. The curing temperature was maintained at 260 °C (500 °F) using a heating tape and insulation. Again, to minimize oxidation a nitrogen blanket was used and in addition, another nitrogen inlet was immersed in the hot blend to purge air from the material and help in mixing. Each nitrogen flow was 11,175 mL/min.

Blends D, E, and F were made by curing 25 percent -20 mesh rubber in 0-100, 50-50, and 100-0 resin-DAO ratios by weight in a Silverson mixer under the same operating conditions as mentioned above. Blend DX was made to duplicate Blend D, only the rubber was cured in a mixture of asphalt solid and DAO, instead of DAO only. After blending, asphalt solid was added in different proportions to achieve an AC-20 target to give a wide range of final Corbett composition. This blending was performed using a drill press as mentioned previously. Since the viscosity after the cut-back was not low enough for Blend E to be an AC-20, a portion of DAO was added.

The blending sequences are summarized in Table 3-19. The base material compositions are given in Table 3-18, Figures 3-14, and 3-15, and the final blend compositions are given in Table 3-20, Figures 3-16, and 3-17. Blend compositions were calculated from Corbett analyses of the base ingredients and the weight percent rubber added. As seen in Table 3-18, Blends A, B, C, and DX were made by blending rubber into the pre-blended base material. Runs D, E, and F were cured at a rubber content of 25 percent and then cut back to the final compositions.

Rheological properties were determined using a Carri-Med CSL 500 dynamic shear rheometer with a 2.5 cm composite parallel plate. All rubber-containing blends were measured with a 1500 µm gap, whereas the gap for the non-rubber blends was 500 µm. The DSR was operated in the controlled-strain mode at the minimum strain level where linear viscoelastic behavior was observed. The viscosities of all blends are given in Table 3-20.

Samples were performance graded in accordance with the AASHTO MP1-93.1B (1996) protocol. Each blend was pre-treated in a RTFO to simulate the hot-mix process and placed in a PAV for accelerated aging. High-temperature properties of non-RTFO and RTFO samples were

Table 3-19. Curing Matrix.

	1550-rpm Mixer (Pre-Curing)				8000-rpm Mixer (Curing)				1550-rpm Mixer (Post Curing)				1550-rpm Mixer			
Blend	Sample	T (°F)	Time (hr)	N[a]	Sample	T (°F)	Time (hr)	N[a]	Sample	T (°F)	Time (hr)	N[a]	Sample	T (°F)	Time (hr)	N[a]
A	Asphalt Solid, Resin	350	1.0	B	Base A, -20 mesh	500	6.5	B S	-	-	-	-	-	-	-	-
B	Asphalt Solid, DAO, Resin	350	1.0	B	Base B, -20 mesh	500	6.5	B S	-	-	-	-	-	-	-	-
C	Asphalt Solid, DAO, Resin	350	1.0	B	Base C, -20 mesh	500	6.5	B S	-	-	-	-	-	-	-	-
D	-	-	-	-	DAO, -20 mesh	500	6.5	B S	Cure D, Asphalt Solid	350	1.0	B	-	-	-	-
DX	-	-	-	-	DAO, Asphalt Solid, -20 mesh	500	6.5	B S	-	-	-	-	-	-	-	-
E	-	-	-	-	DAO, Resin, -20 mesh	500	6.5	B S	Cure E, Asphalt Solid	350	1.0	B	Hard E, DAO	350	1.0	B
F	-	-	-	-	Resin, -20 mesh	500	6.5	B S	Cure F, Asphalt Solid, Resin	350	1.0	B	-	-	-	-

[a] B = Nitrogen Blanket
S = Nitrogen Sparger

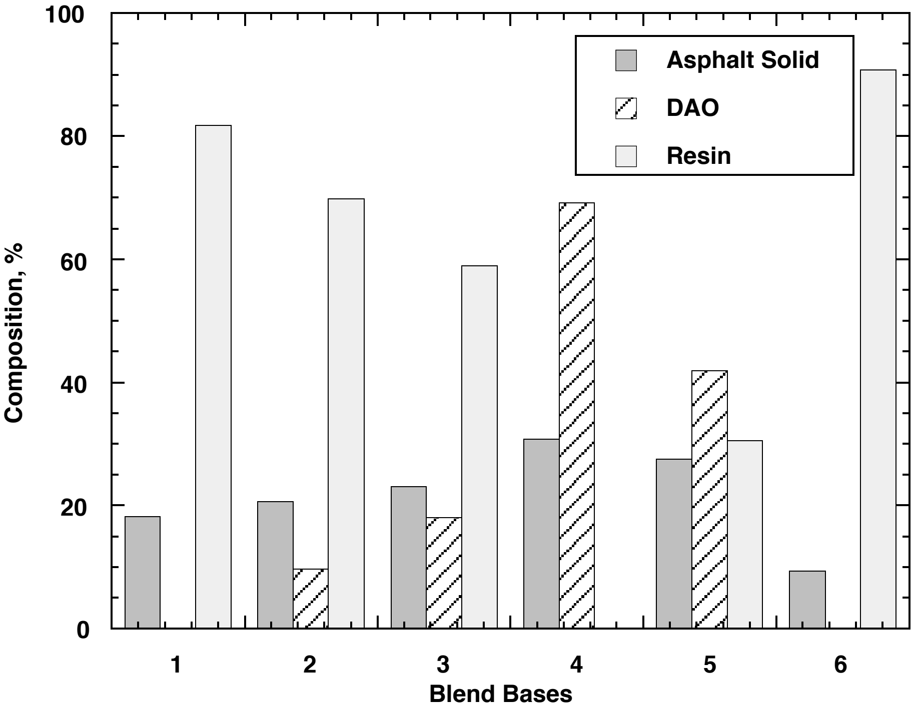

Figure 3-14. Refinery Fraction Compositions of Base Materials.

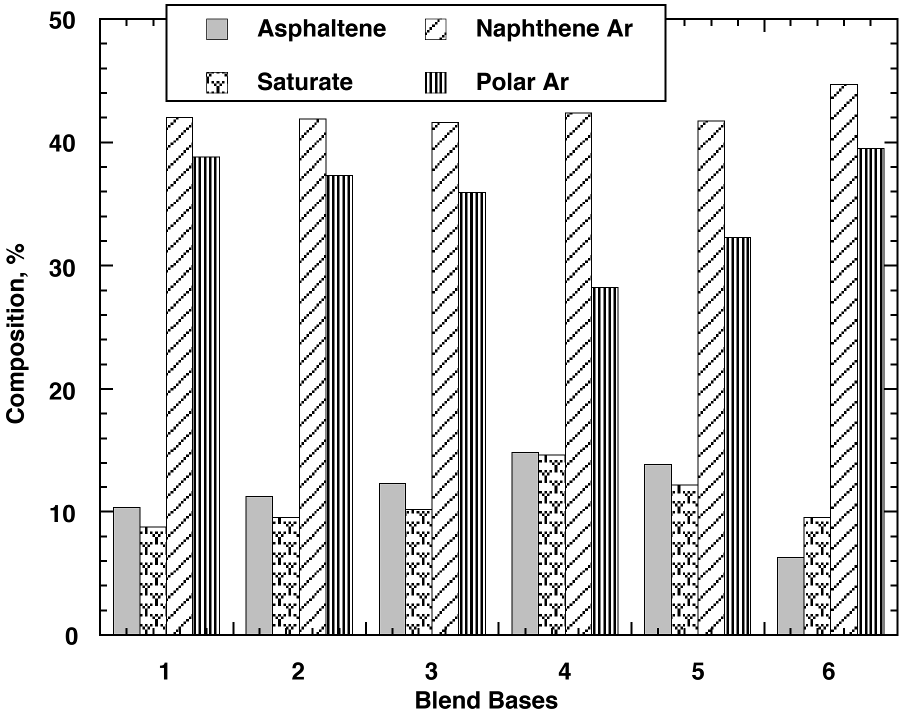

Figure 3-15. Corbett Compositions of Base Materials.

Table 3-20. Blend Refinery Fraction Compositions, Corbett Compositions, and Settling $^{\text{Results}}$.

	Asphalt Solid	DAO	Resin	% Rubber	As	Sat	NA	PA	η* (60 °C, 1.0 rad/s) (Poise)	η* Bottom/ Top Ratio	δ Bottom/ Top Ratio
Blend A	16.39	0.00	73.63	9.98	9.33	7.91	37.84	34.95	4229	1.11	0.981
Blend B	18.50	8.67	62.85	9.98	10.13	8.59	37.72	33.57	3590	1.17	0.978
Blend C	20.81	16.19	52.97	10.02	11.05	9.14	37.45	32.33	3792	1.43	0.952
Blend D	25.11	56.39	0.00	18.50	12.08	11.91	34.52	22.98	2145	1.18	0.939
Blend DX	25.11	56.39	0.00	18.50	12.08	11.91	34.52	22.98	2720	1.00	1.001
Blend E	22.87	34.8	25.42	16.91	11.50	10.12	34.67	26.81	2828	1.87	0.887
Blend F	7.57	0.00	73.69	18.73	5.10	7.74	36.33	32.09	1680	0.86	1.002

[a] As = Asphaltenes; Sat = Saturates; NA= naphthene aromatics; PA = polar aromatics

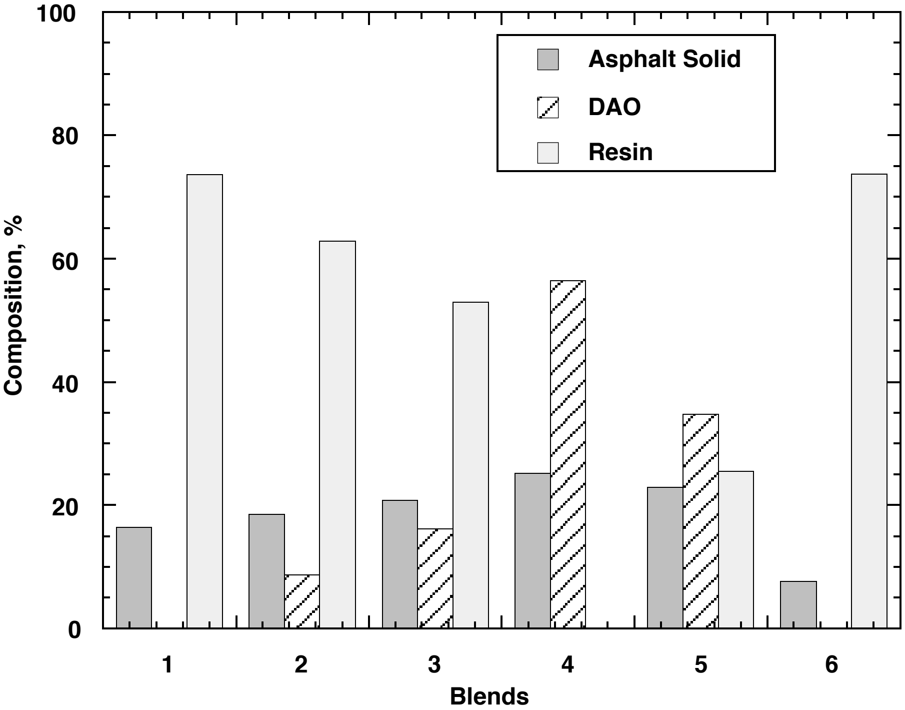

Figure 3-16. Refinery Fraction Compositions of Final Blends.

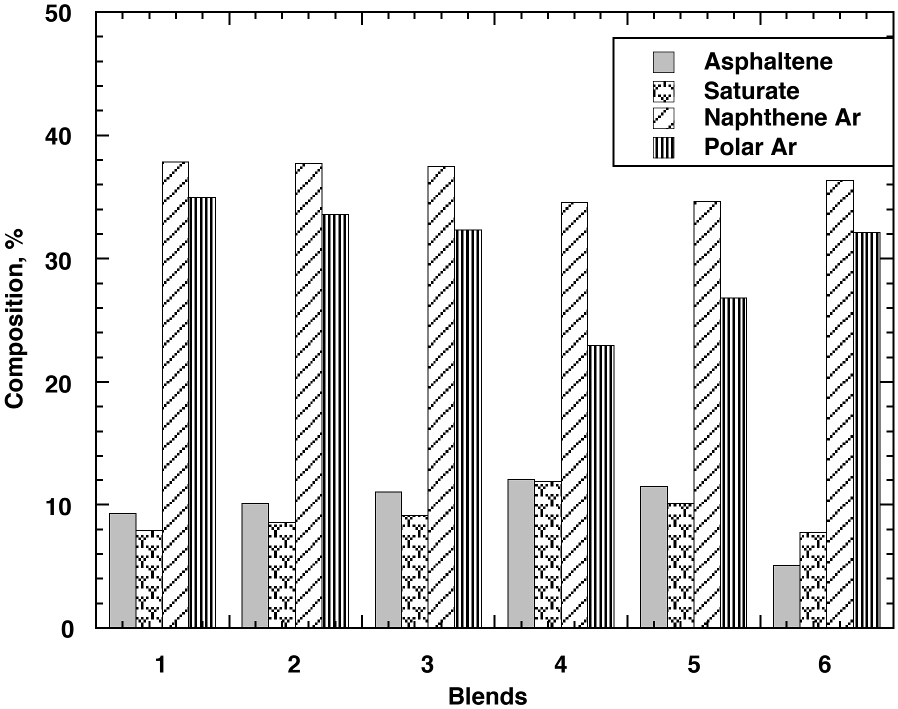

Figure 3-17. Corbett Compositions of Final Blends.

measured with DSR. The G*/sin δ values were evaluated at 10 rad/sec. Low-temperature properties of the blends were tested using a bending beam rheometer. The beams were prepared from blends that had been PAV aged.

A portion of each blend was set aside for a settling study using the Texas Settling test. A 350 g sample of each asphalt-ground rubber blend was poured into a quart can measuring approximately 89 mm in diameter and 102 mm in height. This sample was stored for 48 hours at 163 °C (325 °F) and then allowed to cool to room temperature. A sample was then taken from the top and bottom of the can to determine softening points based on the ASTM D36-95 (1997) procedure. A difference between the softening points of the top and bottom samples of 4 percent or more, based on the average of the top and bottom softening points (in °F), constitutes separation. In addition, the rheological properties of the top and bottom sections were measured using a Carri-Med CSL 500 rheometer as previously described. The Texas Settling test was performed to assure that the asphalt-ground rubber blend was at the desired high-cure consistency, and that road implementations would run smoothly.

Results and Discussion

Effect of Composition on Performance Grade

All base materials were graded at PG 58-28 except Blend A base (PG 58-22) and Blend F base (PG 52-28). Continuous grades, also shown in Table 3-21, were calculated by interpolating parameters to the passing criteria (Table 3-21). In general, the highest top grade corresponds to the higher viscosity. Figure 3-18 shows the top continuous grade plotted versus 60 °C (140 ^{o}F) viscosity. As these asphalts were designed to have similar 60 °C (140 ^{o}F) viscosity, the top grade was not studied further. Though Blend A base has the highest viscosity and poorest bottom grade, there is no general trend of bottom grade with viscosity.

The top performance grades of rubber Blends A, B, and C are 64, and those of Blends D, DX, E, and F are 58, 58, 64, and 58, respectively, as shown in Table 3-22. The top grades seem invariable because of the experimental design. The blends were produced to meet certain viscosities. Blends A, B, C, and DX were made by curing 10 percent (or 18 percent for Blend DX) rubber in an AC-20 asphalt. The viscosities of the end products were higher than those of the neat materials. On the other hand, Blends D, E, and F were cured with 25 percent rubber, and cut back to make AC-20 like material. As a result, the rubber content was reduced to approximately 18 percent, except for Blend E which was 17 percent because of an addition of asphalt solid to increase the resulting viscosity to an AC-20. Since the viscosities of Blends A, B, and C are higher than Blends D, DX, E, and F, the top performance grades of the former are higher than the latter. Blend E has a higher top PG than Blends D, DX, and F perhaps because of its high viscosity. The continuous grades show a similar trend. Again due to the experimental design, the top continuous grades of Blends A, B, and C are the same, they were all 67, while

Table 3-21. Performance and Continuous Grades for the Bases.

	Performance Grade	Span	Continuous Grade	Span
Blend A Base	58-22	80	61-27	88
Blend B Base	58-28	86	60-29	89
Blend C Base	58-28	86	60-28	88
Blend D Base	58-28	86	58-31	89
Blend DX Base	58-28	86	58-31	89
Blend E Base	58-28	86	59-30	89
Blend F Base	52-28	80	54-28	82

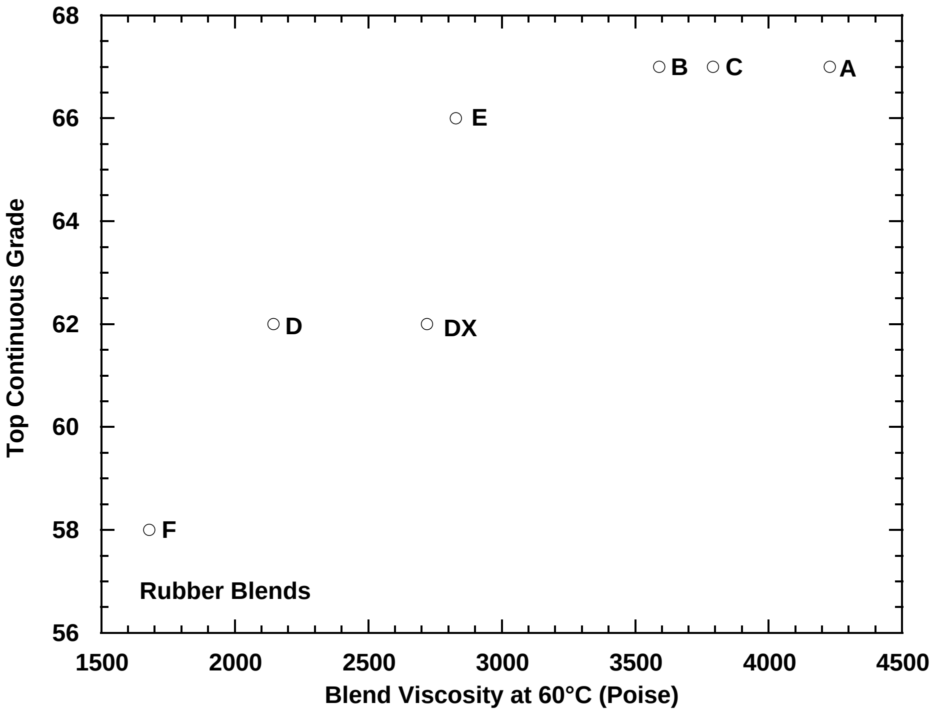

Figure 3-18. Effect of Viscosity on Top Continuous Grade.

Table 3-22. Performance and Continuous Grades for the Rubber Blends.

	Performance Grade	Span	Continuous Grade	Span
Blend A	64-16	80	67-20	87
Blend B	64-22	86	67-23	90
Blend C	64-28	92	67-31	98
Blend D	58-34	92	62-38	100
Blend DX	58-34	92	62-39	101
Blend E	64-28	92	66-31	97
Blend F	58-28	86	58-31	89

those of Blends D, DX, E, and F were 62, 62, 66, and 58. Among the latter blends, Blend E has the highest top continuous grade. Blend F, however, has the lowest top grade because it has the lowest viscosity compared to the others.

The bottom grades of Blends A, B, C, D, DX, E, and F are -16, -22, -28, -34, -34, -28, and -28, respectively. As suspected, Blends D and DX, which are high in saturates and low in heavy aromatics, have the best bottom grades. This is consistent with the findings of Domke et al. (1999a) where they observed that higher saturate content yielded better low-temperature properties.

The continuous grade span differences between the base and the blend are tabulated in Table 3-23. Blends C, D, and DX showed significant increase after curing. Blend C improved on the top grade, whereas Blends D and DX improved on the bottom grade. It is possible that the low polar aromatic content of Blend C compared to Blends A and B helps improve the top grade. On the other hand, Blends D and DX contain more saturates and light materials compared to Blends E and F, which enhance the bottom grade.

A statistical analysis (SAS System for Windows ver 6.12) was performed to determine the linear correlations between the grades and the rubber, asphalt solid, DAO or resin compositions. The correlation coefficients represent in what sense two variables are linearly correlated and how well they are correlated. The values of correlation coefficients range from -1 to 1. A correlation coefficient of one signifies a perfect linear correlation between two variables with the sign indicating the direction of the relationship. The negative sign indicates an increase in one variable is compared by a decrease in the other. On the other hand, the positive sign

Table 3-23. Increase of Grade Due to Curing.

	Rubber Content	Performance Grade Span Increase	Continuous Grade Increase		
			Span	Top	Bottom
Blend A	9.98	0	-1	6	-7
Blend B	9.98	0	1	7	-6
Blend C	10.02	6	10	7	3
Blend D	18.50	6	11	4	7
Blend DX	18.50	6	12	4	8
Blend E	16.91	6	8	7	1
Blend F	18.73	6	7	4	3

indicates the two variables increase or decrease together. The correlation coefficient is defined in equation 3-3 as (Lapin, 1997):

$$\rho = \frac{\Sigma\, XY - n\,\overline{XY}}{(n-1)\; s_x\; s_y} \tag{3-3}$$

where X and Y are variables under study, n is number of data points, and s_x, s_y are standard deviations.

The analysis indicates that the effect of resin and DAO on span are of similar magnitude but opposite direction. The correlation coefficients between span and rubber, asphalt solid, DAO, and resin contents are 0.47, 0.82, 0.91, and -0.91, respectively. Each component seems to have positive correlation with the span except for resin; an increase in resin reduces the span. Between asphalt solid and DAO, the latter correlates more strongly with the span than asphalt solid. Asphalt solid helps improve the high-temperature properties, but DAO lowers the bottom grade temperatures more.

The correlation coefficient between bottom grade and rubber, asphalt solid, DAO, and resin, respectively, were -0.79, -0.49, -0.84, and 0.84. The more the DAO content the lower the bottom grade. Although not as strong as DAO, asphalt solid also appears to help the bottom grade, but this likely is really the effect of DAO because as the asphalt solid was added DAO also had to be added to achieve the target viscosity. Here DAO helps bottom grade more than asphalt solid hurts it.

A similar analysis was made on the Corbett composition. Since asphaltenes greatly increase viscosity and saturate addition similarly lowers it, they are strongly correlated; a higher asphaltene content generally is accompanied by a higher saturate level in order to keep the grade, therefore the sum of the two was used as an independent variable. The resulting correlations between total PG spans in terms of rubber content, a combination of asphaltenes and saturates, naphthene aromatics, and polar aromatics are 0.48, 0.70, -0.70, and -0.76, respectively. The naphthene aromatic content, though large, varies so little that any correlation is doubtful, and Table 3-23 shows the ambiguity in the effect of rubber.

Among the original blend constituents, increasing resin content at the expense of asphaltenes and saturates rather consistently produces a poorer span while no single original component correlates well with bottom grade. For Corbett fractions, polar aromatics correlate well with decreasing PG span except for Blend C, which has a better span than predicted. Saturates also correlate with increasing PG span except for Blend C which again is better than expected. The bottom grade correlates well with (As+SA) except for Blend F which is better than predicted. The bottom grade correlates negatively with polar aromatics, but both Blends E and D are better than expected.

Because of the strong interdependence among component fraction compositions - if more light components are added, heavy components must be added to maintain target viscosities - an attempt was made to correlate PG with some variation of the compatibility index (Serfass et al., 1992; Gotolski et al.,1968; Traxler, 1960). Asphaltenes and saturates are immiscible, and in asphalt, are made miscible by the aromatics. The usual form is (NA+PA)/(As+S) but two other forms PA/(As+S), I, and PA/S, II, were tried. Figures 3-19, 3-20, and 3-21 show all three correlated with total PG grade span, and the simplest PA/S is the best overall. The grade span of the base asphalt blends (0 percent rubber) seems nearly unaffected by composition, except for F which lies beneath the trend in all three figures. Interestingly, the grade span of neither Blend A nor B is helped by rubber addition, but it is not simply the result of less rubber as asphalt Blend C is much benefited.

Figure 3-22 shows a similar plot for bottom grade. This figure shows that the problem of Blend A and B is a negative effect of rubber on the bottom grade offsetting a similar gain in top grade. Blend E gained only 1° at the bottom but 7° at the top (Table 3-23). As observed later, the top grade may be affected by less complete curing. In Figure 3-21, very good fits were obtained for continuous grade span increase versus PA/S. However, Blend F appears quite anomalous regarding span increase, Figure 3-23. In fact, in Figures 3-22 and 3-23, it is hard to decide whether to weight E more or F more as both are anomalous, E on the top grade increase and F on the bottom. Yet the total grade span versus compatibility plots well for each, Figure 3-21. The low viscosity of Blend F may partly account for the anomaly. One may be inclined to believe the results of Blend E for otherwise extrapolation of low- and high-rubber content show the low rubber giving a higher span improvement than high rubber at low PA/S (Figure 3-23).

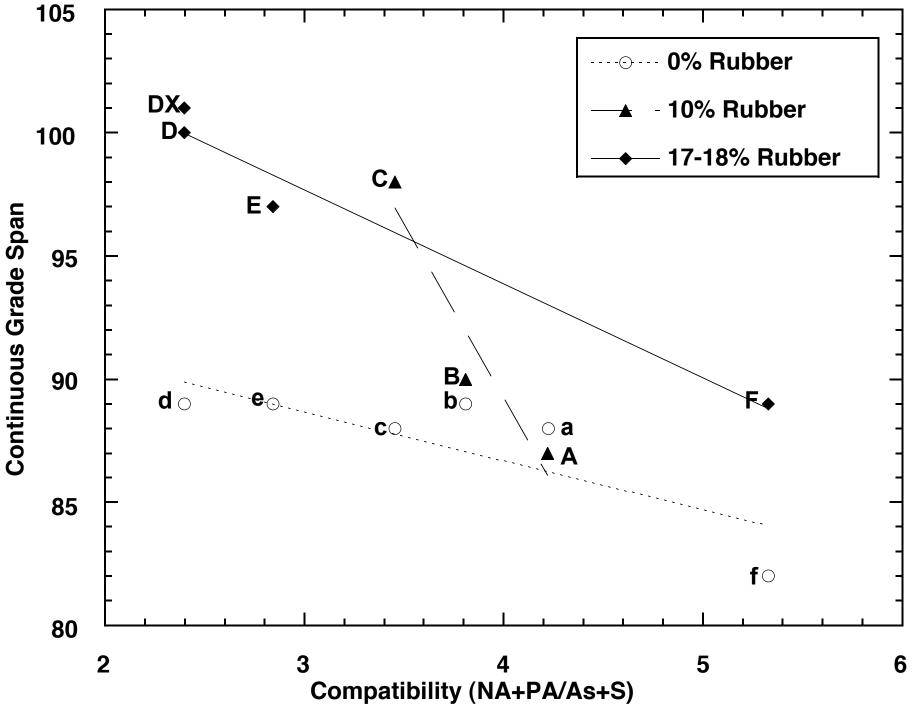

Figure 3-19. Effect of Serfass Compatibility on Continuous Grade Span.

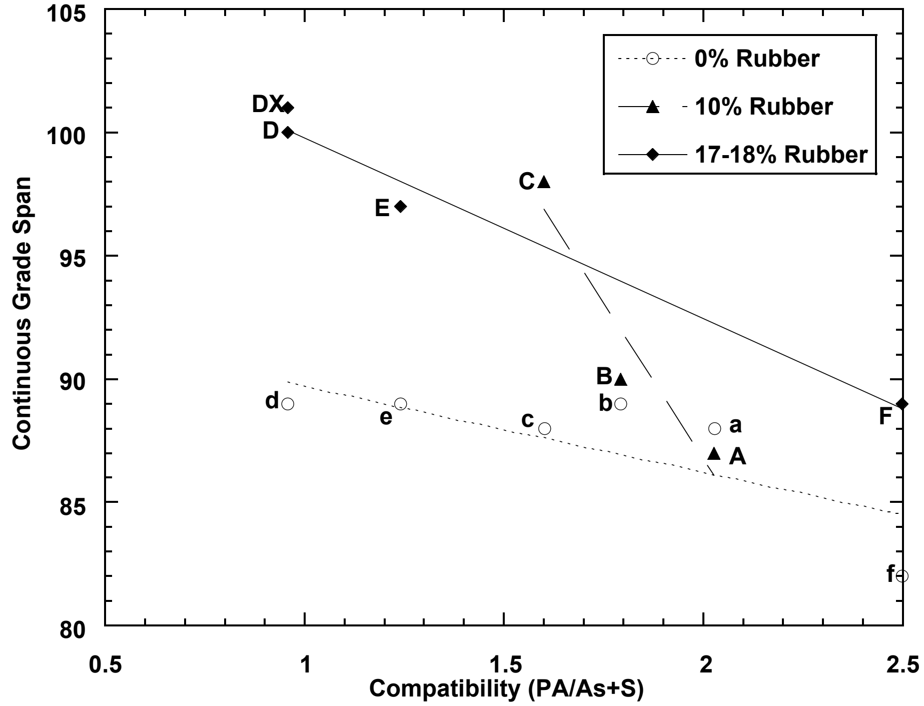

Figure 3-20. Effect of Compatibility I on Continuous Grade Span.

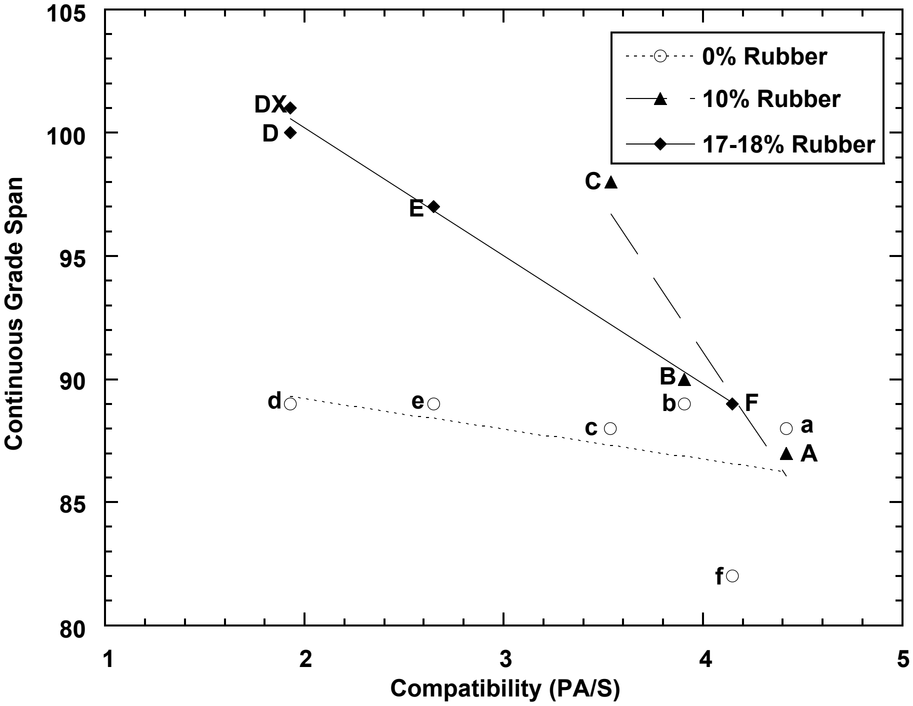

Figure 3-21. Effect of Compatibility II on Continuous Grade Span.

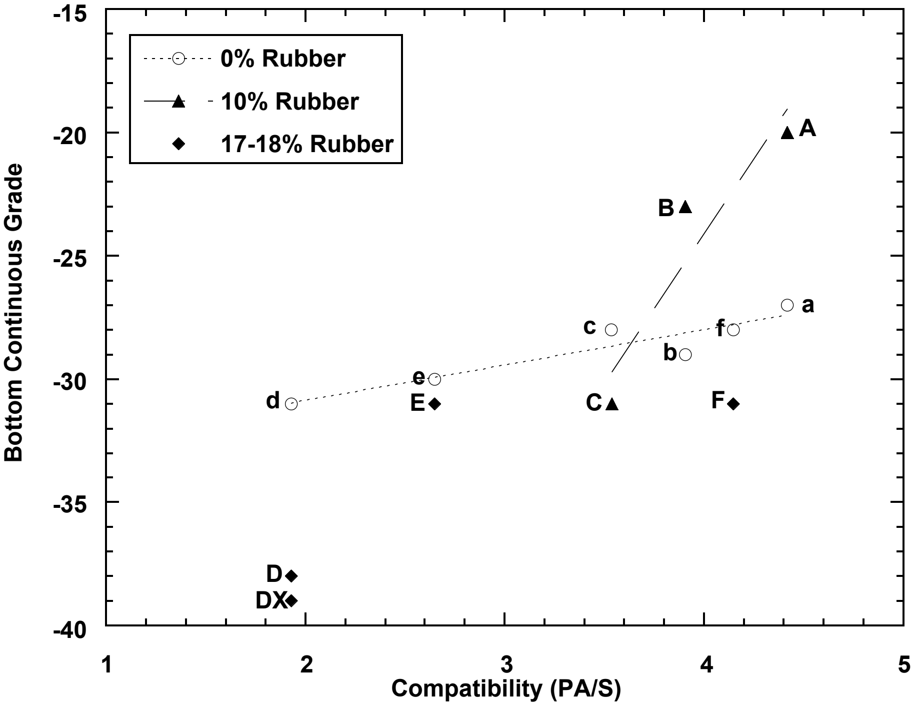

Figure 3-22. Effect of Compatibility on Bottom Continuous Grade.

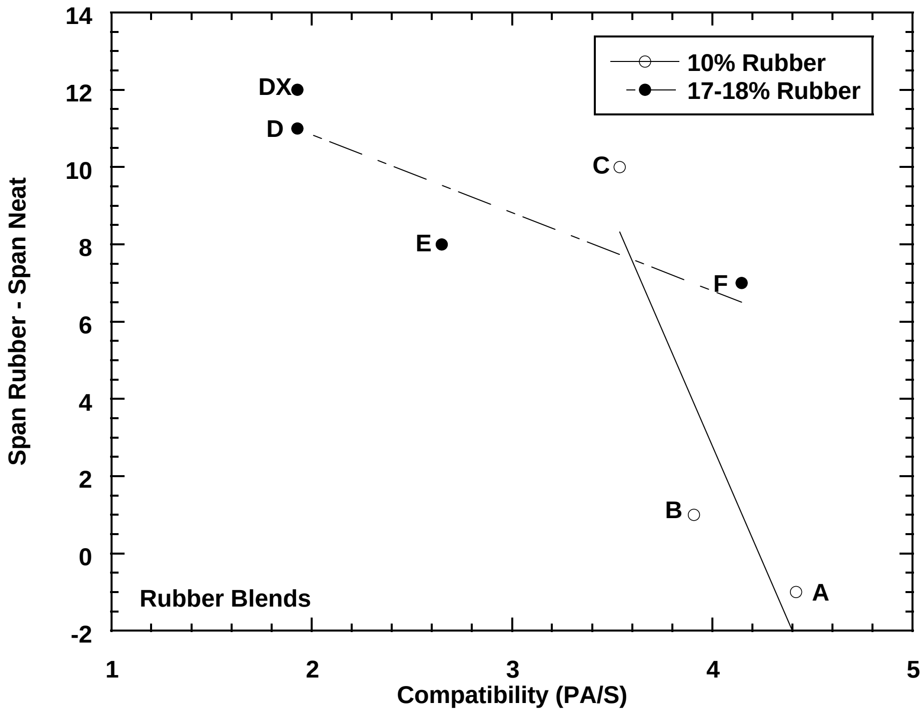

Figure 3-23. Effect of Compatibility on Span Increase.

Effect of Composition on Settling

Blend E failed the Texas Settling specifications in that the difference between the top and bottom ring and ball temperature of the settled sample was greater than 4 percent. The ring and ball difference did not seem a particularly sensitive measure as the temperature span is small. Consequently, rheological properties of top and bottom samples of the settled blend were measured, and the bottom-over-top ratios of viscosity and phase angle were measured. These ratios are given in Table 3-20. Figure 3-24 shows that the viscosity ratio varies inversely with phase angle ratio, and either can be used as a measure of settling.

As with PG grade it is difficult to correlate settling measures with individual components so correlation was again attempted with a compatibility index. It turned out again that the simplest, PA/S, was as good or better than the others. This correlation is complicated in that Blends D, E, and F were not cured in their final composition. Figures 3-25 and 3-26 show the viscosity ratio correlated in terms of curing composition and final composition, respectively. The correlations do not appear bad except for Blend E which is much worse than expected. Similarly, Figures 3-27 and 3-28 show results for the phase angle ratios. Notice that the phase angle ratio for both DX and F are near one, indicating very good curing (low settling) for both in spite of considerable composition differences.

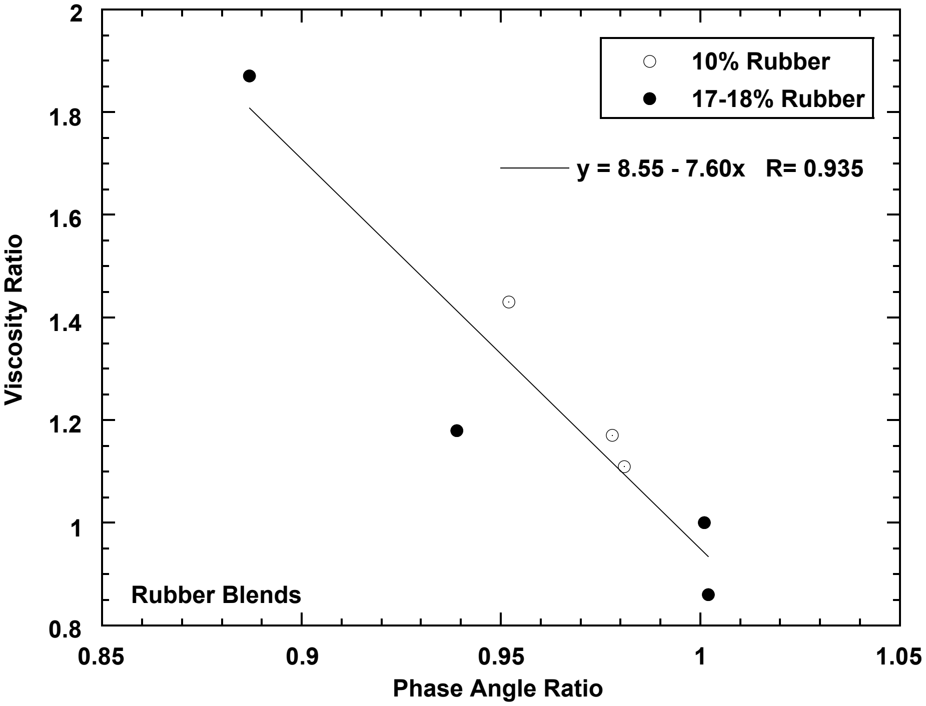

Figure 3-24. Relationship between Viscosity and Phase Angle Ratios.

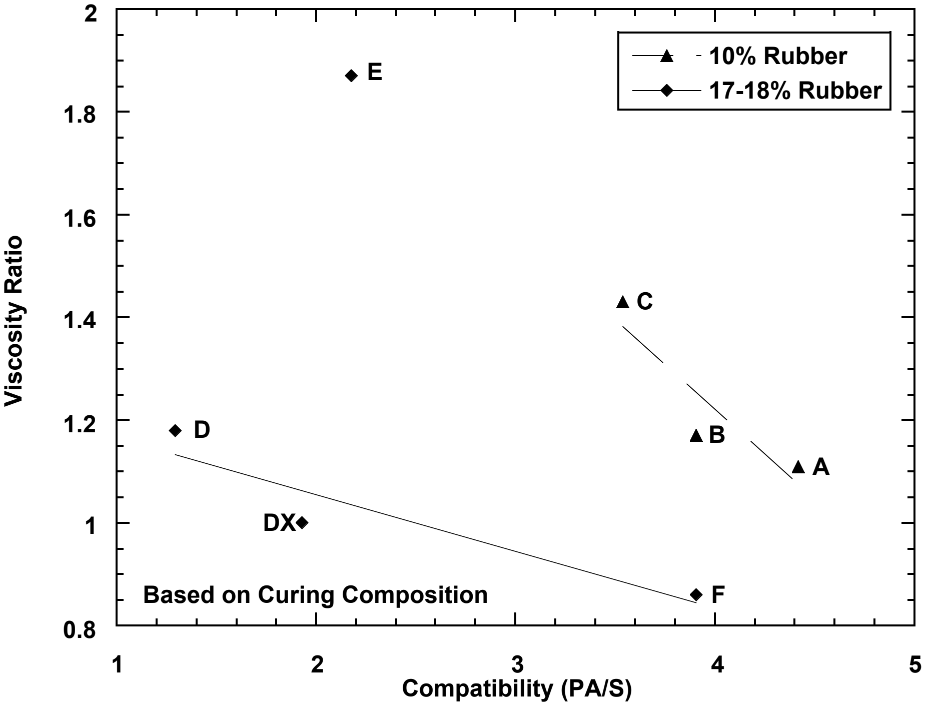

Figure 3-25. Effect of Compatibility Based on Curing Composition on Viscosity Ratio.

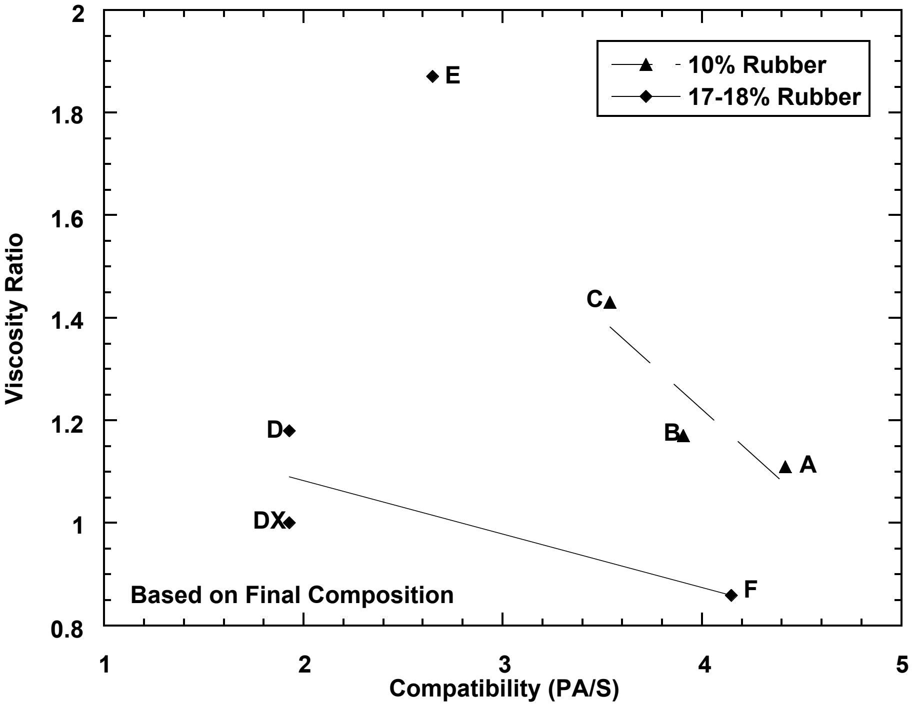

Figure 3-26. Effect of Compatibility Based on Final Composition on Viscosity Ratio.

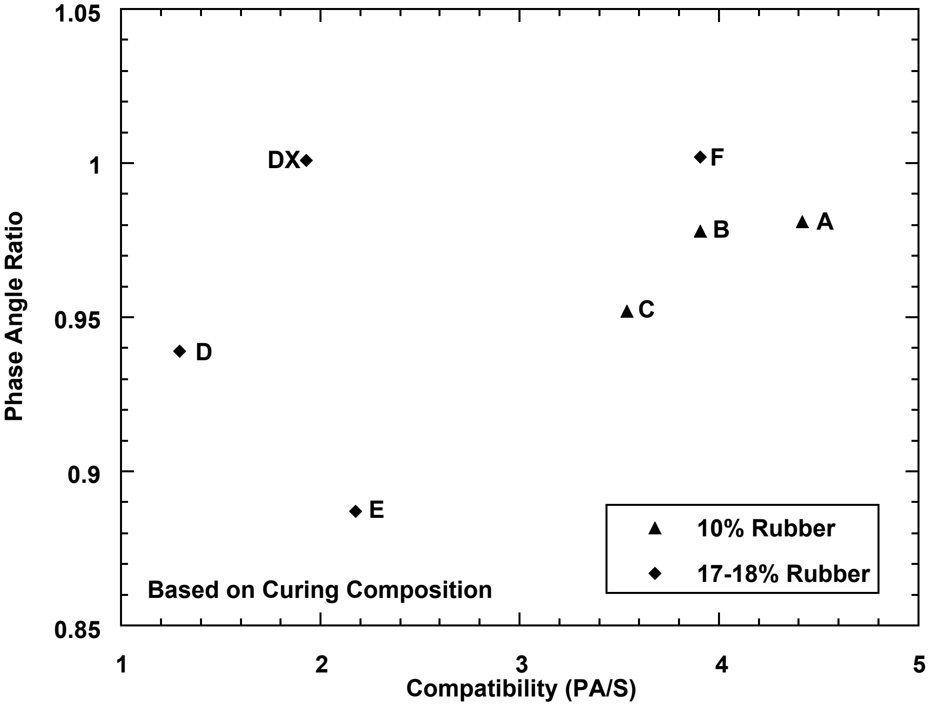

Figure 3-27. Effect of Compatibility Based on Curing Composition on Phase Angle.

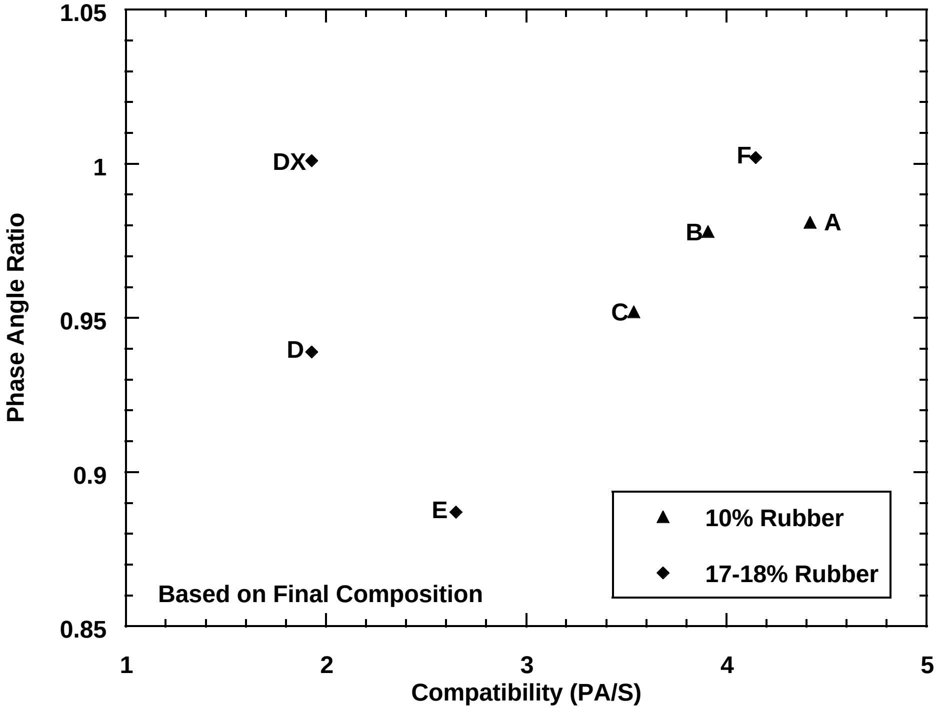

Figure 3-28. Effect of Compatibility Based on Final Composition on Phase Angle Ratio.

The performance of Blend F is unusual in that the top sample is more viscous than the bottom, and Table 3-20 shows the top to be slightly more elastic. This would indicate that the asphalt was denser than the rubber. This could be as the blend contained no DAO. The curing was done in pure resin which was then cut back with asphalt solids.

Figure 3-29 shows that, except for Blend E, the grade span increases with viscosity ratio. Regarding curing method, improved curing affects the settling and reduces the grade span, as shown by Blends D and DX.

In an attempt to explain the very poor settling of Blend E, phase angle data for samples taken during curing of Blends D, E, and F are presented in Figure 3-30. All samples were cured with 25 percent rubber and cut back to the final compositions. It does appear that E is curing less well than D and F, but as its composition is between those of D and F it is not clear why. The final settling data are consistent with these results; however, the blending sequence of E may also be a factor. It was cut back with some DAO and a considerable amount of asphalt solids, and the subsequent blending might have been insufficient to completely dissolve the asphaltenes. Notice that Blend D is also inferior in settling to Blend DX which was not cut back but cured like Blends A, B, and C.

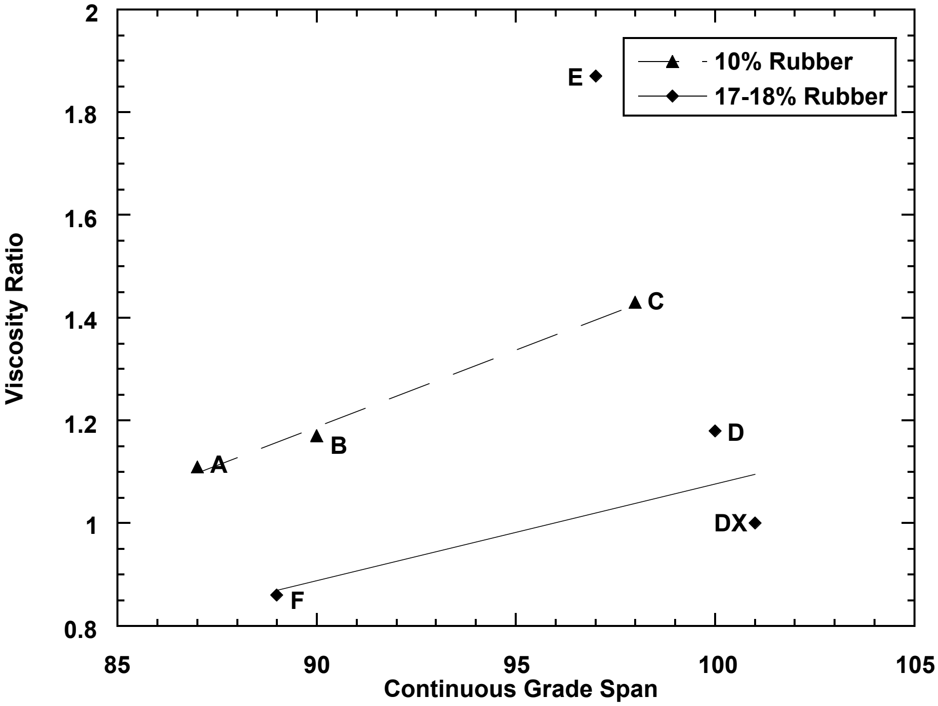

Figure 3-29. Relationship between Viscosity Ratio and Continuous Grade Span.

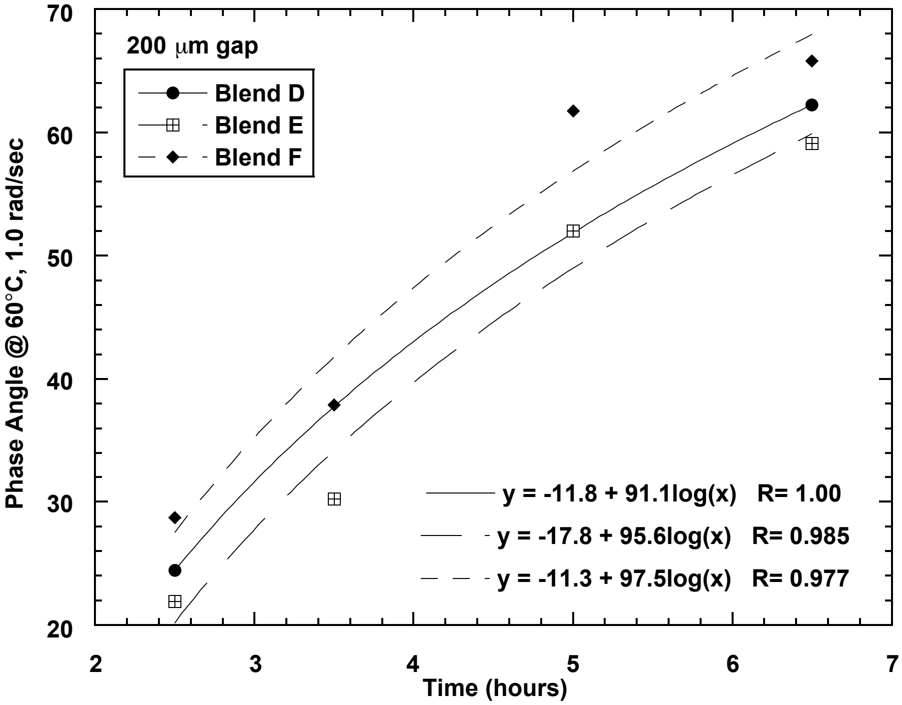

Figure 3-30. Progression of Phase Angle during Curing Process.

To the extent that settling is a function of composition, it seems to run counter to good PG grade (Figure 3-29). Blend F is the best at settling but exhibits the poorest grade span of the high rubber content blends. Blend A is the best at settling but the poorest with respect to grade span among the lower rubber content blends.

These data seem to indicate that curing composition, rubber concentration, and cut back procedure may each have significant effect on the final settling properties. In particular, Blend DX which exhibits an excellent PG grade span also exhibits superior settling properties.

Conclusions

The Corbett compositions affect the PG of high-cure asphalt rubber. Asphaltenes and saturates increase the PG span by lowering the bottom grade while polar aromatics decrease the PG span by increasing the bottom grade. Naphthene aromatics on the other hand did not show significant effects on the PG.

High-cure crumb-rubber modified asphalt produced from neat asphalt having a low asphaltene and saturate content and, correspondingly, having a high polar content exhibits better dissolution of rubber.

Interestingly, except for Blend E, the higher rubber content asphalts settled less than the lower ones. These data are complicated by the sensitivity to curing mode. It does appear that settling is better at high aromatic levels which runs counter to the compositions effect on grade. It could well be that the improved curing is actually reducing the grade span.

LABORATORY DEVELOPMENT OF INDUSTRIAL PREPARATION TECHNIQUES

The study of CRMA in the laboratory is not complete without a set of scale-up procedures. The reason for this necessity relates to the installation problems documented by many authors (Allison, 1967; Jiminez, 1982; Linden et al., 1989). One of the problems with conventional asphalt rubber is its viscosity is too high; consequently the binder does not coat the aggregate properly and installations fail. Furthermore, due to incomplete blending or due to rubber particle settling while the material is transported to the job site, asphalt-rubber binder samples from the same batch, but from different transports, can have a high degree of variability in HTV. Consequently, adjustments to the binder content on the job may be necessary. Alternatively, adjustments to the mix temperature may be made; however, a substantial temperature change may be required.

Meeting the Optional High-Temperature Viscosity Specification and the Texas Settling Test

To a large degree the high-cure process will eliminate the HTV problem, in that the high-cure HTV values fall about halfway between the neat binder and the low-cure, conventional technique, given equal rubber content. Table 3-7 and Table 3-24 list the high-temperature viscosities of a selection of binders. The blends are indentified numerically by Tables 3-3 through 3-6, and their preparation is described in a previous section. Each of these blends was tested using a four-speed Brookfield Model RVF Viscometer. Some of these data seem somewhat extraordinary, especially at high rubber content. It is believed that a good deal of error may be associated with the high-rubber content, low-cure measurements. Researchers hypothesized uneven temperature profiles and the potential for settling were present and that the viscometer was ill-conditioned for the samples. The long delays to allow for equilibrium contributed to an uncertainty about heating and settling.

The Brookfield Model DV-III Viscometer has been available more recently for sample analysis. It is capable of rotation rates between 0.1 and 250 rpm. A well-designed thermocell complements the spindle design, and the system requires much less material, 13 grams compared to 80-100 grams, both of which enhance the temperature control issue. The DV-III is capable of stand-alone use and computer interface control. Using computer control, a series of multi-speed data points can be attained without user intervention. The data in Table 3-25 present the HTV of asphalt rubber prepared by conventional means (Low-Cure Study #2), various samples related to the 2818 test section, and blends of Air-Blown Flux #1 (F1AB), i.e., F1AB-20, F1AB-68, etc. materials that were sampled at various times during curing, along with a variety of neat binder properties.

Some description of the F1AB asphalts is necessary. About fifteen 2,200-gram batches of a refinery Flux #1 (7 Pas, 70 poise material at 60 °C) were air-blown in one-gallon cans at 204 °C (400 °F), with drill-press mixing at 1550 rpm, and air sparge rate of 4 L/min. The dynamic shear rheometer (DSR) material properties were monitored while air-blowing to achieve the desired AC or PG grade, which was allowed to vary somewhat over the 15 batches. The house air supply varied from day to day, rendering timed runs impractical. Furthermore, while air-blowing continued, a lag of about 20 minutes between sampling and DSR results imposed a considerable challenge in accurately attaining the desired grade. The air-blowing runs were sampled frequently and this monitoring allowed trendlines to be established which allowed endpoints to be predicted with some degree of success.

F1AB-65 was produced by air blowing just one 2,200 gram sample to an actual PG-65 grade, and likewise for F1AB-67 to an actual PG-67 grade, while the target grades were PG-64 and PG-70. Even with this reasonable accuracy, only one unique blending sample was produced, and it became apparent that a mixture of several air-blown repetitions would facilitate the rubber

Table 3-24. High-Temperature Viscosities of High-Cure Blends #301-#314.[a]

High-Cure Blend Description	High-Temperature Viscosity, η (poise)					
	121°C (250°F)	149°C (300°F)	160°C (320°F)	171°C (340°F)	182°C (360°F)	194°C (380°F)
Resin #1	3.38	1.00	0.65	0.60	0.43	0.25
Blend #301	8.83	3.40	1.70	1.38	0.93	0.78
Blend #302	15.75	4.27	3.42	2.25	1.98	1.35
Blend #303	8.68	2.45	1.75	1.18	0.89	0.74
Blend #304	7.65	2.60	1.78	1.43	1.03	0.98
Blend #305	16.48	6.43	4.48	3.05	2.48	1.90
Blend #306	9.48	3.68	1.98	1.34	0.91	0.73
AC-10 #2	7.20	2.60	1.87	1.15	0.85	0.68
Blend #307	13.38	4.75	2.52	2.18	1.70	0.90
Blend #308	15.93	5.72	3.45	2.84	1.87	1.70
Blend #309	16.50	7.12	3.97	2.90	1.80	1.42
Blend #310	13.83	4.42	3.17	1.93	1.50	1.00
Blend #311	45.85	10.35	7.43	5.58	5.58	3.38
Blend #312	13.13	5.20	3.45	1.89	1.35	1.03
Blend #313	6.80	3.18	3.15	2.05	1.58	1.40
Blend #314	9.28	5.03	3.03	2.23	1.73	1.28

[a] - Billiter, 1996.

Table 3-25. HTV of Selected Materials - DV-III Viscometer Measurement.

Material Description			HTV (poise) 135°C (275°F)
Neat Binders	SHRP ABL-2	MRL Library Material	3.8
	Resin #1	Table 3-1	1.6
	AC-10 #2	Table 3-1	2.9
	AC-20 #1	2818 Test Section and Table 3-1	5.6
	ABFA-20	AB Flux A to AC-20	3.4
	ABFA-64	AB Flux A to PG-64	3.8
	ABFA-67	AB Flux A to PG-67	4.4
	ABFB-68	AB Flux A to PG-68	---
Low-Cure Study #2 Drill Press Mixer 177°C (350°F) 500 rpm	Resin #1	10% TG-40	4.0
		20% TG-40	37.2
	AC-10 #2	5% TG-40	4.5
		10% TG-40	8.8
		15% TG-40	23
		20% TG-40	76
2818 Test Section	AC-20 #1 10% RS-80	246°C (475°F) 8000 prm	14.6
	AC-20 #1 15% RS-80	CAMC Design Lab Prep.	33.3
	HM2-13.5% RS-80	AMI Industrial Prep.	20.2
	HM2-17.6% RS-80		38.0
Air Blown Flux Experiments All Samples 12% GF-20 Silverson Mixer Cured at 260°C (500°F) 8000 rpm	ABFA-20	1.5 h	7.1
		3.0 h	6.3
		4.5 h	6.3
	ABFA-64	1.5 h	9.3
		3.0 h	7.6
		4.5 h	6.8
	ABFA-67	1.5 h	9.8
		3.0 h	9.25
		4.5 h	9.0
	ABFA-68	0.0 h	46
		0.5 h	11.3
		1.0 h	10.7
		1.5 h	10.1
		2.0 h	9.3
		3.5 h	8.0

curing analysis. F1AB-20 was produced by mixing three consecutive air-blowing runs in a ratio of 1:1:1, to achieve over 6,000 grams of asphalt binder. The target viscosity of each attempt was 2,000 poise, and the resultant viscosity was 2,018 poise. The binder could then be divided into three samples with identical compositions. Similarly, F1AB-68 was produced by equally mixing seven air-blown replicates. The target viscosity was a PG-70 grade, but only a PG-68 grade was produced. The multiple mixing method also reduced error by allowing the researcher to dilute bad air-blowing runs and to adjust later air-blown runs to compensate for these errors as well.

The low-cure preparations exhibit unacceptably high viscosities at content levels of 15 and 20 percent. The test section preparations are lower and fall in line with respect to rubber content. Interestingly, the 17.8 percent binder produced by Asphalt Materials, Inc. (AMI) has a comparable HTV to that of the low-cure Resin #1 containing 20 percent rubber, 38 versus 37 poise. This should not reflect badly on the AMI curing, given that AC-20 #1 contains seven times more asphaltenes than Resin #1, 21 versus 3 percent (Table 3-10) and is approximately four times its viscosity (Table 3-25). The blends of F1AB show the effect of prolonged curing on the high-temperature viscosity. For a reference, the F1AB-68 data contain a measurement at zero hours of curing with viscosity of 46 poise. This datum was obtained by hand mixing the sample with a ladle, followed by curing it with the Silverson mixer for less than two minutes. The high-cure process rapidly decreases the HTV to around 10 poise by the first sampling point of 0.5 hours. The HTV decreases slightly, but statistically significantly, after further processing. From these data it is seen that the high-temperature viscosity is affected early in the high-cure process, and so it can be brought under control rapidly.

However, the HTV is only one binder specification. The Texas Settling test is a TxDOT testing procedure to gauge separation of modified materials. For the test, 350 grams of modified binder are placed in a pint can. The sealed can is placed in an oven at 163 °C (325 °F) for 48 hours and allowed to settle. After cooling, the samples are removed from the oven. A very thin layer (about 20 grams each) is removed from both the top and bottom of the can. Each of these samples is subjected to ASTM D 36 to determine their softening points. The softening points cannot differ by 4 percent, or more, equation 3-4, or the sample fails Texas Settling. (It should be noted that the outcome of such a calculation will vary based on the temperature scale employed and that the Celcius scale, providing the most stringent results, is used herein.)

$$2\,\frac{sp_{Bot} - sp_{Top}}{sp_{Top} + sp_{Bot}} < 0.04 \qquad (3\text{-}4)$$

Figure 3-31 examines the effect of curing on the Texas Settling outcome for the material F1AB-68. The binder is found to pass the settling test after a little more than 2 hours of curing, well after the HTV (Table 3-25) has reached a sloping plateau. Consequently, based on reasonable levels of rubber in the binder and this type of high-curing, curing that meets the Texas Settling test will also meet the HTV specification. Of course, if the base material viscosity is too high, then this generalization will be invalid.

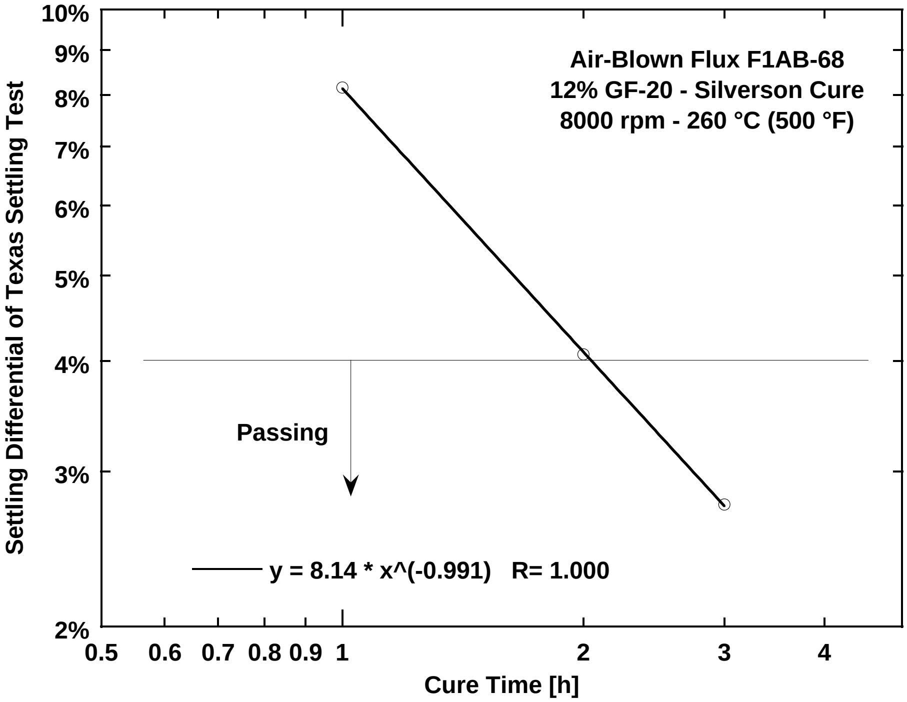

Figure 3-31. Effect of Curing on Texas Settling Test.

Tracking the Curing Process

From a production perspective, it is important to be able to follow the curing process to determine when a desired level of curing has been met, i.e., when the HTV is at the desired level or when the cured binder is at an appropriate level of storage stability. Evidently, a settling test would be preferred over the HTV because the HTV becomes rapidly insensitive to high-curing.

But the two tests are a contrast in convenience. The HTV takes a minimum of only 20 minutes after sampling and requires less than 15 grams of binder. The Texas Test requires 350 grams and 48 hours to settle in addition to the time spent measuring the softening points. Also, the text of the ASTM specfication admits that the softening point is an arbitrary test. The laboratory high-cure process utilizes 2,000 grams of material in total and sizable quantities of binder are sampled during the cure: 4-gram trays, every 15 minutes for 2 hours and every 30 minutes afterward; 70-gram, 3-ounce tins, one or two every 30 minutes. Consequently 140 to 300 grams are sampled each hour. This sampling affects the total binder supply; and sampling the 350 gram settling tests also quickly depletes the batch. In a cure of the ABFA-68 air-blown flux, over 1,050 grams of binder were removed from a single three-hour run just for three settling tests, and nearly 1,500 grams were sampled altogether. The run was stopped at 3.0 hours of curing when the mass in the blend was effectively halved by the 3.0-hour sampling. It is obvious that a curing gauge must consume far less material (at least as a laboratory practicality), assure adherence to the required properties, and be rapidly completed, so that design decisions can be made during production, rather than days later.

Another property found to be affected by curing was the viscosity measurement at 60 °C (140 °F), specifically the phase angle and the range of gaps at which the rheometer could reliably reproduce the results. Asphalt measurements on a dynamic shear rheometer are typically done using a parallel plate geometry, rather than a cone and plate geometry. The parallel plate geometry allows the measurement gap to be changed to accommodate aged and modified materials. Aged materials require higher torques to produce the oscillations of the desired magnitude. Testing the aged material at a wider gap reduces the required torque. Rubber-modified materials contain particles that can affect the measurement adversely if any appreciable fraction of particles comes in contact with both plates. Establishing a wider gap eliminates the chance of bad measurements. However, using size exclusion chromatography, the high-cure process has been shown to increase rubber digestion as curing proceeds, Figure 2-30, for example.

Figure 3-32 illustrates the difference in rheological measurements for a 0.0-hour blend (2 minutes of mixing), when the gap is substantially reduced from the accepted distance of 1,500 µm to 500 µm. Obviously, the 500 µm data are in error from a rheology viewpoint, as a substantial difference can be noted between the 1,500 and 500 µm data, most especially in the phase angle, throughout the tested frequency range, but more especially at 1.0 rad/sec. In fact the 500 µm phase angle data have a positive slope, while the 1,500 µm data have a negative slope. As curing progresses (Figures 3-33 through 3-38) and more gaps are explored, the 500-µm phase angles are shown to reach a zero slope at 0.5 and 1.0 hours of curing (Figures 3-33 and 3-34) and a negative slope at 1.5 hours of curing (Figure 3-35). At 1.5 hours the 500 µm phase angles approach the same values as the 1,000 and 1,500 µm data and have reached those values at 2.0 hours of curing, Figure 3-36. The data confirm that a 500 µm gap is appropriate to measure a high-cure binder, if that binder has been cured for a minimum amount of time. With continued curing (Figures 3-37 and 3-38) the 200 and 400 µm gap data approach the accepted data. A separate cure of ABFA-67 blended for 3.0 hours also shows this effect (Figure 3-39). As curing progresses, the gap at which a positive slope in phase angle is present is decreased.

The data confirm that rubber particle size is decreasing during the curing process, as suggested by their reduced effect on the parallel plate phase angle measurements at any given gap. Contrary to the HTV, this phenomenon can be observed throughout the curing process due to the ability to operate at multiple rheometer gaps, not just at the beginning of curing. Table 3-25 indicates that for ABFA-68 the HTV was already reduced from 46 to 11.3 poise after 0.5 hours of curing, with a final value of 8.0 poise, while the 200 µm phase angle at 1.0 rad/sec was 30 degrees at 0.5 hours, 68 degrees at 2.5 hours, and finally rose to about 76 degrees at 3.0 hours (Figures 3-33, 3-37, and 3-38). Figures 3-40 and 3-41 summarize phase angle measurements as a rapid correlation for tracking settling. Figure 3-40 plots the phase angle at 1.0 rad/sec for various gaps against the Texas Settling test differential temperature. As curing begins, the settling

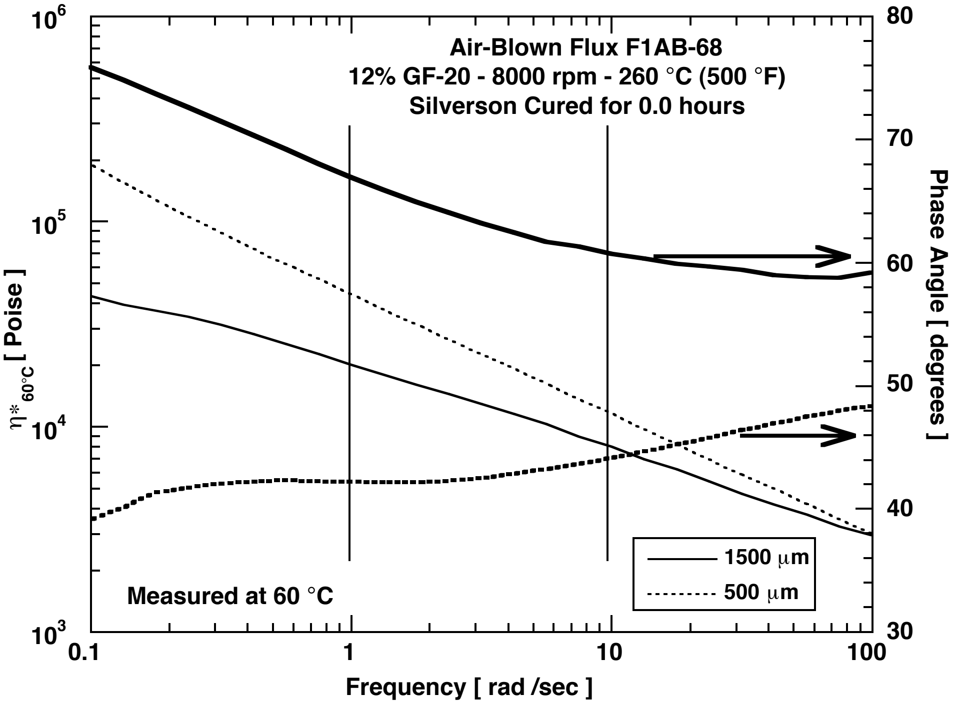

Figure 3-32. Gap Cure Test for Blend of ABFA-68 - Cured for 0.0 hours.

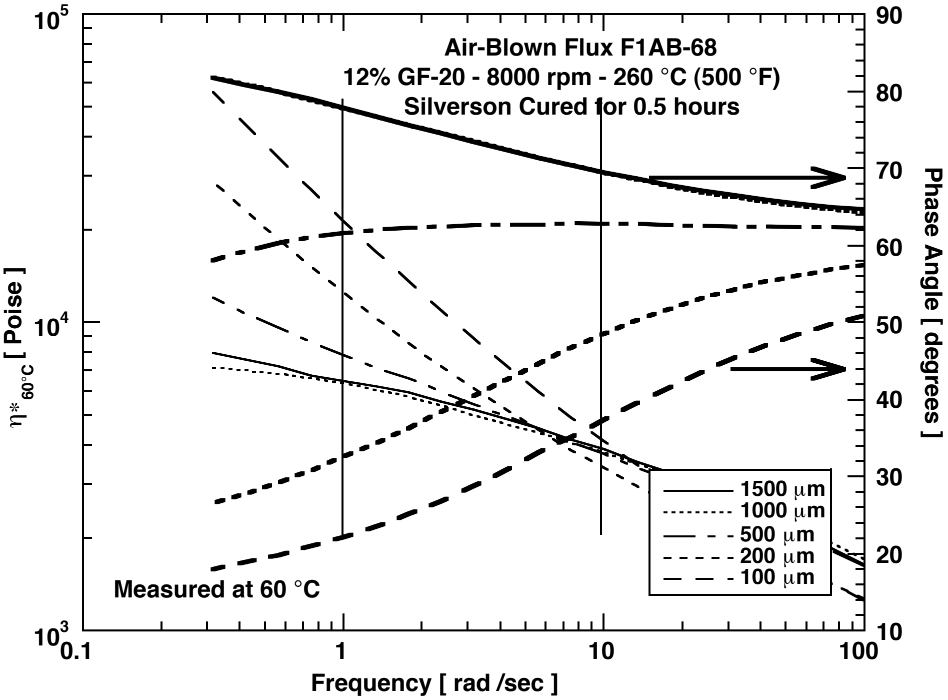

Figure 3-33. Gap Cure Test for Blend of ABFA-68 - Cured for 0.5 hours.

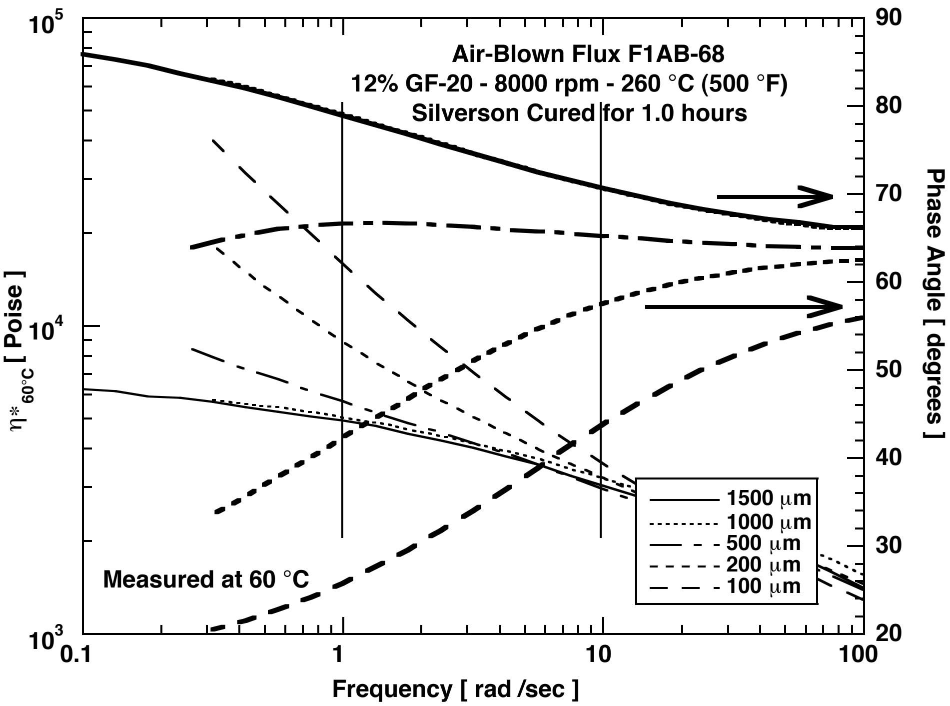

Figure 3-34. Gap Cure Test for Blend of ABFA-68 - Cured for 1.0 hours.

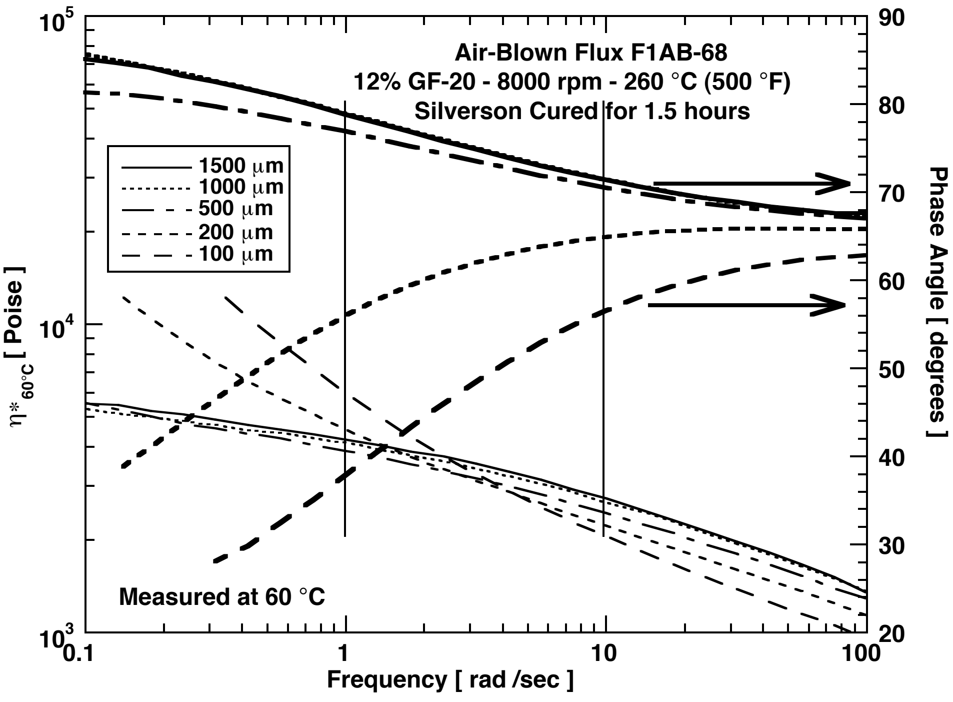

Figure 3-35. Gap Cure Test for Blend of ABFA-68 - Cured for 1.5 hours.

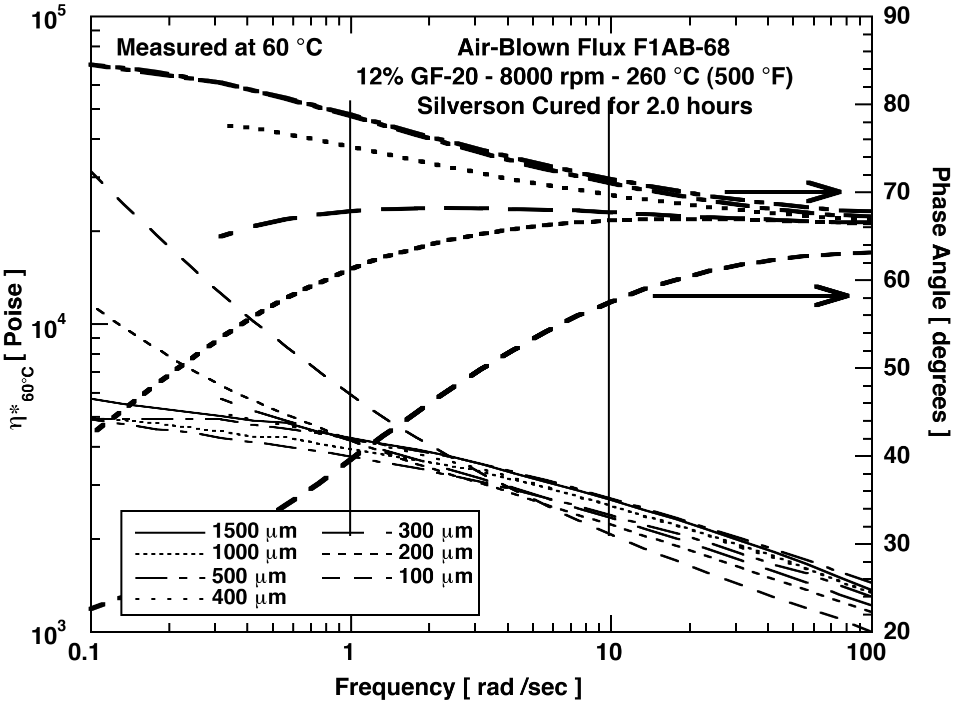

Figure 3-36. Gap Cure Test for Blend of ABFA-68 - Cured for 2.0 hours.

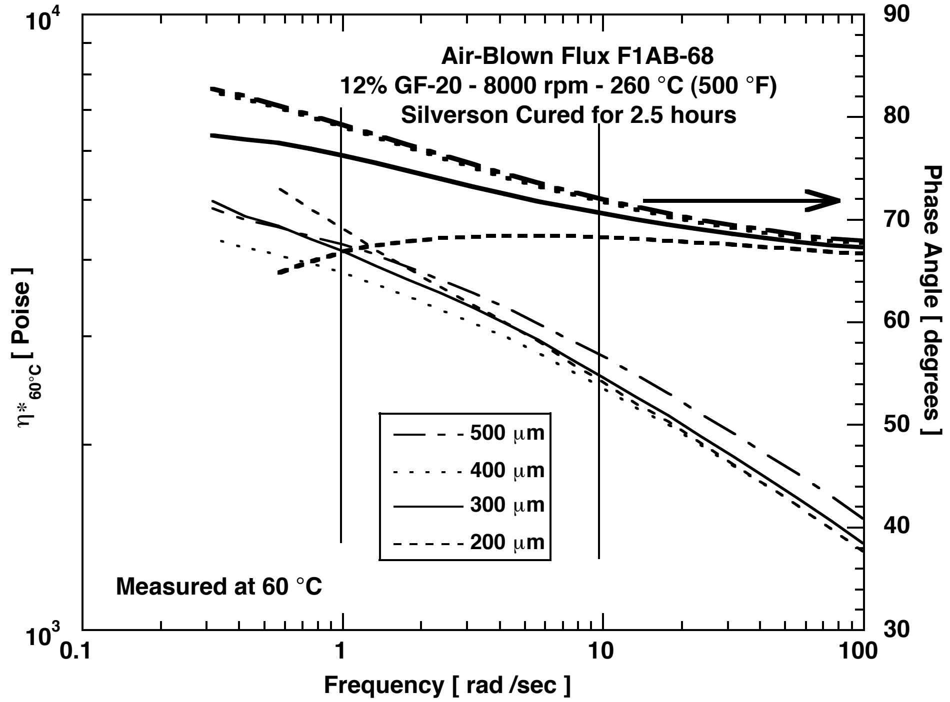

Figure 3-37. Gap Cure Test for Blend of ABFA-68 - Cured for 2.5 hours.

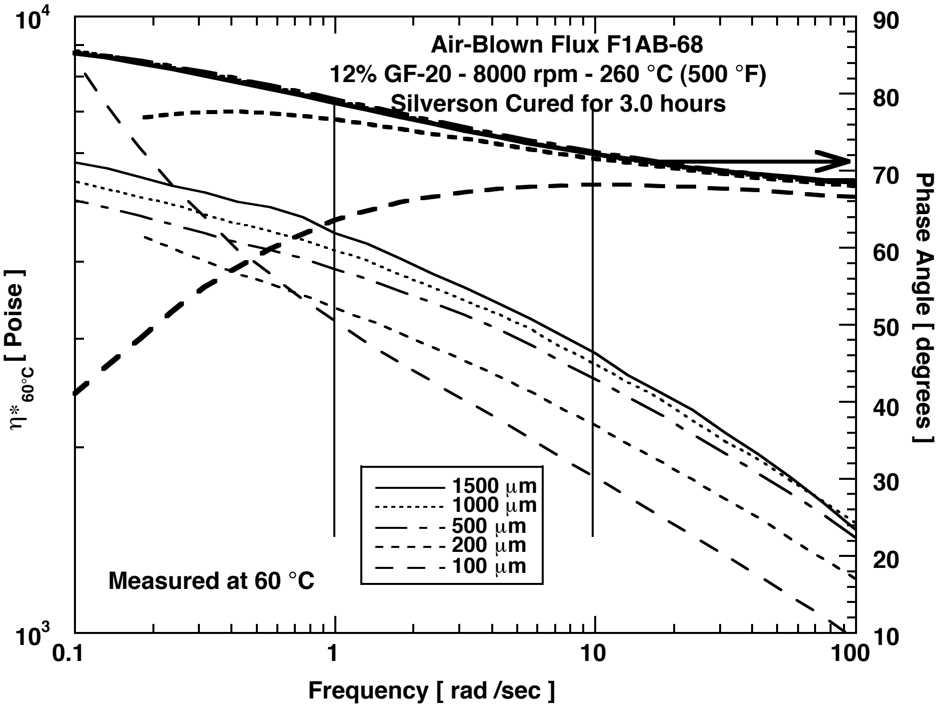

Figure 3-38. Gap Cure Test for Blend of ABFA-68 - Cured for 3.0 hours.

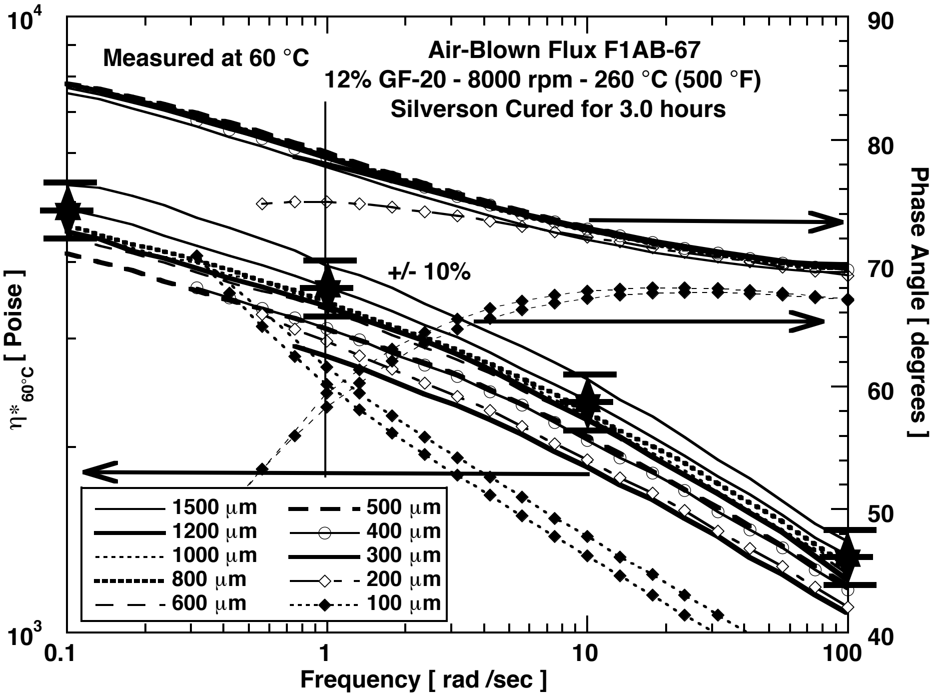

Figure 3-39. Gap Cure Test for Blend of ABFA-67 - Cured for 3.0 hours.

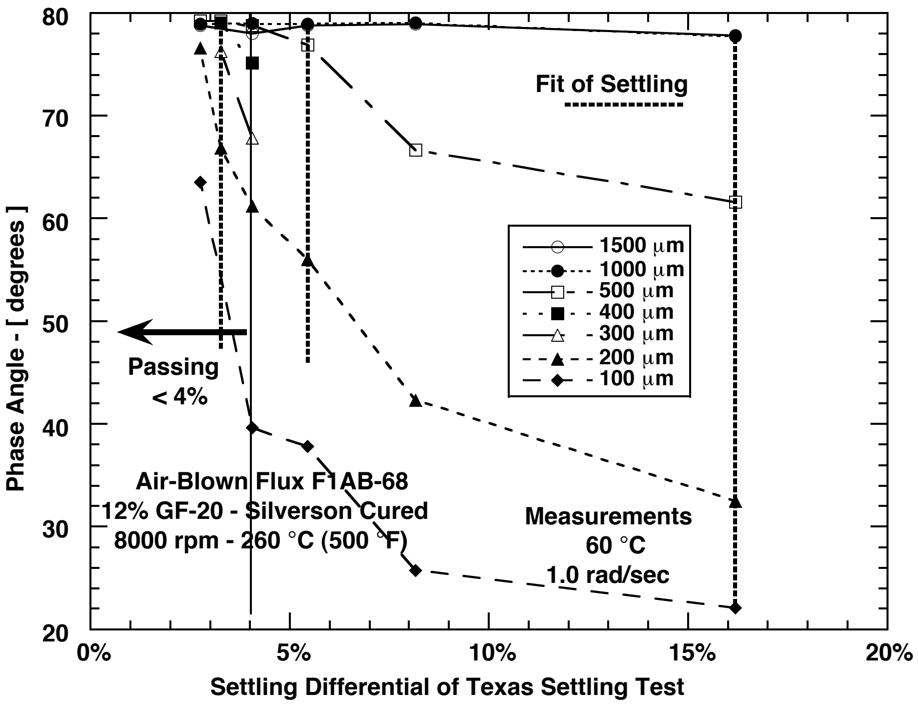

Figure 3-40. Comparison of Reduced-Gap Phase Angle to Settling Properties at Several Gaps and 1.0 rad/sec.

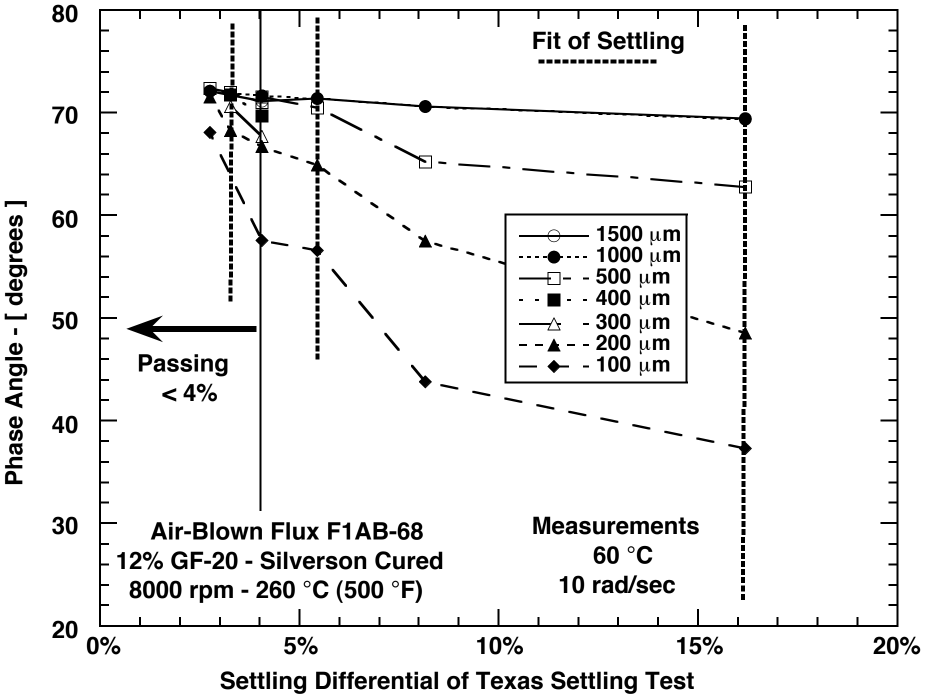

Figure 3-41. Comparison of Reduced-Gap Phase Angle to Settling Properties at Several Gaps and 10 rad/sec.

differential is high, so data at short blending times correspond to a high settling differential and appear at the right on the figure. As curing progresses, the settling differential decreases and blend times increase; therefore, blend times increase to the left. It should be noted that measurements at 1.0 rad/s (Figure 3-41) spread out the gap differences more than measurements at 10 rad/s and therefore appear to be more sensitive to tracking curing.

It must be noted that ABFA-68 was sampled for gap properties at curing intervals of 0.5 hours, but was sampled for settling only at intervals of 1.0 hours because of the material requirement. The fit obtained from Figure 3-41 was used to interpolate additional settling differentials at the missing 0.5 hour intervals, so there is an uncertainty of the ordinate position of these points. Each of these points is marked by a broken vertical line. The phase angle data are not interpolated. Sampling for the Texas Settling test also seems to affect the cure as the phase angle data seem to jump after a settling sample is withdrawn.

The purpose of these types of data, and their value as a curing gauge, is to determine the path followed during curing using reduced-gap measurements, and especially near the 4 percent threshold that indicates passing the settling test. The 100, 200, and 300 µm data at and after the 4 percent line continue to change rapidly with curing and would be a good gauge of the curing process. As an example, an engineer at an industrial facility who is working with 12 percent GF-20 and a material like the ABFA-68 could select a value of 70 or 72 degrees and measure the entire cure at a gap of 300 µm. When the phase angle exceeds 72 degrees, the processing can be ended, as the material is already known to pass on settling (Figure 3-40) and HTV (Table 3-25). For materials that differ from this example in rubber type, content, and binder, a series of laboratory-scale correlation experiments (similar to that described herein) need to be performed to characterize the settling and phase angle properties before industrial preparation.

Further examinations were conducted to study the effect of the initial rubber mesh on the tracking ability of the gap procedure. Figures 3-42 through 3-45 illustrate these efforts. Blends #307 and #310 of AC-10 #2 are described in Table 3-5 and correspond to Blends #8 and #10 of Asphalt #3 in Tables 2-8 and 2-9. Blend #307 is tested at 500 µm throughout the curing process in Figure 3-42. The rubber employed for this blend was TG-10 with a maximum particle size of 1,680 µm. There is a good degree of sensitivity at 500 µm. Similarly, some sensitivity was found with Blend #310 at 500 µm (Figure 3-43). It should be noted that the TG-40 rubber used in this blend was 420 µm or smaller and the sensitivity to gap setting near 500 µm also was less than for the -10 mesh material. Figures 3-44 and 3-45 show blends measured at a gap of 200 µm. In Figure 3-44 the 6.5 hour sample of Blend #307 was also measured at 100 µm. This blend was very highly cured, yet the figure indicates that a particle influence still affects the rheometer at 200 µm, while this is not the case at 500 µm. The sensitivity range for Blend #307 is 300 to 400 µm. In Figure 3-45 there is also some phase angle sensitivity to curing. For both of these blends, the settling properties for the final (6.5 hr) sample are presented in Table 2-9. Clearly, Blend #10 (#310) has better settling characteristics than Blend #8 (#307). This would seem to confirm the phase angle sensitivity results.

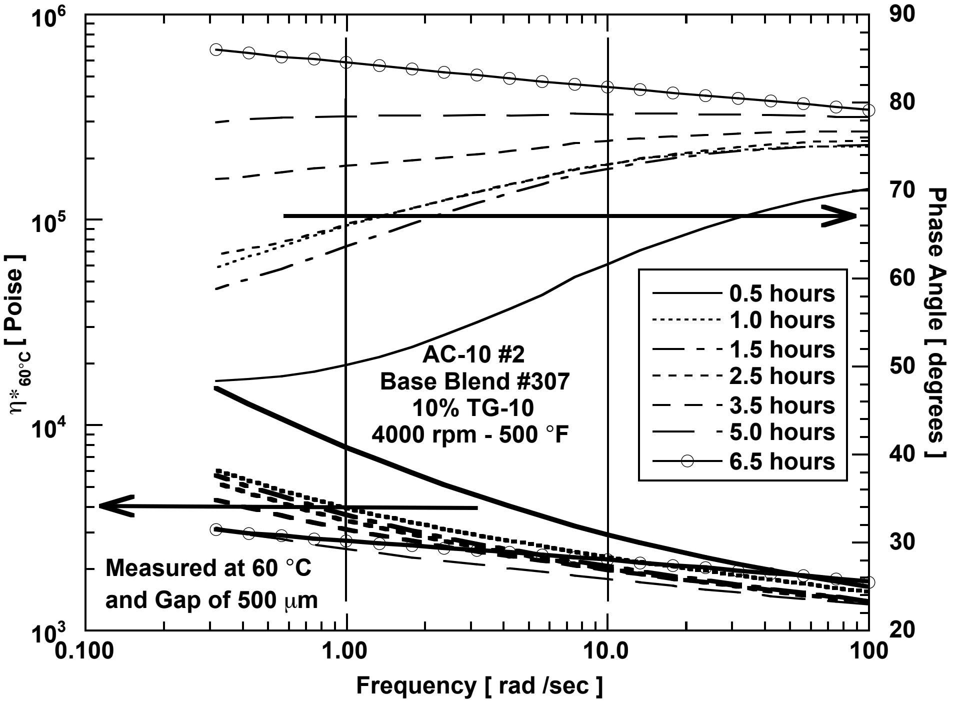

Figure 3-42. Gap Cure Test for Blend #307, AC-10 #2 Base Cure - Measured at 500 μm.

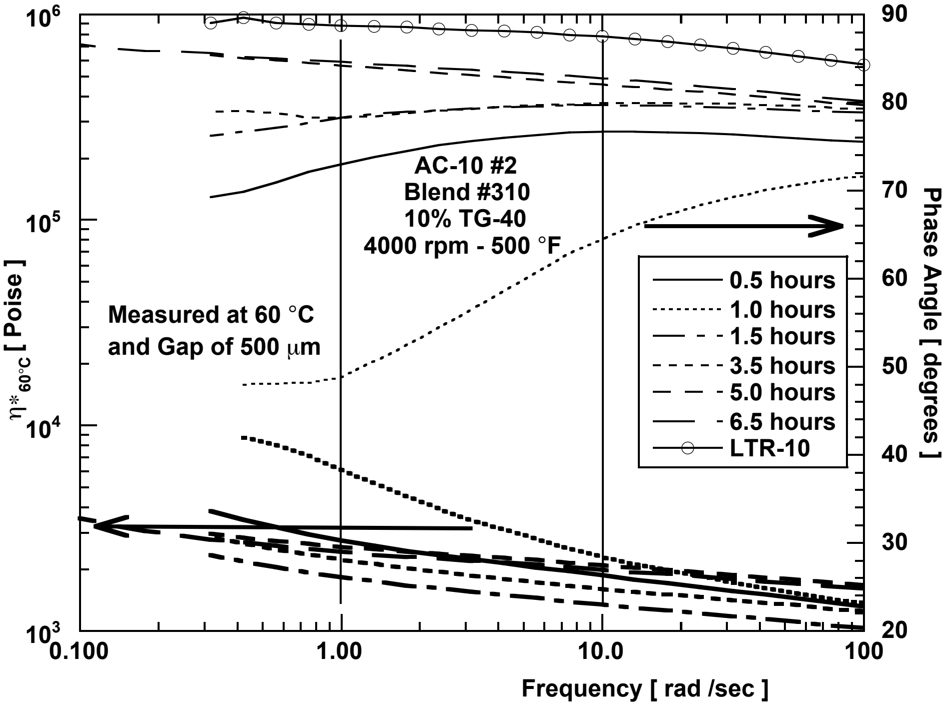

Figure 3-43. Gap Cure Test for Blend #310, AC-10 #2 10% TG-40 - Measured at 500 μm.

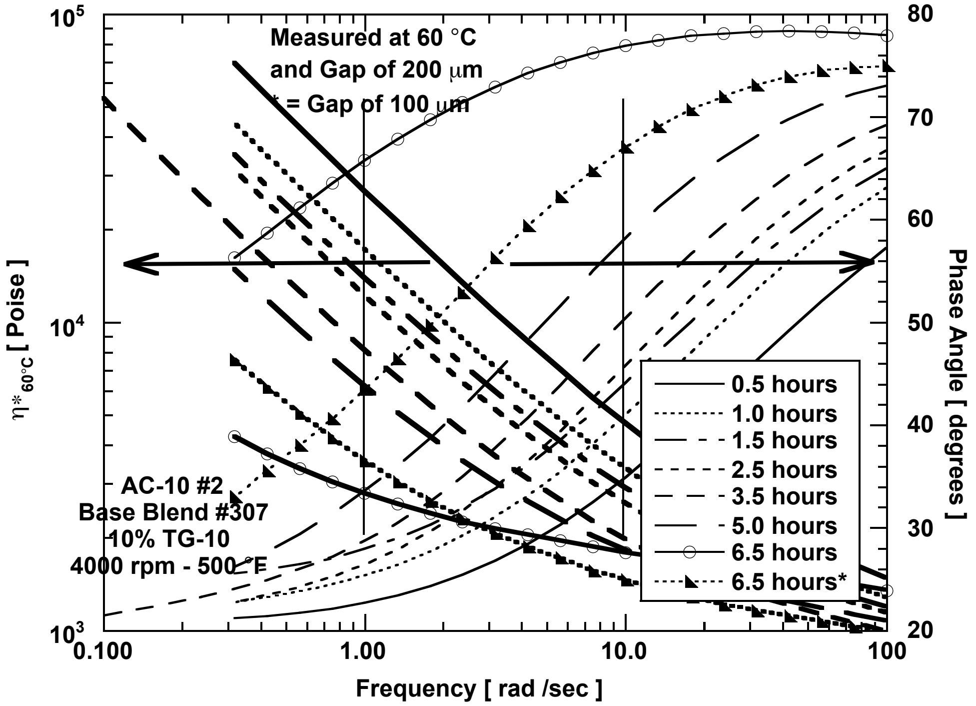

Figure 3-44. Gap Cure Test for Blend #307, AC-10 #2 Base Cure - Measured at 200 μm.

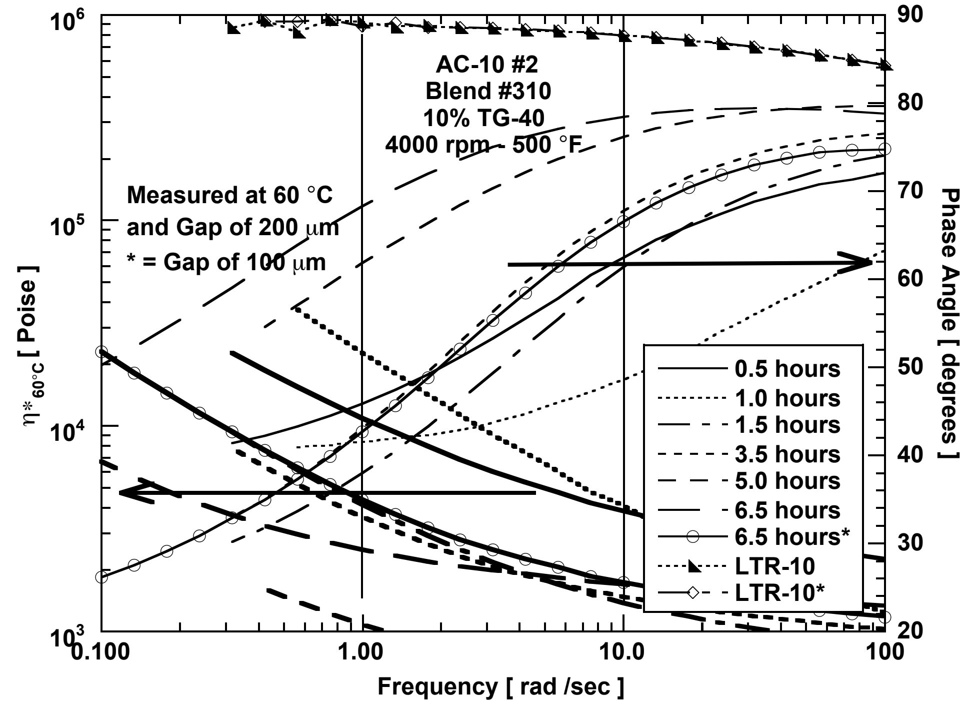

Figure 3-45. Gap Cure Test for Blend #310, AC-10 #2 10% TG-40 - Measured at 200 μm.

To summarize these data, it appears that initial rubber particle size has some influence on the reduced gap measurements, and caution in choosing the gap at which measurements are taken is required. If the gap is too narrow, then the material may be cured too long to reach the desired property; if the gap is too great, then the material may be susceptible to settling.

Conclusions

Three issues associated with industrial preparation of high-cure asphalt-rubber materials were addressed by this study. The optional HTV specification generally was found to be met fairly easily by the high-cure process. The Texas Settling test for storage stability of the binder was found to be met if the curing process is carried far enough. A dynamic shear rheometer at reduced gap settings can be used to track the curing process efficiently and gives a sensitive measure of the extent of cure.

LOW-TEMPERATURE DIRECT TENSION PROPERTIES OF HCAR MATERIALS

As reported in earlier sections in this chapter, the addition of rubber to asphalt provides benefits to the low-temperature PG. In the bending beam measurement, this is reflected in a reduced stiffness (S) and an increased creep parameter (m). But S and m are not the whole story as they do not provide direct measures of failure. The work reported here was performed to add to our understanding of low-temperature failure and the roles of failure stress and failure strain compared to S and m.

Direct Tension Procedure

All asphalt samples were prepared in accordance to industry accepted standards and then tested on an Instron Model BTI-3 Direct Tensile Testing System (DTTS). The DTTS elongated a small “dog bone” shaped sample at a constant rate and produced the corresponding stress-strain curve. Note that the DTTS can only collect data at a strain less than 3.75 percent. Three primary measurements were obtained from the stress-strain curves: failure stress, failure strain, and stiffness modulus. Failure stress was determined as the ratio of the uniaxial load to the original cross-sectional area at the point of failure. Failure strain was determined by dividing the change in specimen length by the effective gauge length at the point of failure. Stiffness modulus or failure stiffness was calculated by taking the slope of the chord connecting the origin to the point of failure. Ideally, an asphalt binder would exhibit high failure stress and failure strain values and a low failure stiffness.

The following procedures were used in testing different asphalt binders and asphalt-ground tire rubber blends (Asphalt Institute, 1995). A control sample was prepared which contained zero percent ground tire rubber for each binder studied. After curing at various conditions, the control and blends were placed in a RTFO at 163 °C (325 °F) for 85 minutes to simulate the oxidation induced during the asphalt manufacturing process. The control and blends were aged in a PAV at 20 atm and 100 °C for 20 hours to simulate longer term aging. The DTTS analysis was performed on the control and blends according to recent protocol. Enough of each control and blend was prepared to insure that samples did not have to be re-used because exact effects of re-use were unknown.

A further word about test conditions is appropriate. In recent years, as the DTTS method has evolved, a considerable number of changes to the test procedure and parameters has occurred. These have involved the fluid used for temperature control, the strain rate, the mold material used to fashion the test specimens, and the end inserts used to hold the sample. Some of these issues are more significant than others, but there is no doubt that individually or collectively, they can cause very significant differences in the failure strain and failure stress values which are obtained from the test. This is the nature of a failure test; any imperfection can cause significantly premature failure. The effects on stiffness or creep properties due to such procedural differences are much less, however, and probably can be neglected. The protocol used at the time of this work called for a potassium acetate bath, cured silicon molds (cured with hot asphalt so that they are saturated with asphalt components), 0.1 mm/min strain (stretch) rate, and epoxy end pieces with steel inserts to reduce holder compliance.

Effect of Rubber on Direct Tension Tests

Figure 3-46 shows direct tension tests for an AC-5 asphalt and blends containing two levels of highly cured ground tire rubber tested at -24 °C (-11.2 °F) and 0.1 mm/min. Without rubber, the base asphalt failed at this temperature at 2 percent strain and about 5 MPa stress, in excess of the required minimum failure strain of 1.3 percent. By comparison, the same base material containing 10 percent rubber was less stiff (lies under the base asphalt curve) and failed at a significantly higher strain, about 3.3 percent. On the other hand, the failure stress was essentially the same, about 4 MPa. With 20 percent rubber, the material was even less stiff at this temperature and did not fail at all. The sharp vertical line at 3.7 percent is not a break, but rather the end of the range of the instrument. Consequently, neither failure stress nor failure strain were reached.

These results are typical of all the tests we have made on these materials. At every temperature, samples with greater rubber content displayed significantly lower stiffness moduli and higher failure strain results than samples with lower rubber content. Typically, 10 percent rubber can reduce the Superpave low temperature grade by approximately three degrees.

Also typical is the fact that the failure stress may be increased somewhat by the addition of rubber. Some samples fail as high as 8 or 9 MPa, especially at higher rubber content, but values in the range of 4 to 5 MPa are more typical. Neat asphalts typically are in the range of 3 to 4 MPa. This suggests that the addition of rubber serves mainly to reduce the stiffness, thereby resulting in better low-temperature performance, rather than improving its cohesion. It should be noted that the PG improvement obtained by the direct tension test typically is consistent with that obtained by the bending beam test and that this result is a direct consequence of the fact that the failure stress is roughly constant for most rubber contents.

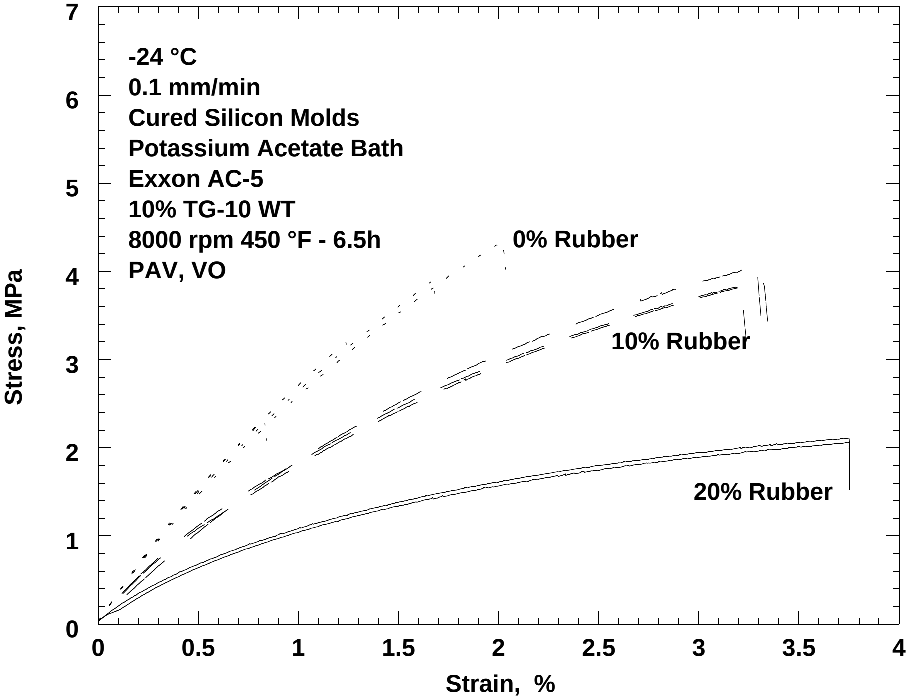

Figure 3-46. Direct Tension Tests - Rubber Content Comparison.

Data for these same materials at three temperatures are shown in Figure 3-47. Note that reducing the temperature increases the stiffness (raises the stress-strain curve) and consequently reduces the failure strain. Note again that the failure stress is constant, near 4 MPa. As before, the lower curve, at -18 °C (0 °F), does not break within the range of the instrument.

Figure 3-48 shows data at two strain rates at the same temperature for the base AC-5 asphalt containing 20 percent rubber. At the higher strain rate, the binder is stiffer than at the lower rate, in accordance with the time-temperature superposition principle. Of particular note in this case is the higher failure stress values, up to 7 MPa.

SUMMARY OF CHAPTER 3

Curing at relatively low temperatures, approximately those of the hot-mix process, and low-shear rates, conditions typical of current industrial practices, leads to a moderate interaction of the rubber material with the asphalt. The blended material has an increased viscosity due to the rubber particles, swollen by absorbed asphalt components. Low-temperature stiffness is improved, high pavement temperature G*/sin δ is increased significantly, and overall, the PG span is considerably widened. However, many low-cure materials do not meet the optional maximum high-temperature viscosity of 3 Pa·s (30 poise) at 135 °C (275 °F), and settling of the swollen rubber particles can be a concern for storage.

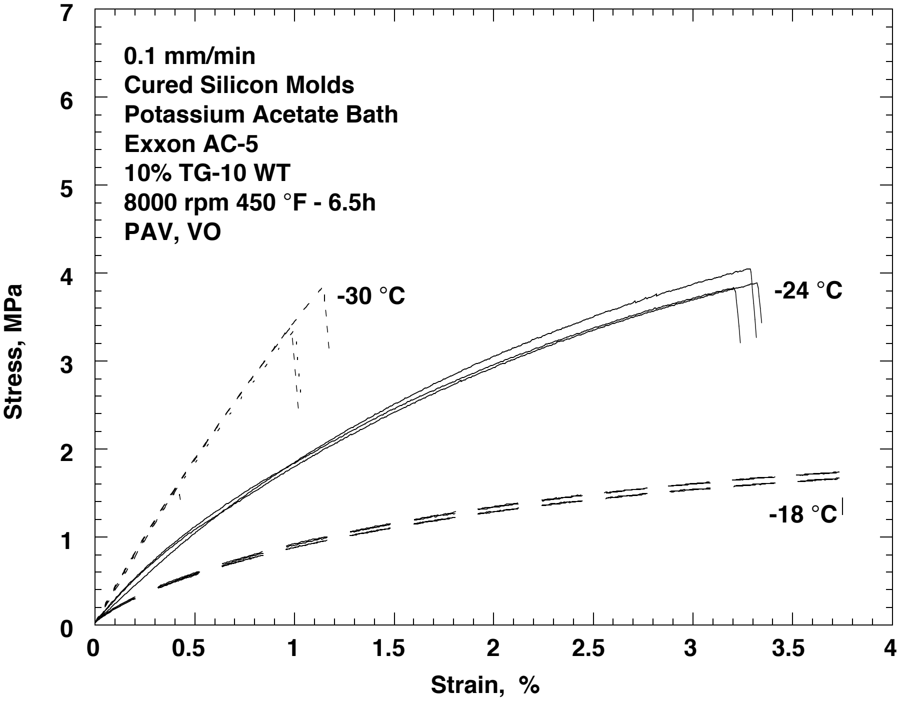

Figure 3-47. Direct Tension Tests - Temperature Comparison.

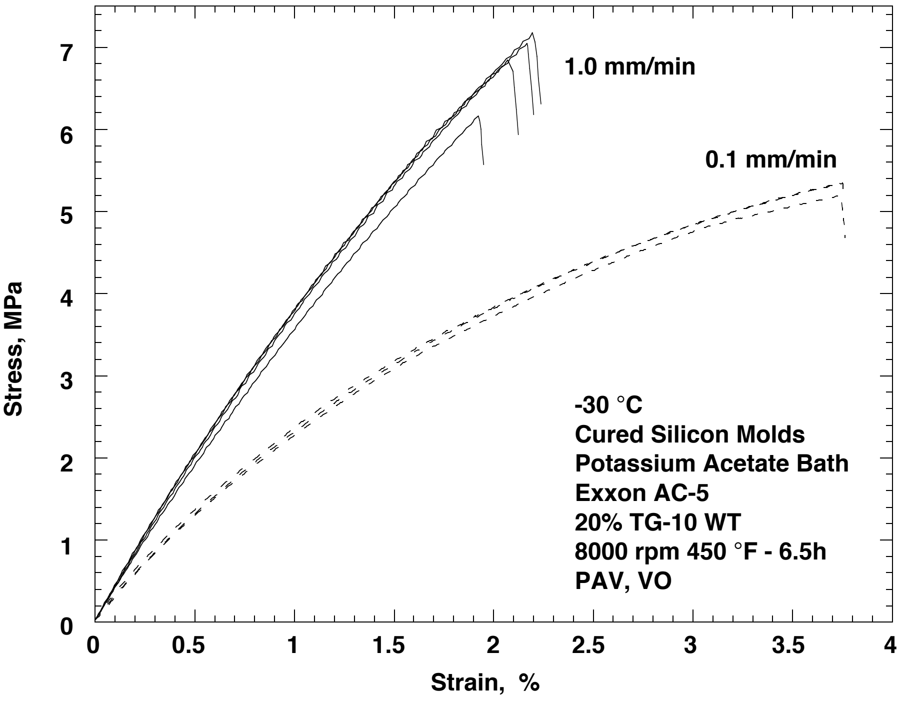

Figure 3-48. Direct Tension Tests - Strain Rate Comparison.

Curing with higher shear mixing and higher temperature further breaks down the rubber particles and digests the long polymer chains and crosslink structures. The blend viscosity decreases with additional curing, but remains elevated above that of the base asphalt material. Resulting viscosities at hot-mix installation and at rutting conditions are reduced compared to the lower shear preparations and can be lowered to the point of meeting the high-temperature viscosity criterion. Low-temperature properties show enhancement as well. However, it certainly is possible to cure too far. Materials produced at the highest level of curing indicate severe polymer degradation. These materials widen the PG span only incrementally when using a continuous grading, or single degree increment basis, but do not always yield improvement on a specification basis.

Curing in the presence of oxygen was found to have primarily two effects. First, oxygen enhanced the rubber curing process, resulting in more rapid digestion of the rubber particles and molecules. Second, the base asphalt material was oxidized to a higher viscosity material, raising the high end PG rating. These two effects together can result in a significantly wider PG span, increasing the upper grade by up to three grades while the rubber serves to hold the low-temperature grade or at least limit its loss.

Base asphalt composition affects both final PG and rubber curing. Asphaltenes and saturates increase the PG span by lowering the bottom grade while polar aromatics decrease the PG span by increasing the bottom grade. Naphthene aromatics on the other hand did not show significant effects on the PG. High-cure crumb-rubber modified asphalt produced from neat asphalt having a low asphaltene and saturate content and, correspondingly, having a high polar content exhibits better dissolution of rubber.

Three concerns associated with industrial preparation of high-cure asphalt-rubber materials have been resolved. First, the optional HTV specification generally was found to be met fairly easily by the high-cure process. Second, the Texas Settling test for storage stability of the binder was found to be met if the curing process is carried far enough. Finally, a dynamic shear rheometer at reduced gap settings can be used to track the curing process efficiently and gives a sensitive measure of the extent of cure.

CHAPTER 4. LONG-TERM DURABILITY OF CRUMB-RUBBER MODIFIED ASPHALT

In Chapters 2 and 3, it was shown that the properties of a ground tire rubber-containing asphalt material vary with the extent to which the rubber is cured with the asphalt. The greater the extent of the cure, the less the viscosities at higher temperatures are increased by the rubber and the less the low-temperature stiffness is reduced. On the other hand, the more the cure, the less settling and the more fluid the binder is at hot-mix and pavement placement temperatures. Hence, the more the cure, the more manageable the binder material is, from both hot-mix and pavement contractors' viewpoints. So, it would appear that there is a tradeoff between achieving enhancements to Superpave grade and producing an easily handled material. (Some would argue that the tradeoff is artificial in that a) the mix design can be adjusted to accommodate the presence of rubber particles, and b) settling can be accommodated by a combination of agitation and shortened storage time. These are adjustments which may add significant cost to the project, however, and which must be evaluated. Cost is discussed further in Chapter 6.)

Apart from Superpave and other physical properties of the binder, another property of the binder must be considered. This is its durability, which is addressed by this chapter.

By durability is meant the ability of the binder to provide acceptable service over an extended period of time. The more durable the binder, the longer the time, of course. A prime component (perhaps *the* prime component) affecting durability is the extent and effect of oxidation on the binder. Oxidation, which results in more chemically polar molecules, inevitably renders a binder stiffer and less ductile than the original material. This increases the stresses which build in a binder due to both low-temperature contraction and traffic loads. With enough oxidation, the stresses inevitably will exceed the sustainable levels of the binder, resulting in either cohesive failure of the binder or adhesive failure of the binder-aggregate interface, or both.

In the work presented in this chapter, it is seen that the effect of rubber in an asphalt generally is to reduce the rate at which a binder deteriorates due to in-service oxidation. This reduction may be due either to a decrease in the oxidation rate (a chemical effect), or to a decrease in the effect of oxidation on the stiffness (the material still oxidizes but the resulting increase in stiffness is less), with the latter effect appearing to be the more common. An extensive evaluation of the PAV as an aging test for CRMA materials shows that errors can be very significant due to these effects of rubber on oxidation and hardening.

In addition to this phenomenon of reduced hardening, there are other, secondary effects of adding rubber to asphalt which appear to improve its durability. While we have not fully quantified these results, they appear to be significant, nonetheless. These are improvements in binder "stickiness," resulting in improved cohesion and adhesion.

A MODEL FOR OXIDATIVE AGING OF RUBBER MODIFIED ASPHALTS AND IMPLICATIONS TO PERFORMANCE ANALYSIS

Abstract

Oxidative aging of asphalt binders is a primary cause of binder-related long-term road failures. Viscosity hardening is primarily due to the oxidative conversion of polar aromatics to asphaltenes, oxidation which is indicated by carbonyl formation. The aging of unmodified asphalts yields a constant, aging-temperature independent “hardening susceptibility” (HS) relation between viscosity change and the growth of the infrared carbonyl peak. CRMA exhibit superior aging characteristics, lower hardening rates and, often, lower oxidation rates, throughout the aging simulation range. However, CRMA materials may exhibit a hardening susceptibility that varies with aging temperature, suggesting either shielding or a kinetic competition between the rubber polymer and the asphalt’s polar aromatics, for the available oxygen. This evidence suggests that the commonly accepted high-temperature, high-pressure, long-term aging technique is of questionable value when applied to CRMA materials.

The aging characteristics of CRMA were found to depend most heavily upon the curing method, the fractional content of the rubber, and the chemical composition of the binder. The curing method has a major effect on the material and chemical properties. Curing at lower temperatures and shear rates leads to a mere introduction of the rubber material into the binder, producing a swollen, gelatinous particle phase, the aging consequences of which are difficult to assess. Progressively higher levels of mixing shear and temperature are shown to degrade the long polymer chains and cross-link structures. Polymer strands freed by thermo-mechanical shear are integrated among the binder’s compositional elements, shielding or altering by competitive means the natural oxidation of the binder.

Introduction

The vast majority of road surfaces, upwards of 95 percent, is composed of asphalt-cement pavements. The federal government allocates about $25 billion per year for all types of roadway construction and repair; 7.2 percent of this spending is designated for the state of Texas (U.S. Public Law 105-178, 1998). This federal expenditure represents about 40 percent of the annual funding by the States and Washington combined, while local entities surely add to the total. The State of Texas spent $2.6 billion for automobile-related transportation in each of fiscal years 1998 and 1999 (Texas General Appropriations Act, 1997). The cost of continued new construction, as well as repair, is sure to rise in the future, and methods of construction that increase the service life at a competitive cost would benefit the nation.

One field of study to improve roadway life-cycle cost is the use of ground tire rubber as an elastic binder additive. An added benefit of such an approach would be to reduce waste and incorporate a thermoset polymer material that is comparatively difficult to otherwise recycle or reuse.

The objective of this section is to present detailed studies on the effect of oxidative aging, as it would occur in pavement service on rubber-modified asphalt physical properties. Such aging behavior is important to long-term pavement durability and thus to projections of life-cycle cost improvement that would be realized from the use of ground tire rubber.

Performance of Asphalt Binders

Asphalt binders are recognized to play a role in three major types of road failure each of which is directly related to the strong temperature dependence of the binder properties and their transient nature caused by oxidation. Rutting may occur when the young road is held under traffic load and at high temperatures for a prolonged time. An older road is attacked at moderate temperatures by transient stresses which may lead to "fatigue" cracking if the binder is excessively stiff and non-compliant due to heavy aging. Finally, thermal cracking occurs during rapid and extreme low-temperature change. When the road temperature changes, the pavement expands or contracts, and the binder must deform and flow to relieve the resulting stresses. If the binder flows too slowly and is too stiff, stresses will accumulate until relieved by thermal cracking.

Many methods have been employed to characterize and predict the material's ability to perform. The Superpave binder specifications, developed by SHRP, are a combination of modern methods of evaluating and predicting the performance of asphalt binders (Asphalt Institute, 1995; AASHTO, 1996). Under this system, the qualified binders must meet specifications designed to make them strong enough at high pavement temperatures to withstand rutting, while soft enough to avoid excessive thermal stresses at low pavement temperatures and fatigue at moderate temperatures. Test conditions are determined by the temperature extremes statistically expected to occur in the installation area during the normal service life (Asphalt Institute, 1995; AASHTO, 1996). Both the probability and rate of failure may be increased as the temperatures become more extreme. The test protocol includes an aging procedure designed to assure that the binder will not age excessively in service. As it is conducted at elevated temperature and pressure, however, the indication of in-service aging is only approximate, at best (Lau et al., 1992; Liu et al., 1996; Domke et al., 1999a) and not reliable at ranking asphalts.

Aging of Asphalt Binders

Several previous studies of thin film asphalt aging have been performed (Domke et al., 1999b; Liu et al., 1998; Liu et al., 1996; Choquet and Verhasselt, 1994; Lau et al., 1992; Peterson, 1984; and Van Oort, 1956). As neat asphalt (asphalt binder that contains no rubber) ages, it quickly passes through a rapid aging rate regime, during which the viscosity and carbonyl area have been shown to rapidly climb. This rapid aging is attributed to the presence of sulfoxide materials and highly reactive carbonyl-forming sites (Peterson, 1993; Lau et al., 1992; Martin et al., 1990). After this initial-jump phenomenon, a constant rate state is reached and the material begins to follow the hardening and aging rates described in equations 4-1 and 4-2:

$$\ln \eta^* = \ln \eta_0^* + r_\eta \, t \tag{4-1}$$

$$CA = CA_0 + r_{CA} \, t \tag{4-2}$$

where η^* denotes the limiting complex viscosity and CA denotes the numerical integral of the FTIR carbonyl region. Subscript 0 denotes the intercept of the regression fit at aging time, t =0. Because of the rapid-aging "initial jump" phenomenon, both intercepts, CA_0 and η^*_0, are greater than the measured values for the unaged material, $CA_{(t=0)}$ and $\eta^*_{(t=0)}$, respectively. Oxidative hardening, illustrated by viscosity measurements, equation 4-1, and oxidative aging, represented by carbonyl group formation, equation 4-2, are important predictors in neat asphalt studies (Lau et al., 1992). Both the hardening rate, r_η, and the oxidative aging rate, r_{CA}, are related to aging temperature by an Arrhenius relation, equation 4-3 (Lau et al., 1992):

$$r_a = A_a \exp \frac{-E_a}{RT} \tag{4-3}$$

where E_a is the activation energy and subscript a is chosen to denote the specific rate in question. Lau also found the HS property, a combination of hardening and oxidation rates, to be a characteristic of the asphalt and independent of aging temperature, equation 4-4 (Lau et al., 1992):

$$\begin{gathered} \frac{d \ln \eta^*}{dt} = \frac{d \ln \eta^*}{d\,CA} \frac{d\,CA}{dt} \\ HS = \frac{d \ln \eta^*}{d\,CA} = \frac{r_\eta}{r_{CA}} \end{gathered} \tag{4-4}$$

Hardening susceptibility is the ratio of ln viscosity increase to FTIR carbonyl growth, where less viscosity growth per unit carbonyl growth is desired. The important objective in an aging analysis is the ability to select the material that has the most favorable hardening rate. The benefit of an aging-temperature independent property is the ability to collect data from rapid, high-temperature aging with the assurance that the data are valid for lower, much slower aging temperatures. HS is a correlation tool, acting as surrogate for the hardening rate.

Lin et al. (1995) examined the effect of asphaltene content on viscosity and found that it obeyed a form of the Pal-Rhodes model (1989), equation 4-5:

$$\eta^* = \eta_m^* \left(1 - K \, \%AS \right)^{-\nu} \tag{4-5}$$

where η^* is the resulting viscosity, η^*_m is the viscosity of the maltene, *K* is related to the asphaltene solubility (or maltene solvent power), and ν relates to the shape of the asphaltene particles. The parameters η^*_m, K, and ν are asphalt dependent and may be determined by varying the fractional asphaltene content, either by aging or laboratory manipulation. The shape factors, ν, from Lin's work compare favorably to other research indicating that asphaltenes are planar molecules stacked closely together. Lin et al. (1995) further related hardening susceptibility to asphaltene content by equation 4-6:

$$HS = \frac{d \ln \eta^*}{d\ (\%AS)} \frac{d\ (\%AS)}{d\ CA} \qquad (4\text{-}6)$$

where $\frac{d\ (\%AS)}{d\ CA}$ is termed the asphaltene formation susceptibility (AFS) and is thought by Lin to be constant for a given asphalt. The effect of asphaltenes on viscosity may be obtained from the Pal-Rhodes model (1989) as equation 4-7:

$$\frac{d \ln \eta^*}{d\ \%AS} = \frac{\nu\ K}{1 - K\ \%AS} \qquad (4\text{-}7)$$

In summary, the aging of conventional asphalts in service results in carbonyl growth. This reaction produces asphaltenes which then harden the material in accordance with the Pal-Rhodes model (1989). The oxidation rate ultimately determines the hardening rate, but the hardening susceptibility, a characteristic of each asphalt, is important for establishing the extent to which oxidation causes hardening.

Crumb-Rubber Modified Asphalt (CRMA) and Asphalt Rubber

Today's rubber tire is produced to give its user constant long-term properties regardless of service temperature, a stark contrast to the temperature susceptibility of asphalt binders. While its composition varies by function and manufacturer, tire rubber consists of about 33 percent carbon black, 40 percent thermoset polymer mixtures, 25 percent extender oil, and the remainder specialty compounds and preservatives (Rosen, 1993). The polymer thermosets are mainly block co-polymers of styrene-butadiene (SBR) and SBS joined by vulcanization at some small fraction of the unsaturated polybutadiene sites. As an impure thermoset, both the ease and value of recycling are significantly reduced, yet several hundred million tires require replacement annually.

The application of crumb rubber in pavements is attractive both because of the possibility of improving binder properties and as a mode of disposing of discarded tires (Takallou and Takallou, 1991). This can be accomplished by reducing the binder's inherent temperature susceptibility, and perhaps by reducing the aging problem as well. Granulated tire rubber has been used in both the dry process, where the tire rubber acts chiefly as aggregate, and the wet process, where swelling and incorporation into the binder take place (Takallou and Takallou, 1991). The wet process is of much greater interest, in that the binder properties are altered significantly. ASTM defines “asphalt rubber” in its “Standard Specification for Asphalt Rubber” (ASTM D6114-97, 1999) as containing at least 15 percent rubber content in the binder and requires a HTV of at least 15 poise at 175 °C (347 °F). The reader should consider “asphalt rubber” as a subset of CRMA, which herein shall be defined as an asphalt binder that contains some fraction of crumb rubber in any state of cure.

Efforts by Billiter et al. (1997a, 1997b, 1997c) have produced CRMA by a wide range of conditions. CRMA that can increase Performance Grade span, improve properties, and resist settling has been produced (Billiter et al., 1997c). At low-cure conditions, there is a large increase in viscosity that is primarily the result of swollen particles, engorged with binder, that dominate system properties. During low-shear mixing the viscosity increases as particles swell. At high-temperature, high-shear curing conditions, the viscosity decreases from the low-cure state as the dispersed particles disintegrate and dissolve. Utilizing more intensive blending conditions leads to a more homogeneous matrix, lowering bulk viscosities, even in the compaction range. The analyses by Billiter and his colleagues examine the effect of various curing levels on unaged material properties. The work presented here is an aging study of Billiter’s CRMA material to determine the important effect of oxidative aging on these material’s properties.

Materials and Experimental Methods

A selection of asphalts is described in Tables 4-1 and 4-2. Table 4-1 identifies the asphalts by viscosity and blind refinery source and describes laboratory modifications performed on the binders to achieve desired properties (Billiter et al., 1997c). Asphalts “House #1” and “House #2” were created to study the effect of compositional differences on blend and aging properties (Corbett, 1970; Peterson, 1993). SC Asphalt #1 originates from materials fractionated in supercritical n-pentane by a method similar to the ROSE process and described by Jemison et al. (1995) and Stegeman et al. (1992). Selected fractions were recombined in a proportion to yield the desired composition or viscosity. Table 4-2 lists the compositional analyses of the asphalts described in Table 4-1 (from Jones, 1993; Billiter et al., 1997c; and Bullin et al., 1996). Minus 10 and -40 mesh rubber were acquired from Granular Products, also known as Tire Gator (TG), a Mexia, Texas, company no longer in business. The -40 mesh material was made from tire buffings and is given the label TG-40, while TG-10 was made from whole tires. In addition, RS-40, a -40 mesh tire rubber, was obtained from Rouse Rubber of Vicksburg, Mississippi. Blends produced ranged from 5 percent to 20 percent rubber by mass.

A description of blending conditions is presented in Tables 4-3, 4-4, and 4-5. The CRMA materials were blended using one of two mixing apparatuses. Materials produced at 500 and 1550 rpm (Tables 4-3 and 4-4) were produced with a 2 inch diameter impeller blade powered

Table 4-1. Description of Asphalts Studied. [a]

Asphalt Name	η* (dPa·s (poise)) 60°C and 1.0 rad/sec	Source Refinery	Laboratory Modifications
SHRP ABM-1	2,409	MRL	None
Resin #1	238.6	A	None
AC-5 #2	636.3	C	None
AC-10 #1	944.0	A	None
AC-10 #2	952.0	C	None
House #1	507.9	A	Resin #1 was blended 1:1 with AC-10 #1.
House #2	561.0	C	AC-10 #2 was blended 47:3 with a commercial recycling agent: η*= 5.5
SC Asphalt #1	634.6	F	Supercritical Fraction of AC-20 (Refin. F)

[a] Portions after Billiter et al. (1997c).

Table 4-2. Compositions of Selected Asphalts.

Asphalt	% Asphaltenes	% Polar Aromatics	% Naphthene Aromatics	% Saturates
SHRP ABM-1[a]	7.1	52.4	29.6	9.0
Resin #1[b]	3.0	38.2	49.6	9.2
AC-5 #2[c]	10.8	31.1	45.5	12.6
AC-10 #1[b]	14.5	30.1	43.4	12.1
AC-10 #2[b]	12.7	26.6	48.4	12.3
House #1[b]	8.7	34.2	46.5	10.6
House #2[b]	11.9	25.8	49.8	12.5
SC Asphalt #1	2.7	35.7	52.6	8.7

[a] Jones (1993). [b] Billiter et al. (1997c). [c] Bullin et al. (1996).

Table 4-3. Low-Cure Blend Matrix. [a]

Asphalts	SHRP ABM-1	Weight Percent Rubber	Rubber Type / Mesh
Blend Designation	#114	5	TG-40
	#117	10	
	#120	15	
	#122	18	TG-10
	#123		TG-40

[a] Curing Temperature: 177 °C (350 °F)
Mixer Conditions: 500 rpm impeller for 1 hour

Table 4-4. Intermediate-Cure Blend Matrix.

Asphalt	Resin #1	AC-5 #2	AC-10 #1	AC-10 #2	Weight Percent Rubber	Rubber Type / Mesh
Blend Designation[a]	---	#201	#205	#209	5	TG-40
	---	#202	#206	#210		RS-40
	---	#203	#207	#211	10	TG-40
	---	#204	#208	#212		RS-40
Blend Designation[b]	#221	#223	#225	#227	10	TG-40
	#222	#224	#226	#228	20	

[a, b] Curing Temperature: 191 °C (375 °F)
[a] Mixer Conditions: 500 rpm impeller for 12 hours - (Long Term)
[b] Mixer Conditions: 1550 rpm impeller for 6 hours - (High Shear)

Table 4-5. High-Cure Blend Matrix. [a]

Asphalt Blend #	Resin #1	AC-10 #2	SC Asphalt	Weight Percent Rubber	Rubber Type / Mesh	Mixer Speed (rpm)	Curing Temperature
	#301	#307	#313	10	TG-10	4000	260 °C (500 °F)
	#302	#308	#314				232 °C (450 °F)
	#303	#309	---			8000	260 °C (500 °F)
	#304	#310	---		TG-40	4000	
	#305	#311	---	20	TG-10		
House #1	#306	---	---	10			
House #2	---	#312	---				

[a] Mixer Conditions: Slotted disintegrating head for 6.5 hours

by a drill press. Blends produced at 4000 and 8000 rpm (Table 4-5) were produced using a Silverson L4RT high-shear laboratory mixer with a 2.25 inch blade and a slotted disintegrating head. For this second mixer the rotation develops a flow of material upward from below the housing into the path of the blade and out between the slots, providing a means of mechanical shearing. For the sake of convenience, the blending strategies employed may be divided into groups. “Low-Cure” blends (Table 4-3) were produced by mixing for only 1 hour at 500 rpm and 177 °C (350 °F); “Long-Term” intermediate-cure blends (Table 4-4, Blends #20x and #21x) were mixed for 12 hours at 500 rpm and 191 °C (375 °F). “High-Shear” intermediate-cure blends (Table 4-4, Blends #22x) were blended for 6 hours at 191 °C (375 °F) and 1550 rpm, and “High-Cure” blends (Table 4-5) were blended for 6.5 hours at 4000 or 8000 rpm and at 232 °C (450 °F) or 260 °C (500 °F).

The intermediate- and low-cure blends study the effect of rubber type and content level on the selected asphalts. The high-cure blends consist of 14 blends. For each of AC-10 #2 and Resin #1, six blends were prepared to study the effect of five parameters on the blend. SC Asphalt #1 was available in limited quantities, so only two blends could be prepared. The base cure for each featured binder is represented in Table 4-5 by Blends #301, #307, and #313: 10 percent rubber content, -10 mesh Tire Gator rubber, 4000 rpm, and 260 °C (500 °F). Then for supplemental blends, one element of the base cure was alternated in turn to one of the following: 20 percent rubber content, -40 mesh Tire Gator rubber, 8000 rpm, and 232 °C (450 °F). Finally, the binder itself was modified by substituting with either House #1 or House #2, a material containing a substantial portion of the featured binder. In presenting the data from these samples, a complete listing of material and cure conditions is rather long, so only the deviation from the base cure is presented, along with the blend designation. Also, “10% TG-10” is used for the designation of the base cure.

Oxidative aging was performed at temperatures equal to or greater than normal roads, to accelerate the aging (Table 4-6). Aging of a 1.0 mm thick film was performed in a tray 4.0 cm wide by 7.0 cm long. Aging at 60 °C (140 °F) was performed in an environmentally controlled room maintained at 25 percent relative humidity. Aging at higher temperatures, 80 °C to 99 °C (176 °F to 210 °F), was performed in pressure oxidation vessels (POVs), as described by Lau et al. (1992). These vessels are contained in an insulated bath of water and triethylene glycol and were designed to maintain temperatures up to 100 °C and pressures up to 20 atmospheres (atm). A variety of gases and gas mixtures may be selected. For this work 20 atm pure oxygen was employed for low-cure blends, and atmospheric air was used otherwise.

Aged binders were evaluated for carbonyl content and complex viscosity. Viscosities were measured using a Carri-Med CSL-500 dynamic shear rheometer with a 2.5 cm parallel plate geometry and a 1500 µm gap. The rheometer was operated at a strain of 50 percent through a 25-point logarithmic frequency range from 100 rad/sec to 0.1 rad/sec. Several polymer modified materials, including CRMA, do not exhibit a low-shear rate limiting complex viscosity; therefore, data reported herein were produced at 1.0 rad/sec. The carbonyl content was measured using a Mattson Galaxy 5000 FTIR with an Attenuated Total Reflectance attachment that allows analysis of opaque materials (Jemison et al., 1992). Reported values of carbonyl area (CA) were determined by the areas under the FTIR spectra between wavenumbers of 1820 and 1650 cm^{-1}, while the baseline was set at 1820 cm^{-1}.

Table 4-6. CRMA Aging Conditions.

Curing Level	Aging Temperature							
	60 °C (140 °F)	80 °C (176 °F)	85 °C (185 °F)	88 °C (190 °F)	82 °C (180 °F)	90 °C (194 °F)	93 °C (200 °F)	99 °C (210 °F)
Low Cure					✔[a]		✔[a]	
Long Term	✔			✔			✔	✔
High Shear	✔	✔	✔			✔		
High Cure	✔	✔	✔			✔		

[a] Aging Conditions: 20 atm O_2

Results

The results of these analyses can be divided into two fields of interest, aging phenomena and performance comparison. First, varied sets of samples are used to emphasize the trends in the data and compare them to those of neat asphalts. The noted phenomena require the blends be analyzed by their hardening rate property. Second, the blends are compared by such variables as level of cure, rubber content, and asphaltene content.

Aging Phenomena - Initial Jump

Neat asphalt ages first by undergoing short-term, rapid hardening. This is followed by a long-term period where the rate of hardening, r_η, (equation 4-1) is constant, likewise for the FTIR carbonyl region. Figures 4-1 and 4-2 illustrate this property for asphalts ABM-1 and AC-10 #2, respectively. Low-cure blends of ABM-1 exhibited a swollen heterogeneous particle, especially above 10 percent rubber content. An important factor in this study is the difference between the intercept of the curve fit and the unaged asphalt viscosity, the initial jump. The initial jump is a measure of the rapid, short-term aging of the binder. Most notable in Figure 4-1, depicting low-cure blends of SHRP ABM-1, is the decrease in this initial jump with increasing rubber content. At aging time zero, the plot shows a range of rubber levels; increased rubber content drives the blend viscosity up substantially. The addition of tire rubber dramatically increases the blend viscosity over that of the neat binder. The hardening rate trend is to decrease with increasing rubber content, and the neat material hardens much more rapidly than any blend. However, as the rubber level increases, the initial jump becomes negligible, and, in addition, the viscosities of the unaged blends are all unacceptably high, varying from the ABM-1 neat material by as much as a factor of 10. The neat binder ABM-1 is also shown in Figure 4-1 to have a dramatic initial jump. This is not surprising given ABM-1 is 7 percent asphaltenes and 52 percent polar aromatics. ABM-1 is predisposed to rapid aging because of its high polar content (Lin et al., 1995). For the blends, however, the rapid initial oxidation and asphaltene production that normally produce a brisk increase in viscosity is masked by the high particle content. The rubber particles are simply dominating the viscosity of the material, so it is difficult to characterize the effect of aging for these blends.

Long-term blends showed no viscosity decrease during curing, even when selected blends were cured for up to 60 hours. Thus, little additional integration of the heterogeneous components was expected (Billiter et al., 1997b). The blend viscosities, therefore, were still rather high compared to the neat material. This suggests some degree of competing viscosity building components during both curing and aging. Comparing Figures 4-1 and 4-2, AC-10 #2 has a smaller initial jump; it contains about half as many polar aromatics as ABM-1 (27 percent) and its initial viscosity is elevated by 13 percent asphaltenes. The pronounced viscosity aging overlap between Blends #209 and #211 (with varied rubber content) suggests that the rubber particles are again dominating the viscosity, without reducing the hardening rate. The hardening properties at road conditions (Figure 4-2) are not observed to improve appreciably over the neat

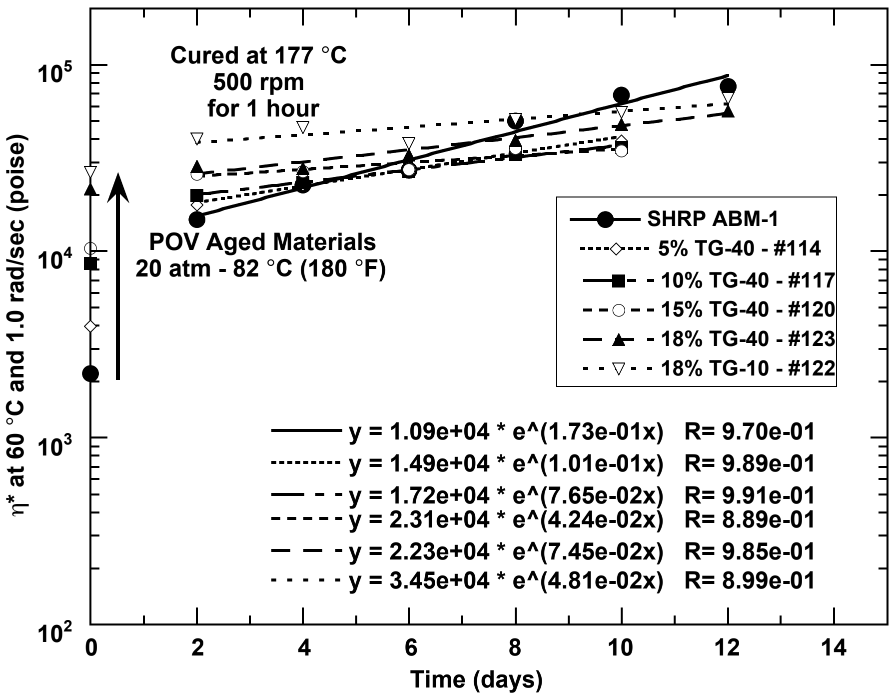

Figure 4-1. Hardening Properties of Low-Cure Blends of SHRP ABM-1.

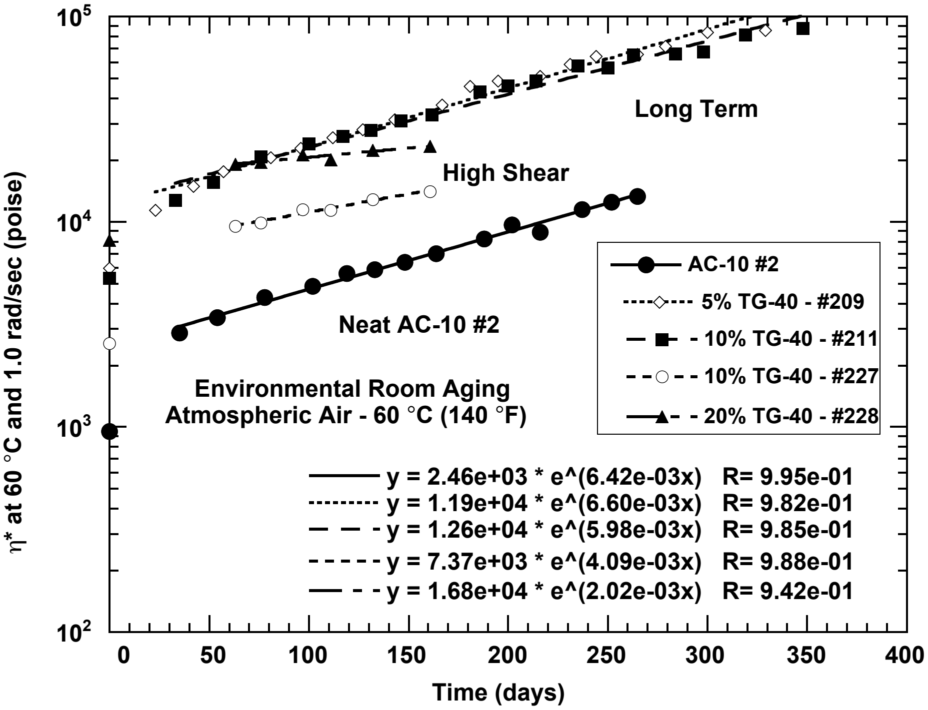

Figure 4-2. Hardening Properties of Intermediate-Cure Blends of AC-10 #2.

material, and hardening rate improvement over the neat material was most significant at the higher aging temperature in Figure 4-3.

High-shear and high-cure blends were prepared as specified in Tables 4-4 and 4-5. One important characteristic of these materials was that as curing continued, a decrease in viscosity was observed (Billiter et al., 1997a, 1997c). The suspended swollen particles were being mechanically sheared during the blending process, and as the suspended particles began to decrease in size, rubber material entered the binder “fluid” phase, increasing its characteristic viscosity. But at the same time, the dominance of these shrinking particles on the bulk viscosity is rapidly diminished. This combined effect leads to lower blend viscosities, as shown in Figures 4-2 and 4-4 at aging time zero. With the reported results from the unaged material, it is easy to predict that the initial jump phenomenon of aging will be observed, even at high rubber content, as asphaltene production becomes the principle viscosity building component. This is exactly what is observed in the higher levels of curing (Figures 4-2 and 4-4). In addition it is important to note that the hardening rates have fallen by 30 to 60 percent (Blend #228, Figure 4-2). Either some reduction of asphaltene formation is occurring, or the rubber particles are being reduced in size by the oxidative aging.

At the highest curing level studied, a change was made from TG-40 to TG-10 mesh rubber particles. The larger particles posed no problem in either curing or aging. The disintegrating head mixer mechanically integrated the particles substantially, reducing the blend viscosities to less than twice the neat source viscosity, including that of a 20 percent tire rubber blend (Figure 4-4). The initial jump due to aging is a prominent indication that asphaltene growth dominates viscosity, while the decreased hardening rates suggest some type of shielding. In addition, size exclusion chromatography, Figure 4-5, indicates that oxidation reduces the rubber molecular size (Billiter et al., 1996; Leicht et al., 2000). This suggests a mechanism for the observed reduction in hardening rate, that oxidative cleaving of polymer bonds subsequent and in addition to mechanical shearing, leads to a relaxation in the rubber matrix. This cleaving would reduce the viscosity, even as the binder ages, so hardening is reduced. At the least, there is some reaction at sites not seen before that does not contribute to viscosity growth. In either case the polymer chain is soaking up some portion of the oxidation and reducing its effect.

Aging Phenomena - Hardening Susceptibility Temperature Dependence

Lau et al. (1992) found that the HS parameter, a measure of hardening and carbonyl growth is important in neat asphalt studies. Aging time, in equations 4-1 and 4-2, is eliminated and viscosity is plotted against its corresponding carbonyl area, producing a fit whose constant slope is the hardening susceptibility. Although different materials have different hardening susceptibilities, this property has been found to be independent of aging temperature for all neat materials studied, as well as for various recombinations of Corbett and other fractions (Figure 4-6).

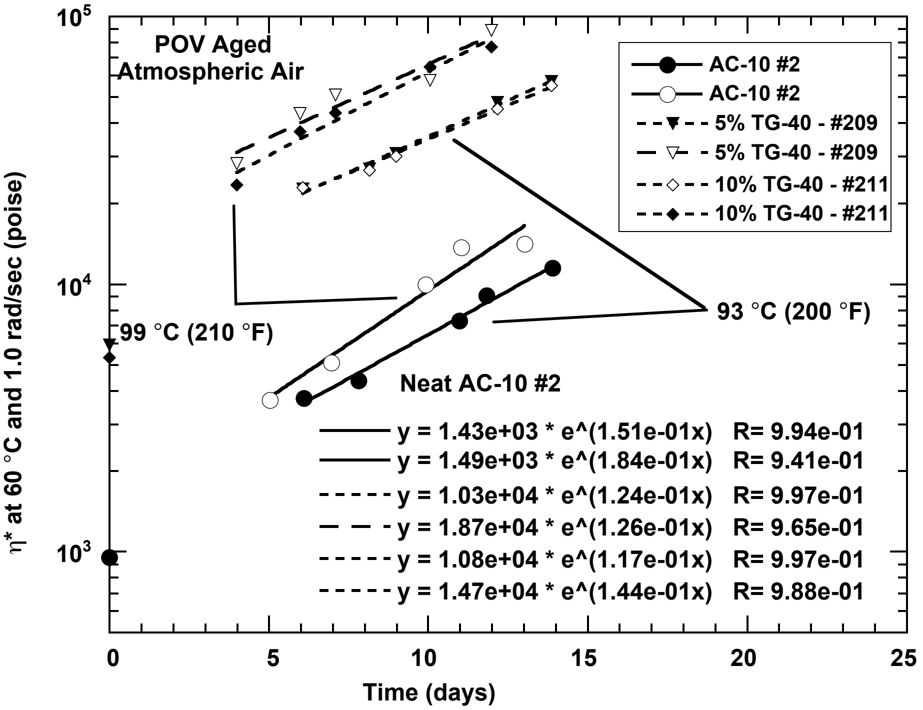

Figure 4-3. High-Temperature Hardening Properties of Intermediate-Cure Blends of AC-10 #2.

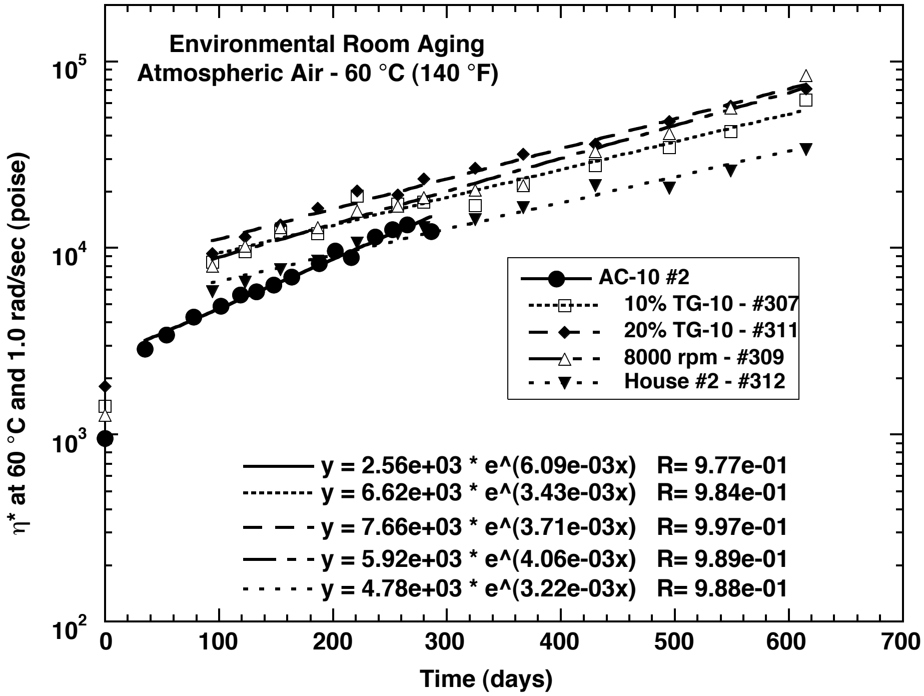

Figure 4-4. Hardening Properties of Selected High-Cure Blends of AC-10 #2.

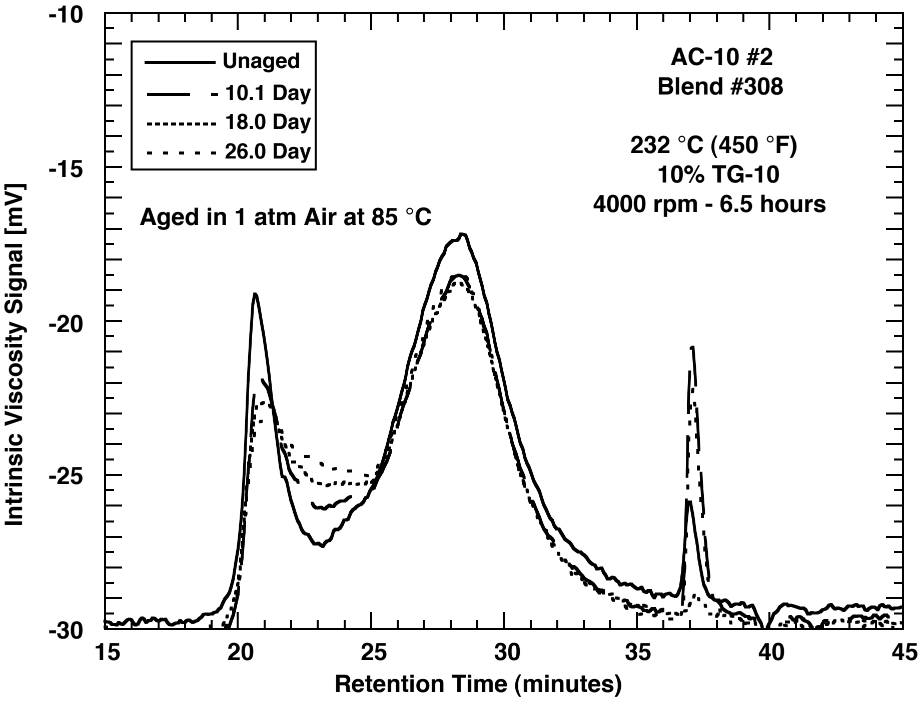

Figure 4-5. Viscotek Response of Blend #308 - Aged at 85 °C.

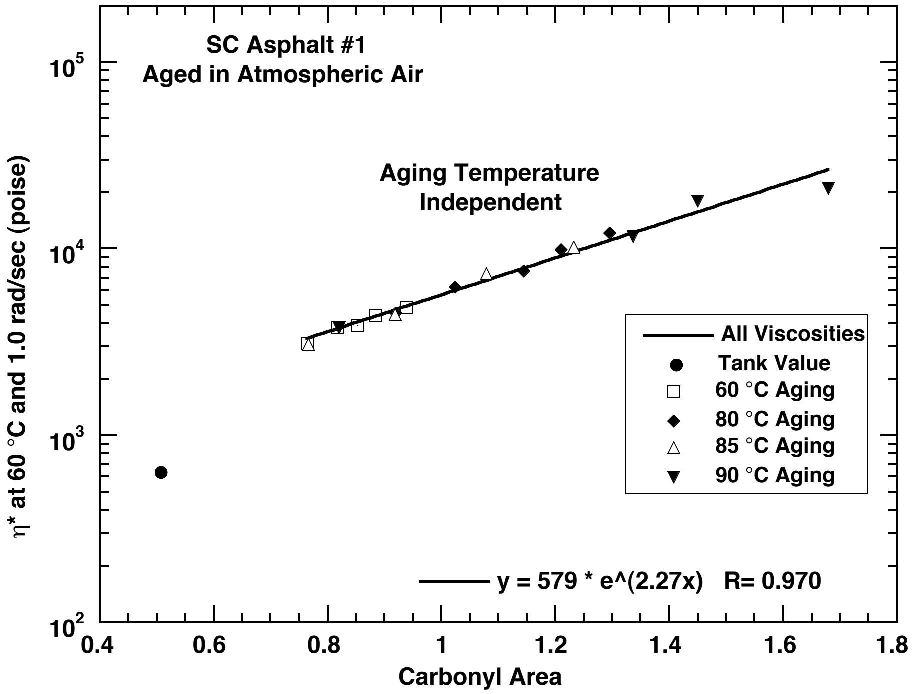

Figure 4-6. Hardening Susceptibility of SC Asphalt #1.

This is not the case for CRMA, however. In order to avoid low-cure complications, such as particle dominance of viscosity, it is best to consider the high-shear and high-cure blends. Figure 4-7 shows two illustrations of the hardening susceptibility phenomenon. Note that for these blends the hardening susceptibility decreases with increasing temperature over this range. This is an indication that at higher temperatures the rubber is absorbing more of the oxygen than at low temperatures.

Because HS was found to be constant regardless of aging temperature, at least under 100 °C (212 ºF), high-temperature aging has been used to rank and compare conventional binders. Figure 4-8 shows the difficulty of applying this idea to CRMA materials. Blend #222 has the lowest HS at every temperature except 60 °C (140 ºF), where it is significantly higher than the other blends and higher than the neat binder. This figure shows the danger of ranking blends using high-temperature aging properties.

In addition, the hardening susceptibility trend for high-cure blends indicates an appreciable minimum between 85 °C (185 ºF) and 90 °C (194 ºF). This may suggest a changing kinetic mechanism around 90 °C (194 ºF). Given that Performance Grade aging is conducted at 163 °C (325 ºF) for short-term hot-mix aging and at 90 °C (194 ºF) and 100 °C (212 ºF) for long-term aging simulations, this transition is very important and raises questions about the reliability of aging tests in relation to CRMA.

The observed temperature dependency of the hardening susceptibility leads to a further analysis of activation energies than that performed by Lau et al. (1992). The theoretical dependence of hardening susceptibility on temperature arises from the Arrhenius model. Combining equations 4-3 and 4-4:

$$\frac{d \ln HS}{dT} = \frac{E_{\eta} - E_{CA}}{RT^{2}} \tag{4-8}$$

Lau’s work with neat materials is an argument for the special case of equation 4-8, where both activation energies are equal. Equation 4-8 predicts that the hardening susceptibility temperature dependency relies on a substantive difference between hardening and aging activation energies, which is suggested in Figure 4-9. Plotting hardening and aging rates versus inverse temperature, the neat material has two nearly identical slopes representing hardening and aging activation energies. The outer markers indicate AC-10 #2, while the inner markers indicate Blend #311. CRMA consistently shows lower hardening rates, lower aging rates, and higher activation energies with the resulting difference in activation energies the important finding with respect to the validity of high-temperature aging tests.

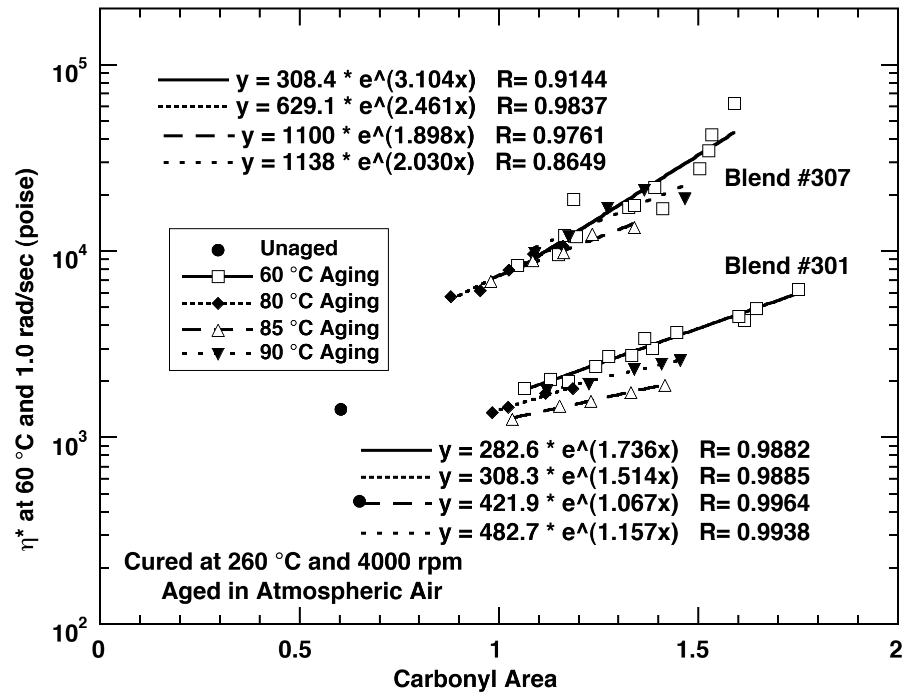

Figure 4-7. Hardening Susceptibility of Select High-Cure Blends.

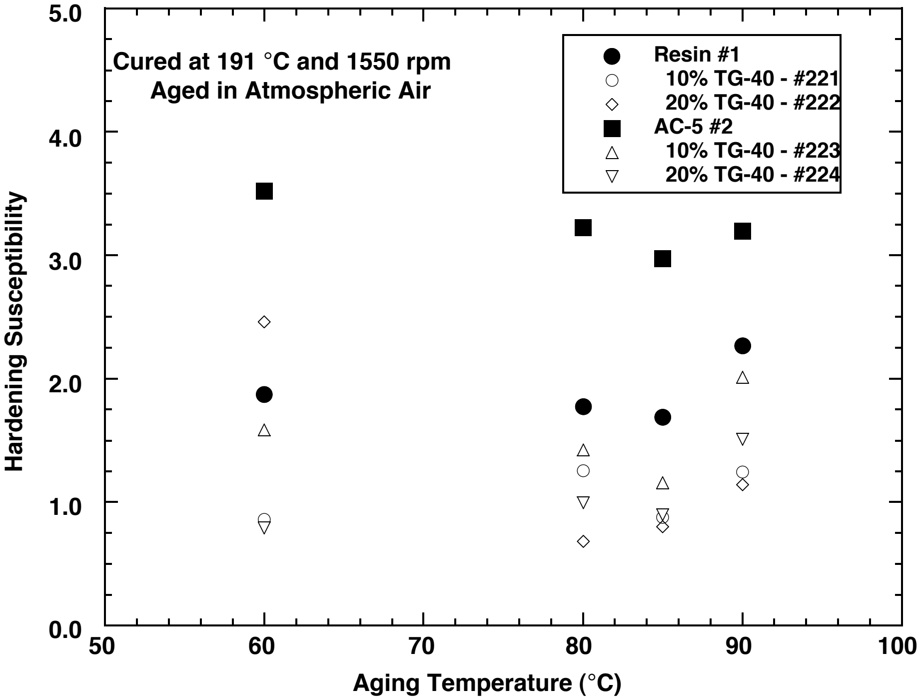

Figure 4-8. Effect of Aging Temperature on Hardening Susceptibility - Selected High-Shear Blends.

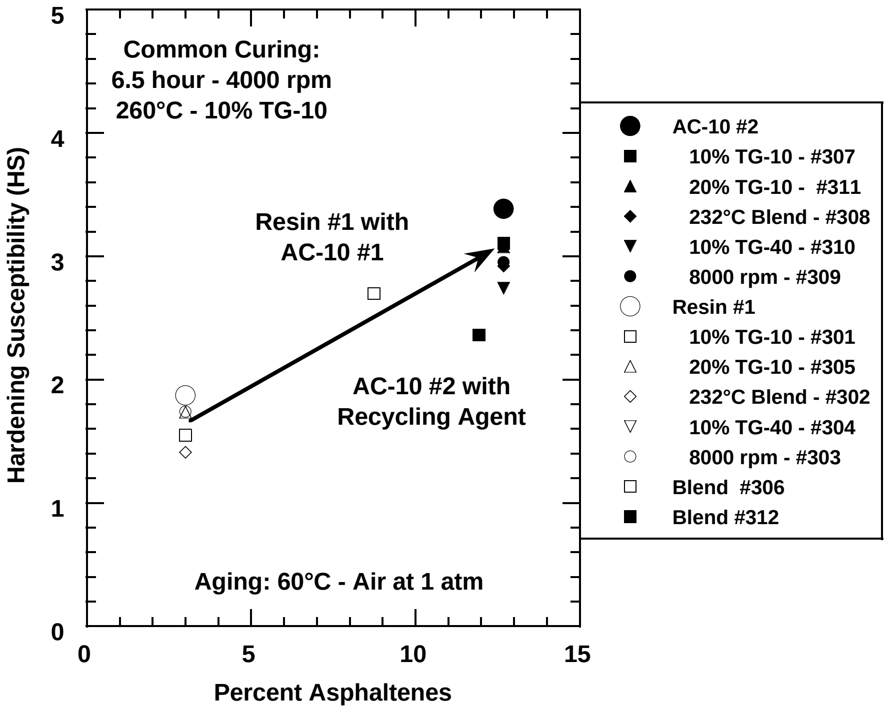

Figure 4-9. Comparison of Activation Energies for AC-10 #2 and Blend #311.

Aging Phenomena - Hardening Susceptibility at 60 °C (140 °F)

The previous section illustrated that hardening susceptibility varies with aging temperature. The remaining discussion examines aging performed at 60 °C (140 °F), because the focus of this analysis should consider data that best approximate the road conditions.

Figures 4-10 through 4-12 examine the effect of selected curing variables on the 60 °C (140 °F) hardening susceptibility property. HS is beneficially reduced, to some degree, for each of the following trends: increasing rubber content (Figure 4-10) and decreasing asphaltenes content (Figure 4-11). Figure 4-12 compares hardening susceptibility to the level of curing. Note that the curing level axis spacing is arbitrary, and that there is no intention to obtain a fit line, but rather to examine the trend. The trend of the data is perplexing because the high-shear data seem to constitute a local minimum. The high-cure HS values are only slightly lower than the neat materials (Figures 4-11 and 4-12). Other studies of these blends indicate that higher curing levels produce a more homogeneous material that, once produced, is easier to utilize (Billiter et al., 1997c; Leicht et al., 2000). Further examination of these data in the following discussion leads to an interesting finding on hardening susceptibility.

Figures 4-13 through 4-16 graphically display the hardening susceptibility by plotting hardening rate versus oxidation rate. The HS of any data point is the slope of the line drawn from the origin to that point. Thus, all points lying on such a line have the same hardening

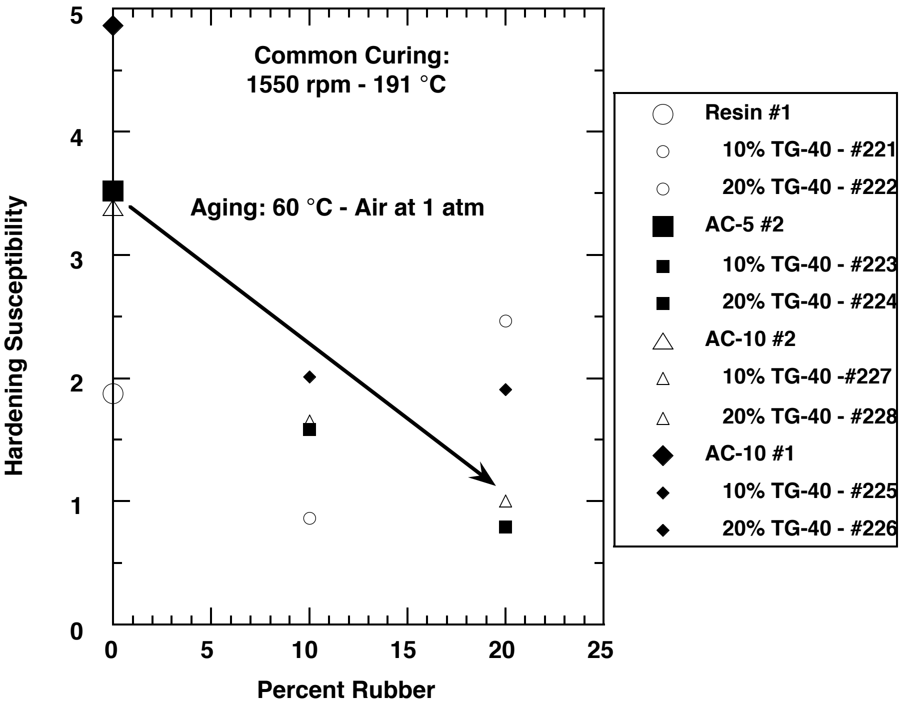

Figure 4-10. Effect of Tire Rubber Content on Hardening Susceptibility - High-Shear Blends.

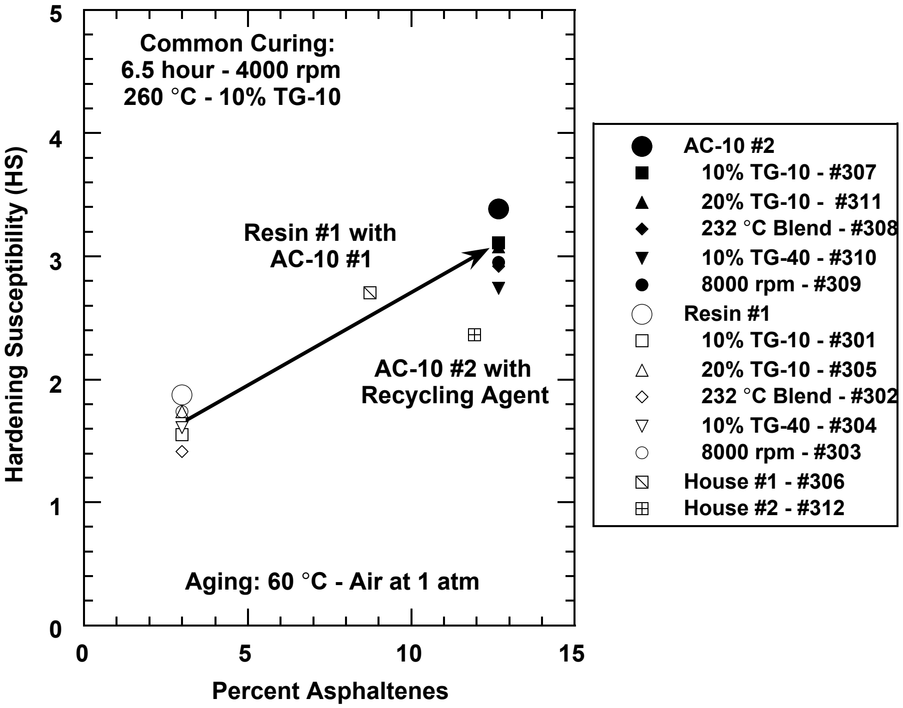

Figure 4-11. Effect of Asphaltene Content on Hardening Susceptibility - High-Cure Blends.

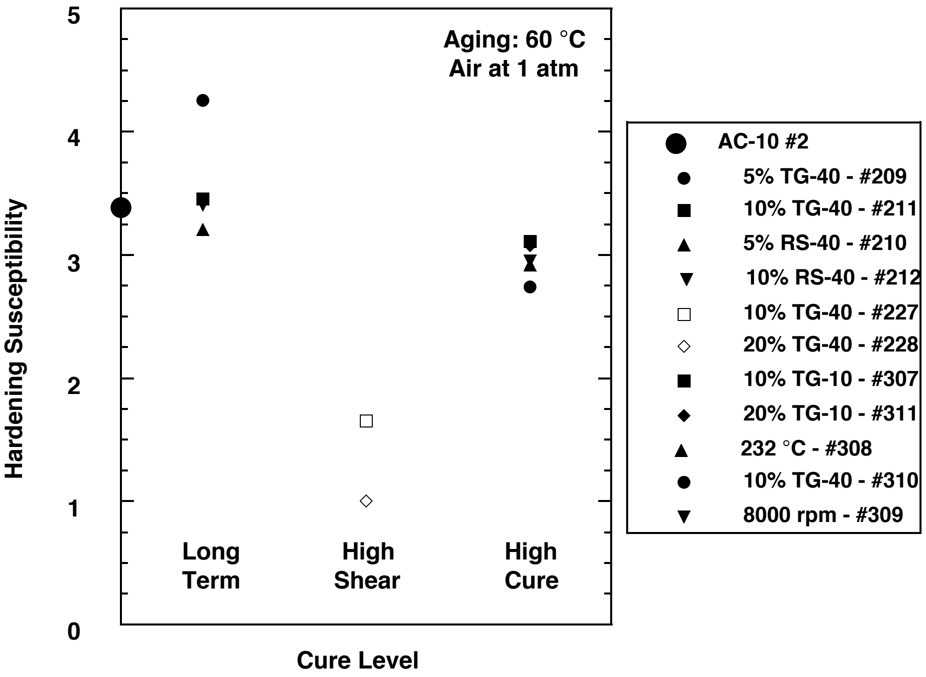

Figure 4-12. Effect of Cure Level on Hardening Susceptibility - AC-10 #2 Blends.

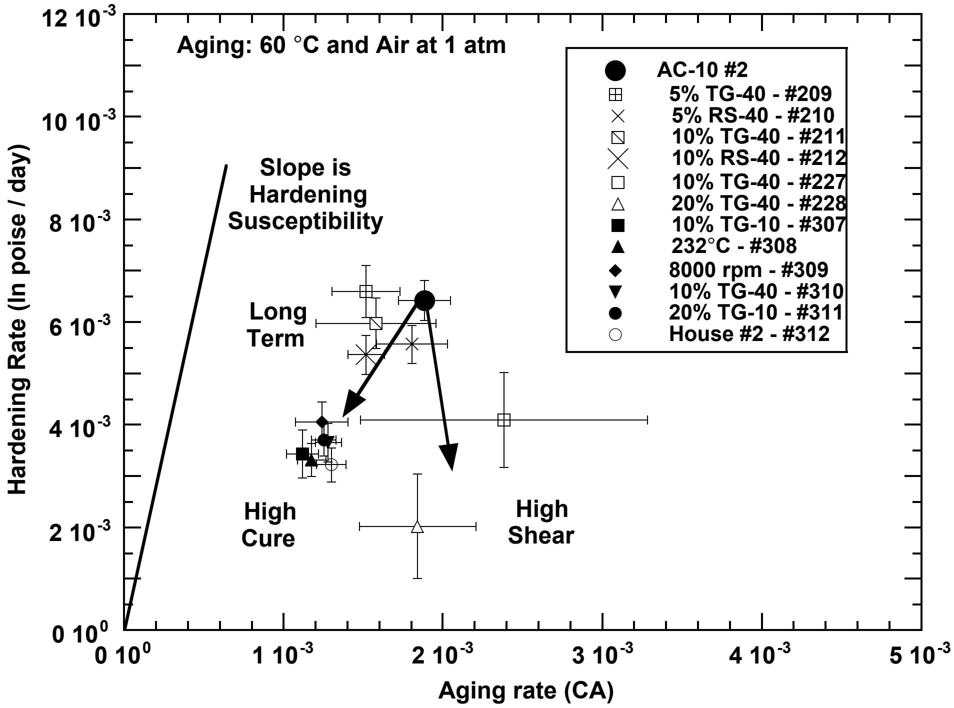

Figure 4-13. Graphical Hardening Susceptibility of AC-10 #2 Blends.

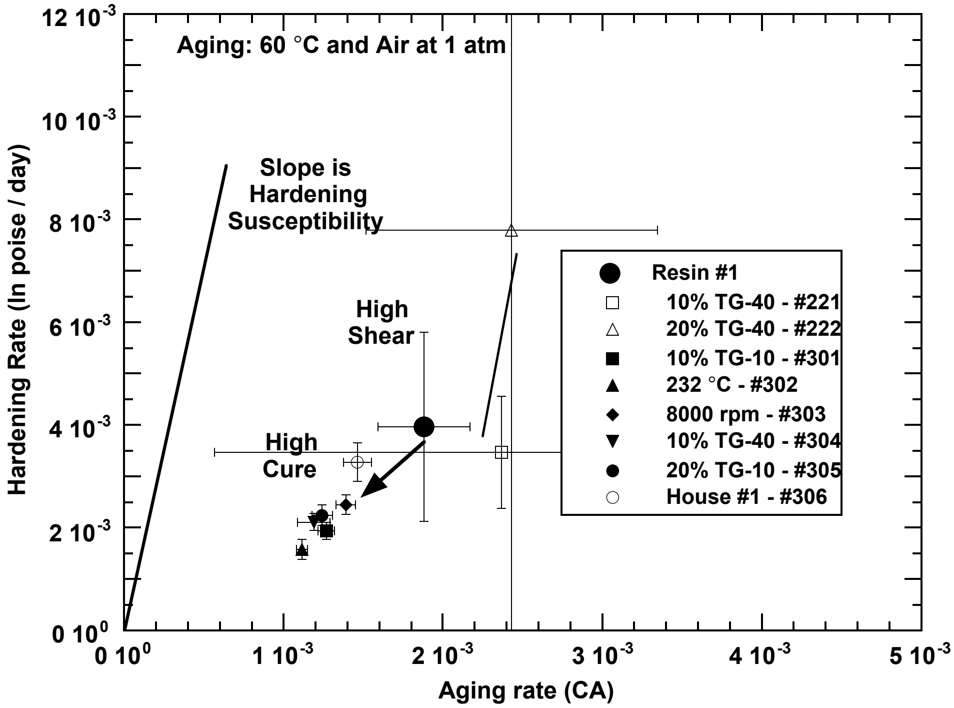

Figure 4-14. Graphical Hardening Susceptibility of Resin #1 Blends.

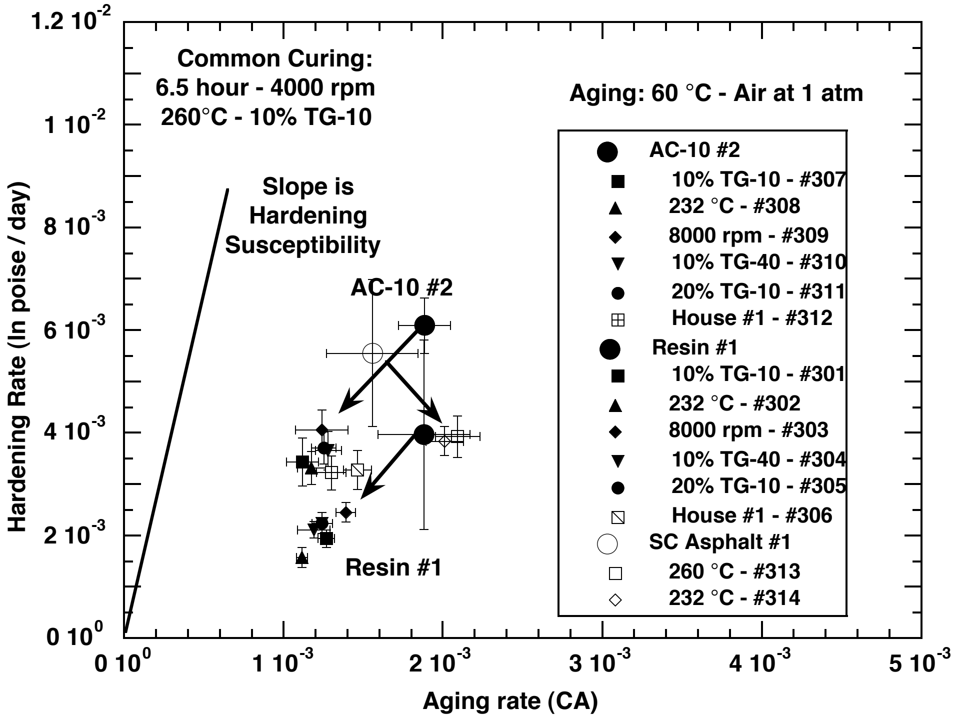

Figure 4-15. Graphical Hardening Susceptibility of High-Cure Blends.

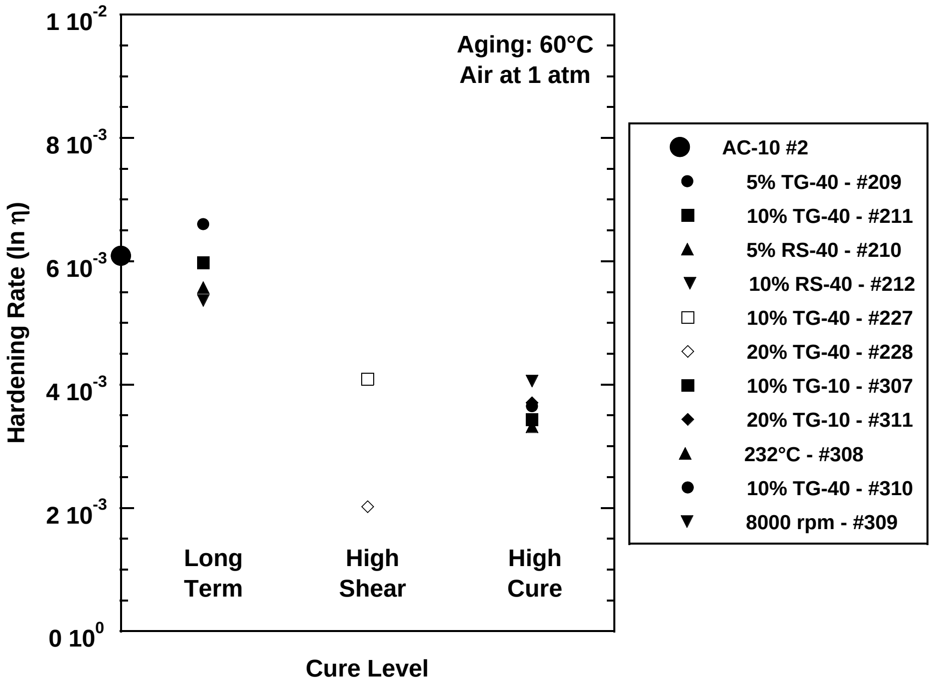

Figure 4-16. Graphical Hardening Susceptibility of High-Shear Blends.

susceptibility, regardless of the magnitude of the aging rates. The error bars on these and subsequent plots indicate the 95 percent confidence interval for the linear least squares fit of equations 4-1 or 4-2, as appropriate. The rates measured at 60 °C (140 °F) required very long times in a shared environmental room subject to occasional upsets. At these low temperatures, diffusion effects in the 1 mm films may be present and could affect rates. Even so, the results are consistent enough to reach some interesting if qualitative conclusions.

Figure 4-13 examines the hardening susceptibility of AC-10 #2 blends prepared at various curing levels. It is very significant that both the high-cure and high-shear material have lower hardening rates than the more conventional long-term blends. In addition, the high-cure data points in Figure 4-13 are shown to be reduced in both hardening rate and oxidation rate, but the relative reductions are about the same for each. This leads the HS to appear “flat,” or unaffected by the rubber additives and processing, while the material is particularly well improved in its hardening rate. The HS measurement developed by Lau is not sensitive to this type of property enhancement. In contrast are the long-term and high-shear samples where there is little change in the carbonyl formation aging rate, but a considerable reduction of the hardening rate and thus the hardening susceptibility.

Figures 4-14 through 4-16 examine the graphical hardening susceptibility for more varied materials, Resin #1 in Figure 4-14, high-cure blends in Figure 4-15, and high-shear blends in

Figure 4-16. Virtually every point of each figure shows improvement in hardening rate, while the insensitivity problem with hardening susceptibility continues. A particularly notable observation is the trend in the oxidative aging rate. Most high-shear samples show a slight reduction in carbonyl formation rate, but some show an increase. This suggests that a different aging mechanism may be present in the high-cure binders. The high-cure process is thought to break rubber particles and incorporate polymer structure into the binder phase. If this is the case, the polymer backbone may have been rendered more accessible to oxidation. While vulcanization would have created a few sulfur cross-links, the vast majority of the poly-butadiene double bonds would still be intact. In addition, the oxidation could cleave the polymer chains as well. This is suggested by Figure 4-5. While the sample is aged at a higher temperature than 85 °C (185 °F), the Viscotek size exclusion chromatograph emphasizes high molecular weight constituents. The unaged rubber peak is eluted at about 21 minutes. Rubber particle size is shown to decrease with aging as the median of the rubber content shifts to longer retention times.

The hardening susceptibility analysis has given hints to the mechanical nature of the curing process, but has not been adequate in providing a means of ranking asphalts on their aging properties. No further meaningful results can be drawn from the HS property. The overwhelming data indicate that hardening rates must be used to gauge the relative rates of aging.

Performance Comparison

Figures 4-17 through 4-20 reexamine the aging comparisons made in Figures 4-10 through 4-12. The new figures remove the oxidation rates from the analysis and focus only on the hardening rates. Overall the hardening trends that seemed partially ambiguous can be clarified.

Figure 4-17 stands in contrast to Figure 4-12. The trend apparent here is that the hardening rate decreases with the increased level of cure. The hardening rate for high-cure blends of AC-10 #2 is reduced by at least 30 percent. Figure 4-18 compares to Figure 4-10. Here the selection of the source binder is found to affect the aging properties, at least where asphaltene content is concerned. The hardening rates for the high-cure blends are substantially less than those of the source binders. Figures 4-19 and 4-20 examine the effect of rubber content on binder properties. The high-shear preparations (Figure 4-19) yield reduced aging properties at both 10 and 20 percent rubber content. However no appreciable difference is seen in the two high-cure blends prepared at 20 percent rubber, compared to the various 10 percent preparations.

Discussion

This analysis requires some speculation primarily because of an inability to compositionally separate the rubber solids from asphaltenes by reliable means. First, the mechanism by which rubber particles interact with the asphalt must be considered. Then, the effect of these materials on aging should be examined.

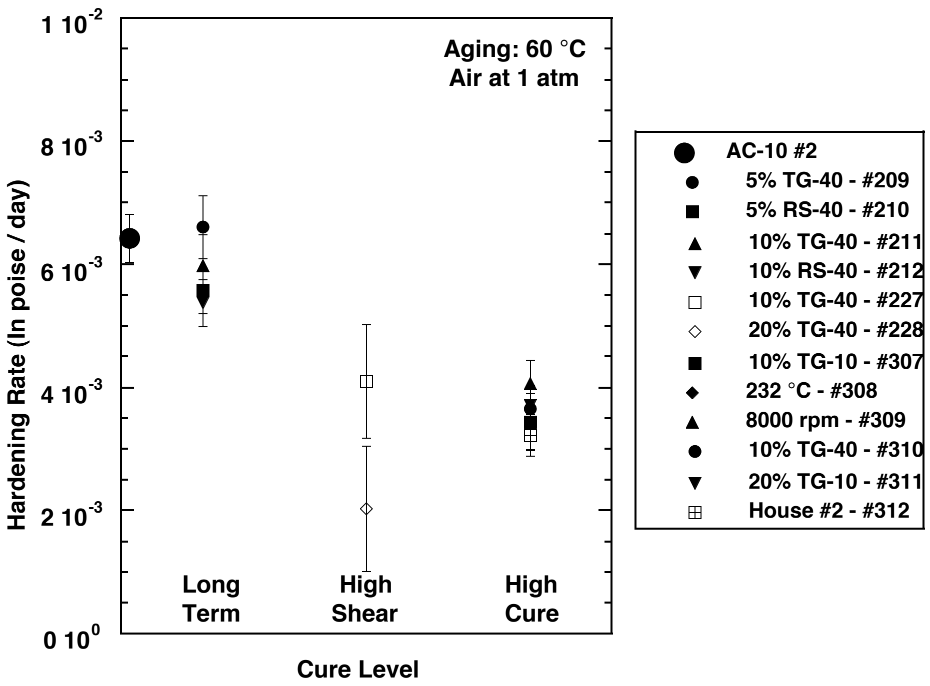

Figure 4-17. Effect of Cure Level on Viscosity Hardening Rate - AC-10 #2 Blends.

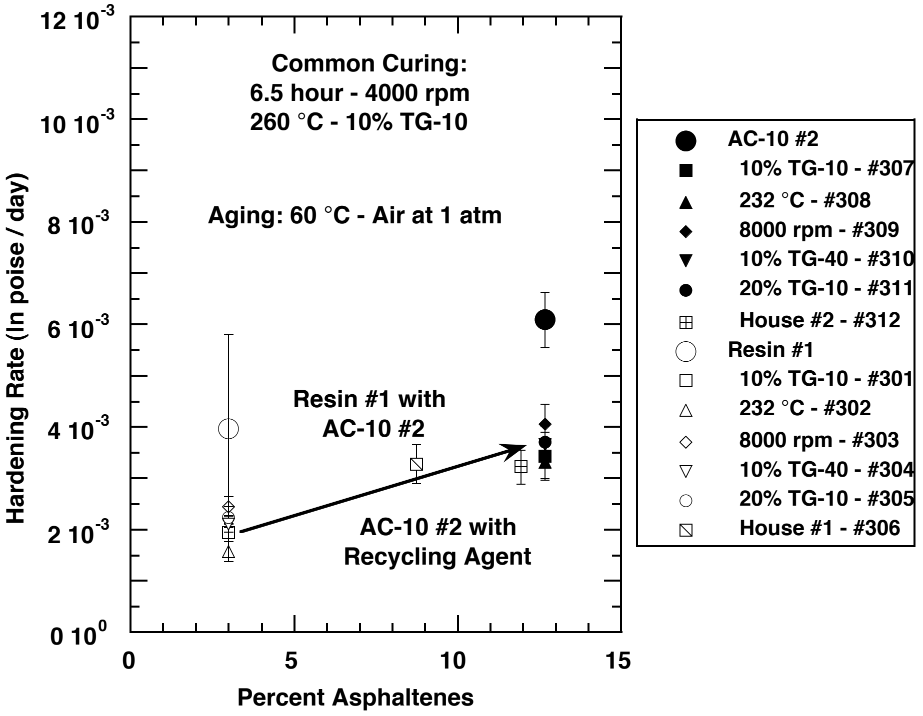

Figure 4-18. Effect of Asphaltene Content on Hardening Rate - High-Cure Blends.

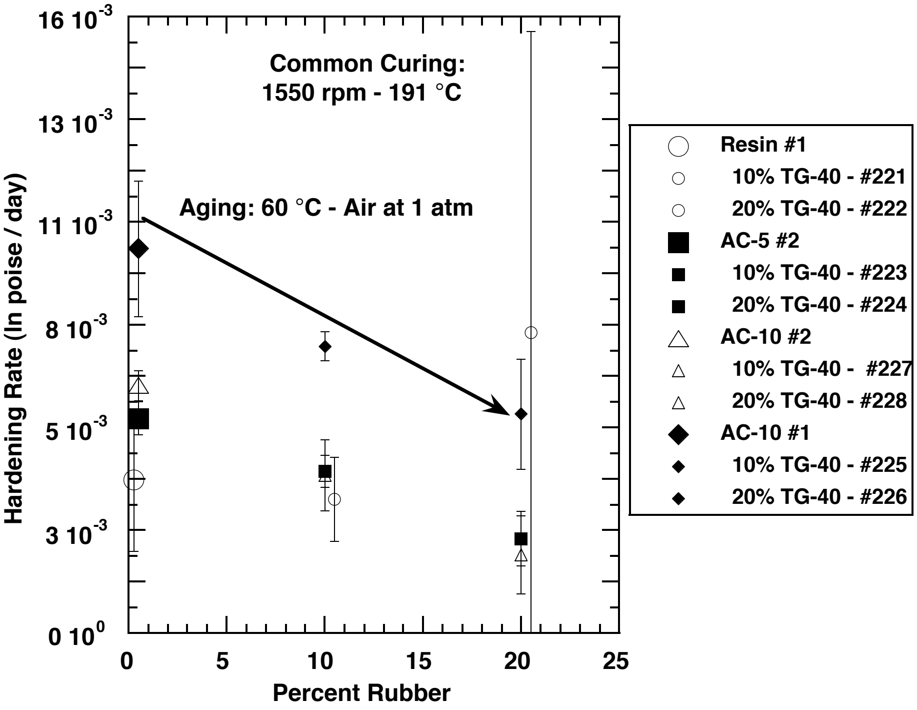

Figure 4-19. Effect of Tire Rubber Content on Hardening Rate - High-Shear Blends.

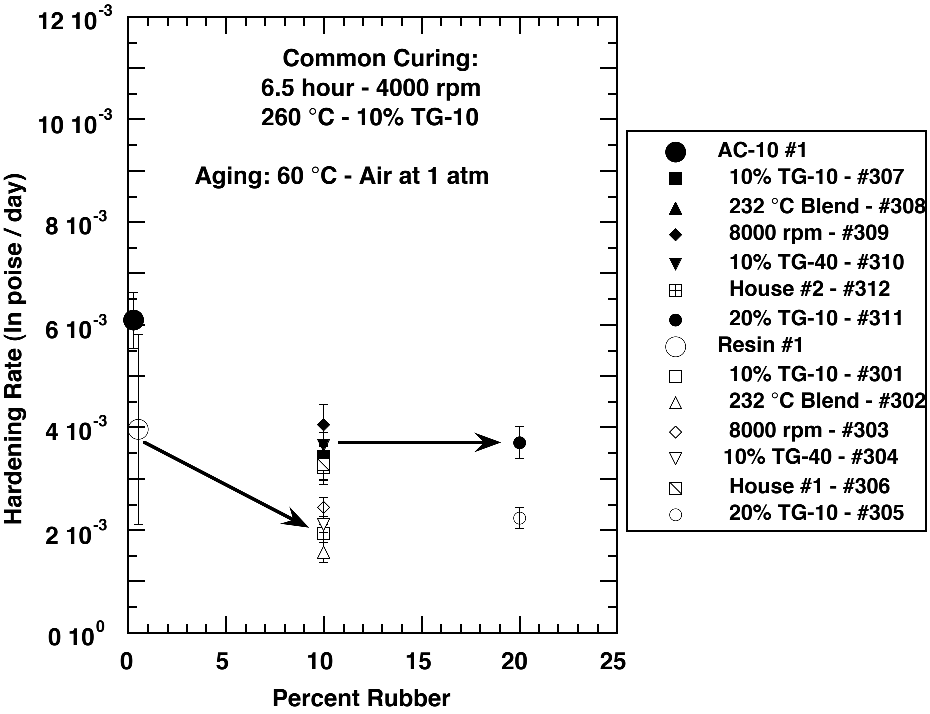

Figure 4-20. Effect of Tire Rubber Content on Hardening Rate - High-Cure Blends.

It has been shown that asphaltenes are planar molecules that stack to form larger, viscosity building structures and that these asphaltene structures behave as particles obeying a modified Pal-Rhodes model. It has also been shown (Lin et al., 1995; Liu et al., 1998) that hardening in asphalt is almost entirely caused by the oxidation of more reactive polar molecules to form asphaltenes. The polars are also planar molecules and are more likely to stack once reacted. Dispersed rubber particles would be expected to act similarly; however, the stacked asphaltene structures in neat binder must be compared to macromolecule rubber particles to complete the analogy. Considering the presence of two distinct and separable types of viscosity building particles in a Pal-Rhodes form, we can rewrite equation 4-5 as:

$$\eta^* = \eta_m^* (1 - K_1 \ \%AS - K_2 p)^{-\nu_{avg}} \tag{4-9}$$

where K_1 and K_2 are association constants for asphaltenes and rubber, respectively, and p is the fraction of tire rubber. This of course is a very approximate, first order approximation as we are ignoring asphaltene-rubber interactions, and ν_{avg} is a (positive) mean shape factor. This equation as well as equation 4-5 ignores the changes in η_m as polar aromatics are converted to asphaltene and as some rubber is so disintegrated that it becomes part of the maltene fraction. Even so equation 4-9 gives a qualitative basis for explaining the behavior of these systems. Oxidation has very different effects on the viscosity building components of equation 4-9, K_1 %AS and K_2 p. The oxidation of heavy polar aromatics rapidly produces molecules which associate to form asphaltenes.

However, as indicated in Figure 4-5, aging also reduces rubber particle size. It has been shown previously (Leicht et al., 2000; Flanigan, 1995) that oxidation greatly accelerates the curing process resulting in much reduced particle settling rates indicating the more extensive disintegration of larger rubber particles. This in turn will reduce the contribution of the rubber to the mixture viscosity. Probably both K_2 and p are reduced; p only slightly as some rubber is sufficiently disintegrated to become part of the maltene fraction, as indicated in Figure 4-5, but primarily K_2 is reduced by a decrease in particle size as the bulk of the rubber is still in particle form.

As shown in Figures 4-12 through 4-17 there is a marked difference in the aging effects of long-term, high-shear, and high-cure materials. For the long-term material both oxidation rate and hardening rate are little changed from that of neat material. The high-shear material has a reduced hardening rate that results almost entirely from a reduced value of HS. The high-cure material also has a reduced hardening rate but for this material it results from a reduced oxidation rate while HS is about equal to that of neat material.

Taking the log and then the derivative of equation 4-9 with respect to carbonyl and with the assumptions that K_1 and ν_{avg} are constant, yields:

$$HS = \frac{\partial \ln \eta}{\partial CA} = \frac{\nu_{avg}\left(K_1 \frac{\partial \%AS}{\partial CA} + \frac{\partial K_2 p}{\partial CA}\right)}{1 - K_1 AS - K_2 p} \tag{4-10}$$

Considering the number of variables involved it is remarkable that the HS still remains constant during oxidation as it does for neat material even though it is no longer temperature independent. As oxidation proceeds ∂%AS/∂CA tends to decrease as reactive material is consumed and K_1%AS in the denominator of equation 4-10 increases. For neat materials this yields off-setting changes that leave the ratio in equation 4-9 unchanged (Lin et al., 1995). Even with the addition of terms in equation 4-10 it still remains constant. As oxidation proceeds, K_2p decreases and the term $\partial K_2p/\partial CA$ becomes less negative and there may be other changes not accounted for, but they all remarkably interact to keep HS constant as oxidation proceeds.

It is interesting to consider the effect of curing on the subsequent oxidation and hardening. There is almost no effect on either for the long-term cured materials. As this is the least cured material, K_2p will be at a maximum. It is also likely that $\partial K_2p/\partial CA$ is at or near its maximum negative value as the large rubber particles are reduced in size by oxidation. Most of the oxidation probably still occurs in the asphalt as the carbonyl formation rate is little changed. At any rate the value of K_2p is offset by the negative effect of $\partial K_2p/\partial CA$ and perhaps by a small decrease in ∂%AS/∂CA.

The minimum in HS exhibited by the high-shear material, relative to the other curings, is hard to explain (Figure 4-12 but also Figures 4-13, 4-14, 4-16, 4-17). Within the error there is no change in oxidation rate, probably indicating only a small decrease in ∂%AS/∂CA. One would expect both K_2p and its rate of decrease to be lower than for less cured material, though the results would indicate an appreciable negative value for $\partial K_2p/\partial CA$. The results for this curing are clouded by the appreciable data scatter.

The high-cure material (Figures 4-12, 4-13, 4-14, 4-15, 4-17) is most interesting. In the first place it is the best material from the standpoint of less settling and lower viscosity at compaction temperatures, so it is particularly attractive that it experiences less oxidative hardening at road conditions. It is likely that both K_2p and $\partial K_2p/\partial CA$ are now sufficiently low that equation 4-10 is nearly reduced to equation 4-7 and the HS approaches that of the neat asphalt.

As mentioned earlier, the reduction in hardening rate for the high-cure material, unlike the less cured material, results from a lower oxidation rate. It has been shown that associations in asphalt affect the oxidation rate. For instance, a mixture of naphthene aromatics and polar aromatics reacts more slowly than values calculated from the reaction rates of the components (Liu et al., 1998). It is postulated that the less reactive naphthene aromatics are associating with and shielding the polar aromatics. In the high-cure material, particle disintegration is significantly more complete and there are many more polymer chains available to shield reactive sites. The polymer chains are sufficient in number and structure to operate analogous to additional naphthene aromatics, to retard oxidative aging and keep hardening rates low. Therefore the hardening susceptibility is essentially that of the neat material and the oxidation that overcomes the shielding to produce carbonyls is also producing asphaltenes.

Conclusions

Low-cure blends have very low hardening rates and decreased hardening susceptibilities, mainly due to the predominance of suspended particles that elevate bulk viscosity, while not necessarily improving the asphalt phase. The suspension contains competing species that react selectively. While these kinetics are not completely understood, they are temperature dependent. As the curing level increases, the effect of the suspension on bulk properties is diminished. This is evidence that migration into the asphalt phase is occurring. Improved hardening continues, but because the suspended phase is still present, kinetic selectivity still poses a mechanism problem.

High-cure CRMA materials, by comparison to the source materials, exhibit superior aging characteristics (lower hardening and carbonyl formation rates) throughout the aging simulation range, but HC-CRMA exhibits no characteristic hardening susceptibility, rather one varying with temperature. The changing carbonyl formation rates cloud the data analysis rendering hardening susceptibility a less useful property for comparing asphalt hardening properties. Hardening rate improvement is demonstrated with three user customizable properties. Rubber content of at least 10 percent and high-cure preparations are recommended. Aging can further be retarded by utilizing low-asphaltene source binders, although this would somewhat affect the materials' rutting resistance.

The experiments conducted provide a much more rigorous examination of hardening properties than the single data point approach of the current Superpave aging evaluation. These data challenge the foundations of current performance evaluations and their accuracy with regard to CRMA. The temperature dependence of CRMA aging does not support the high temperatures and pressures utilized in Performance Grade analyses. The discussion details the importance of the hardening rate as the final criterion for aging comparison. Neither aging CRMA at higher temperatures, nor an attempt to develop a representative hardening property were found to be reliable for road aging predictions. This finding is a setback for the development of a rapid and dependable aging test for CRMA and asphalt-rubber materials.

ACCELERATED AGING TESTS FOR CRUMB-RUBBER MODIFIED ASPHALTS

Devising an aging procedure that is rapid and yet simulates road aging of asphalt binders has been a major effort of this study and many others. Though badly needed, obtaining a really satisfactory procedure has been a very intractable problem. Even neat asphalts can respond very differently to changes in temperature and pressure (Liu et al., 1996; Liu et al., 1997; Liu et al., 1998; Domke et al., 1997; Domke et al., 1999a; Domke et al., 2000).

The oxidation of asphalt has been shown to occur in a rapid initial phase that is characterized as the initial jump, and this is followed by a lengthy phase during which the oxidation rate is constant at a given temperature and pressure (Lau et al., 1992). During this phase log viscosity varies linearly with time. The carbonyl formation rate is also constant, and when carbonyl is plotted versus ln viscosity a straight line is obtained which is independent of oxidation temperatures below about 100 °C (212 °F). The slope of this line, which we call the HS, is a definite property of each asphalt. Though independent of temperature for neat asphalts, the HS value does vary with pressure.

The initial jump is also temperature independent but it is a function of pressure. The value of the initial jump is obtained by extrapolating the constant hardening rate data back to zero time, and the difference between this value of the viscosity and the initial value is the initial jump.

In this work the hardening rate of thin asphalt films aged at 60 °C (140 °F) and 1 atm of air is assumed to represent road hardening. Thin films reduce the complication of diffusion, and 60 °C (140 °F) is a compromise. It is at the upper end of actual road temperatures, but most of the hardening occurs at higher temperatures, and at lower temperatures the hardening rate is just too slow. Even at 60 °C (140 °F) it takes about a year to obtain the degree of hardening actually found in some old roadways. Obviously this is impractical as a routine test but it serves as a benchmark for evaluating aging at other conditions.

Even for neat asphalts accelerated procedures are complicated by the fact that initial jump and hardening susceptibility are pressure dependent, but this dependence varies considerably for different asphalts. While the initial jump and HS are not temperature dependent, activation energies do vary so that different asphalts respond differently to an increase in temperature. Thus an asphalt that hardens more slowly than others at test conditions may actually be a relatively poor performer at road conditions. We have compared aging in the PAV at various times with 60 °C (140 °F) and atmospheric pressure aging for a number of neat asphalts in a previous study (Domke et al., 1997). While there was a general trend, some asphalts appear relatively much better and some considerably worse in the PAV as compared to the 60 °C (140 °F), 1 atm aging.

For asphalts containing crumb-rubber, this situation is greatly complicated in that now both the initial jump and HS are temperature and pressure dependent as discussed previously. In an asphalt-rubber mixture both asphalt and rubber are oxidizing, and the relative oxidation of each responds differently to temperature and pressure, percent rubber, and particle size. Furthermore, oxidation of the rubber may actually reduce the viscosity by breaking up the particles (Chapter 2).

Evaluation of PAV as an Aging Procedure for CRMA Materials

Table 4-7 shows the time required at various temperatures to reach the same viscosity as obtained in the PAV. The 60 ºC (140 ºF) data were obtained in the environmental room and the

Table 4-7. Number of Aging Days to Obtain PAV Viscosity.

Aging Temperature	60 °C (140 °F)	80 °C (176 °F)	85 °C (185 °F)	88 °C (190 °F)	90 °C (194 °F)	93 °C (200 °F)	99 °C (210 °F)
AC-5 #2							
Blend #203	107			10.0		7.91	6.85
223	115	16.9	21.7		17.4		
AC-10 #1							
Blend #225	79.5	12.1	15.5		11.4		
Resin #1	-52.5	-5.6	-5.24	2.3	-3.13		
Blend #221	116	24.9	21.6		17.4		
301	-188	8.14	2.98		4.34		
302	-73.7	18.2	-5.49		-2.53		
303	-109	15.2	7.15		3.79		
304	-59.2	20.4	9.39		5.75		
305	-99.3	5.86	8.76		-1.32		
306	-12.5	20.6	9.55		6.80		
AC-10 #2	112	18.2	10.9	10.22	6.46	8.39	6.62
Blend #211	-6.78			2.63		0.98	-1.33
227	121	20.0	21.8		17.6		
307	0.76	17.5	8.69		3.02		
308	-2.74	14.9	7.25		6.09		
309	17.6	17.0	6.47		5.89		
310	-88.2	11.3	1.42		1.25		
311	-37.2	9.08	4.09		2.88		
312	-73.8	16.1	5.74		5.36		
313	12.7	20.7	16.6		2.90		
FM 2818 Samples							
HM 10% S1	110						
AMI 10%	130						
HM 15% S1	139						
AMI 15%	70						

others in the POV. All were aged in about 1 mm thick films at one atmosphere. The PAV was operated at 100 ºC, 20 atm air.

To evaluate the PAV as an aging procedure, comparison is made to the 60 ºC (140 ºF) data. Ideally the time at 60 ºC (140 ºF) for each asphalt or blend to reach its own PAV viscosity should be the same. This will be true if the PAV accelerates aging for each asphalt by the same percentage, and this must be approximately true if the PAV is to tell us anything about relative road aging rates.

Some explanation is due the negative values in Table 4-7. These times were obtained by extrapolating or interpolating the constant rate data at 60 °C (140 °F) to the viscosity of the PAV. The negative values indicate that the PAV viscosity is still in the initial jump region for the 60 °C (140 °F) data and thus below the zero time intercept for the 60 °C (140 °F) data. These negative values occur, we believe, when the rubber is oxidized so rapidly relative to the asphalt that its disintegration rate largely offsets asphalt oxidation so that little hardening occurs. This effect can be much greater at PAV conditions than at 60 °C (140 °F) and 1 atm.

It can be seen that in general the results in Table 4-7 are disastrous as the aging times at 60 °C (140 °F) vary from -188 days to 139 days. The results are not too bad for the intermediate cures except for Blend #211 which is totally off and Blend #225 which is also unsatisfactory. The neat AC-10 #2 is close to these but Resin #1 is totally off. The samples from the FM 2818 test section are also fairly good for the most part. These materials were actually cured less than intended and probably are like the intermediate-cure samples. All the high-cure runs are completely off.

Considering all these effects and the extreme conditions of pressure and temperature, it would indeed be extraordinary if the PAV, or the RTFOT for that matter, could reasonably be expected to consistently simulate road or hot-mix conditions respectively for asphalt-rubber blends.

Aging in the POV at Other Temperatures

In Figures 4-21 to 4-36 we have plotted the times required to reach a series of specified viscosities at 60 °C (140 °F) versus the time it takes at other temperatures in the POV to reach the same viscosities. Obviously the lines should go through zero. In general the failure to do so represents different initial jumps. For neat asphalts where the jump is not a function of temperature, it represents scatter. There is always some scatter in the rate data and this can have a significant effect on the intercept at zero time. For the rubber blends the initial jump is very temperature dependent and this causes great difficulty for an accelerated procedure.

Figures 4-21 through 4-23 show the effect of 10 and 20 percent rubber in high-shear blends with asphalts AC-10 #1 and AC-10 #2. As seen, there is a large effect of rubber content further affected by the nature of the base asphalt. The greatest effect is temperature with the results getting worse as the temperature increases from 80 to 90 °C (176 to 194 °F). Actually the results for the neat asphalts are quite good at 85 and 90 °C (185 and 194 °F) but all the rubber modified blends show very large divergence. The trouble is primarily in the initial jump. Figure 4-24 shows similar results for Resin #1 and AC-5 #2. Again the two neat asphalts behave fairly well but there is gross deviation for the rubber-containing material, though the two 10 percent rubber blends agree with each other. However, at 80 °C (176 °F) (not shown) agreement is much poorer. Figure 4-25 shows four high-shear, 10 percent rubber blends aged at 90 °C (194 °F), which incidentally show better mutual agreement than at either 80 or 85 °C (176 or

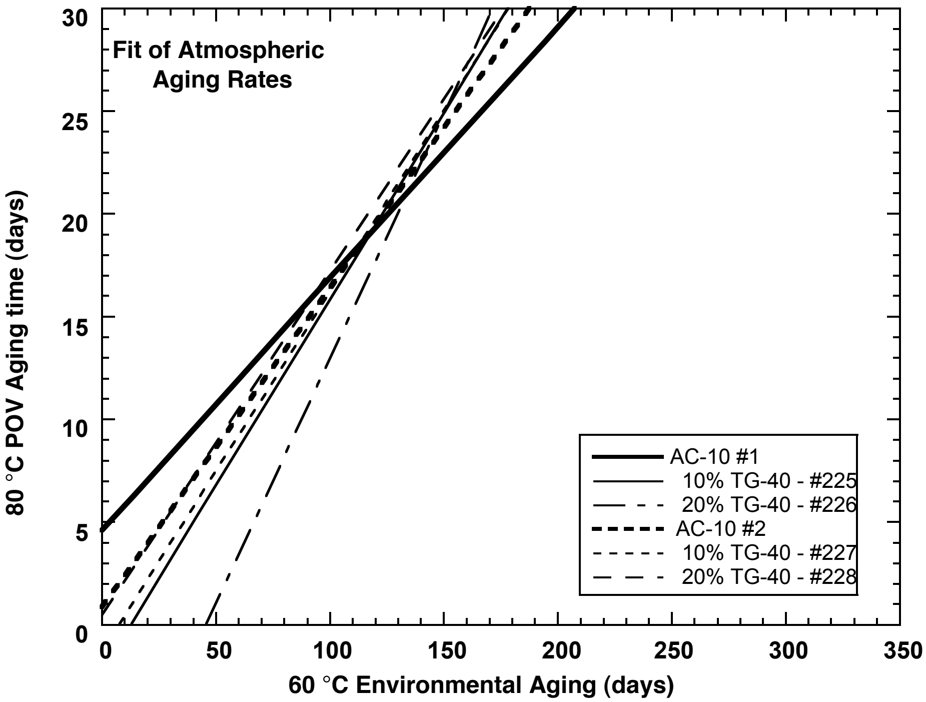

Figure 4-21. 80 °C Aging Index of High-Shear Blends of AC-10 #1 and #2.

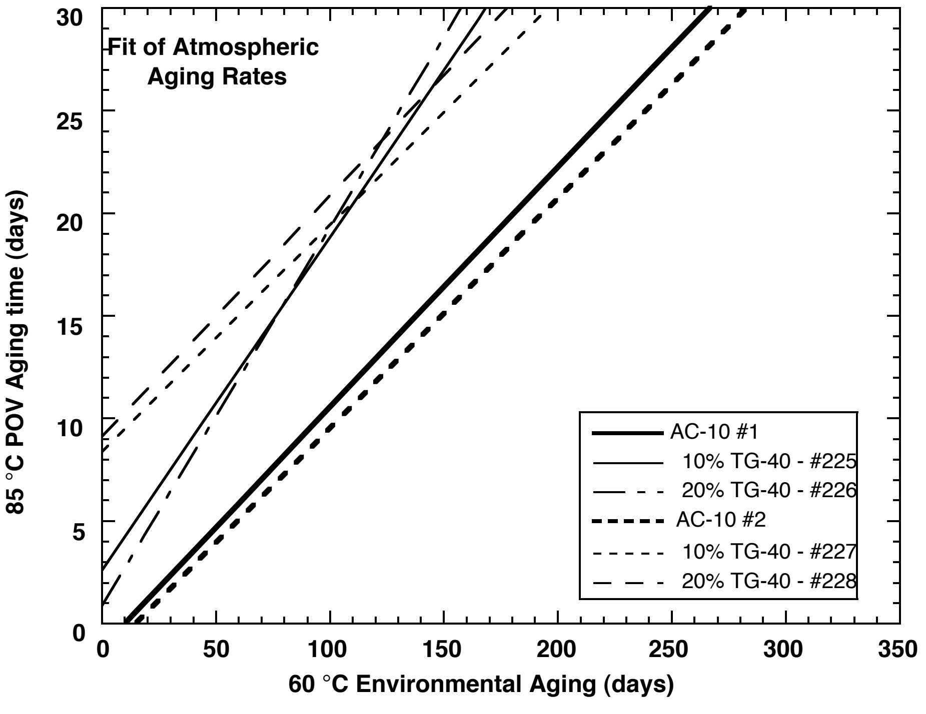

Figure 4-22. 85 °C Aging Index of High-Shear Blends of AC-10 #1 and #2.

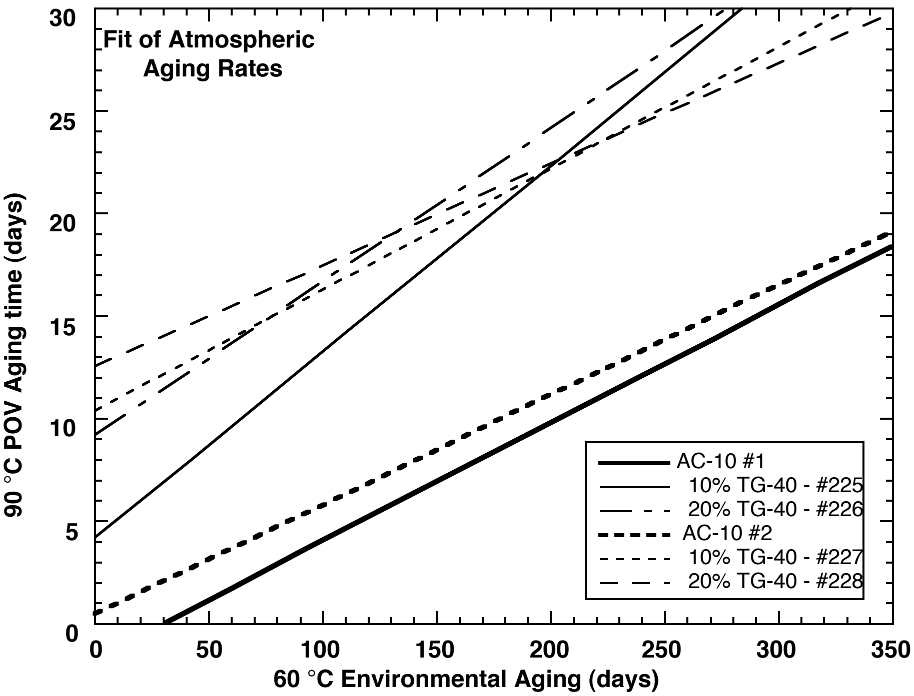

Figure 4-23. 90 °C Aging Index of High-Shear Blends of AC-10 #1 and #2.

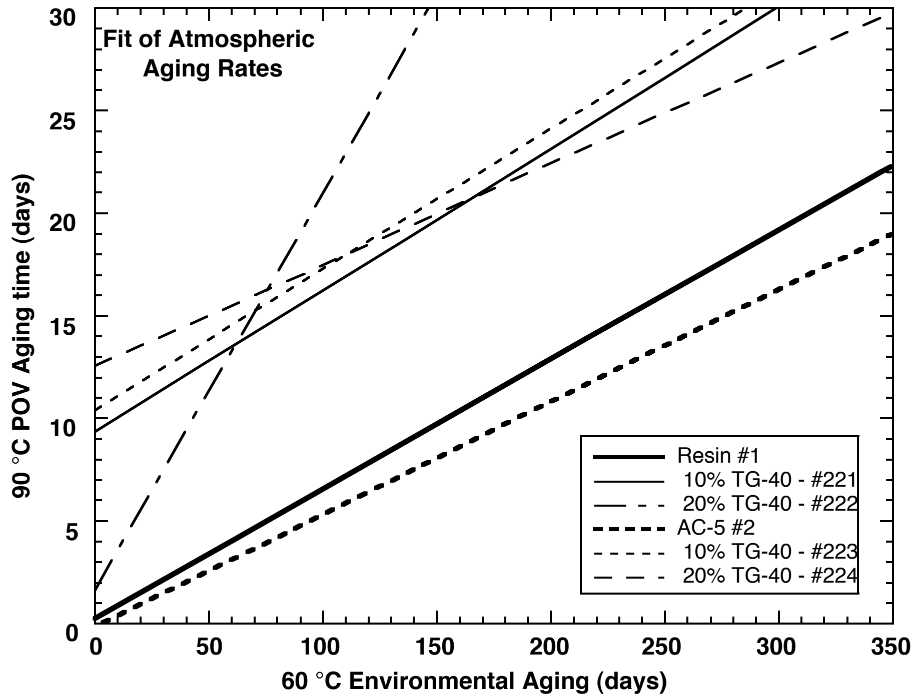

Figure 4-24. 90 °C Aging Index of High-Shear Blends of Resin #1 and AC-5 #1.

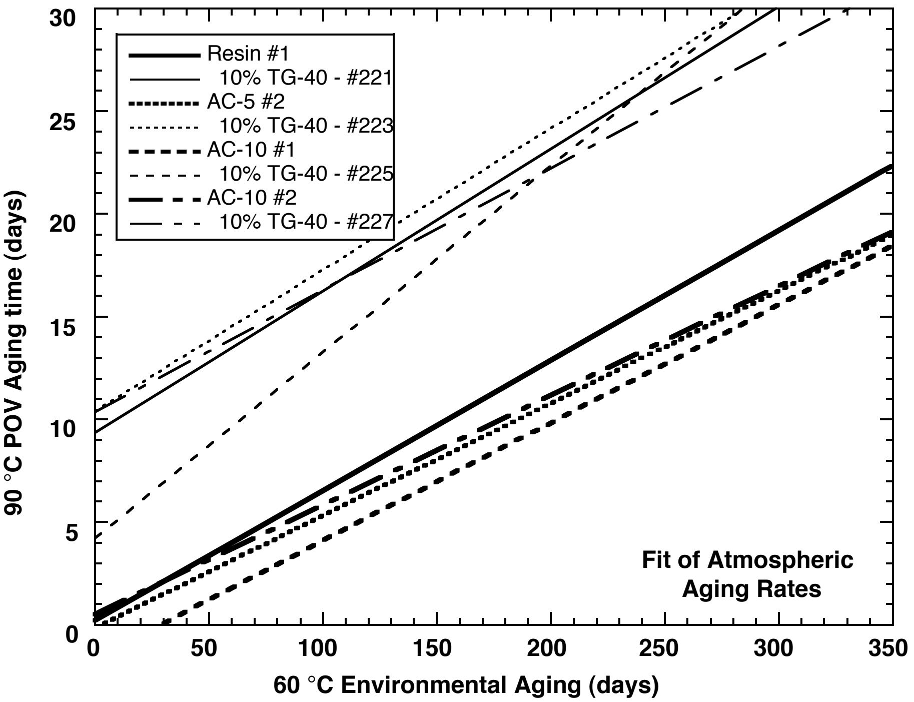

Figure 4-25. 90 °C Aging Index of High-Shear Blends Containing 10% TG-40.

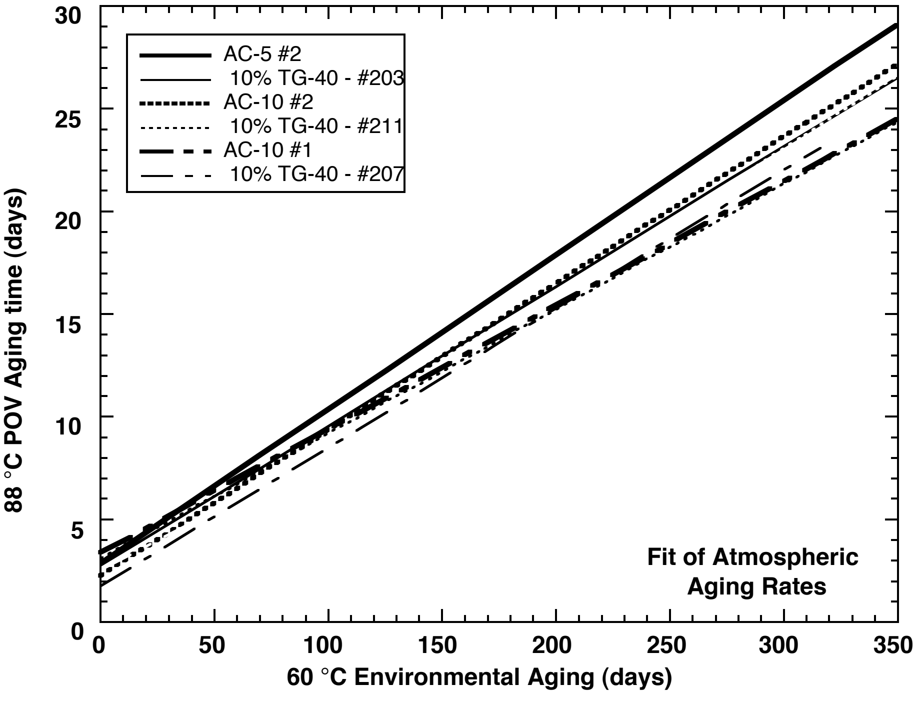

Figure 4-26. 88 °C Aging Index of Long-Term Blends Containing 10% TG-40.

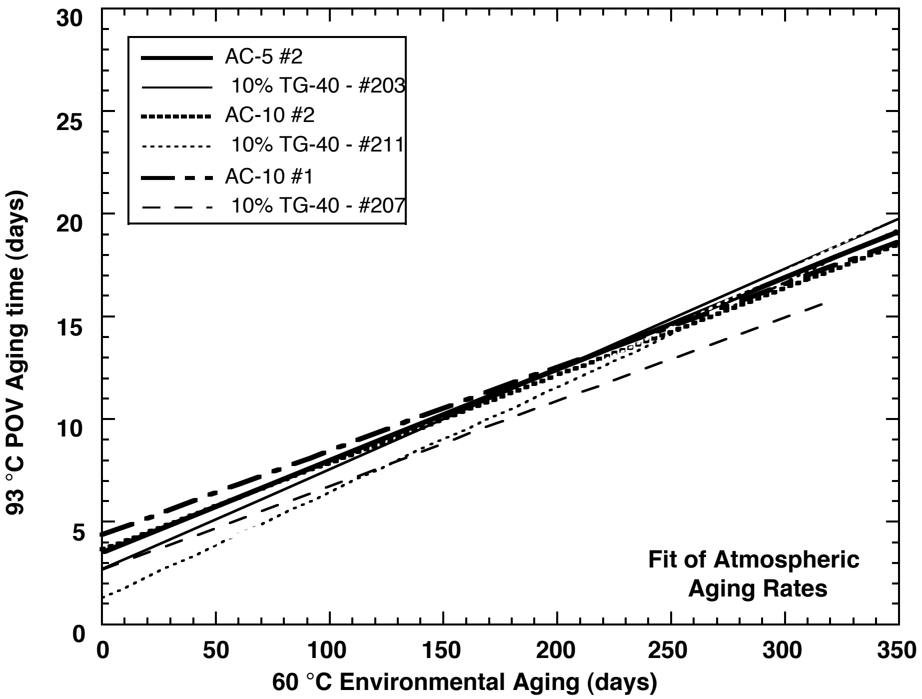

Figure 4-27. 93 °C Aging Index of Long-Term Blends Containing 10% TG-40.

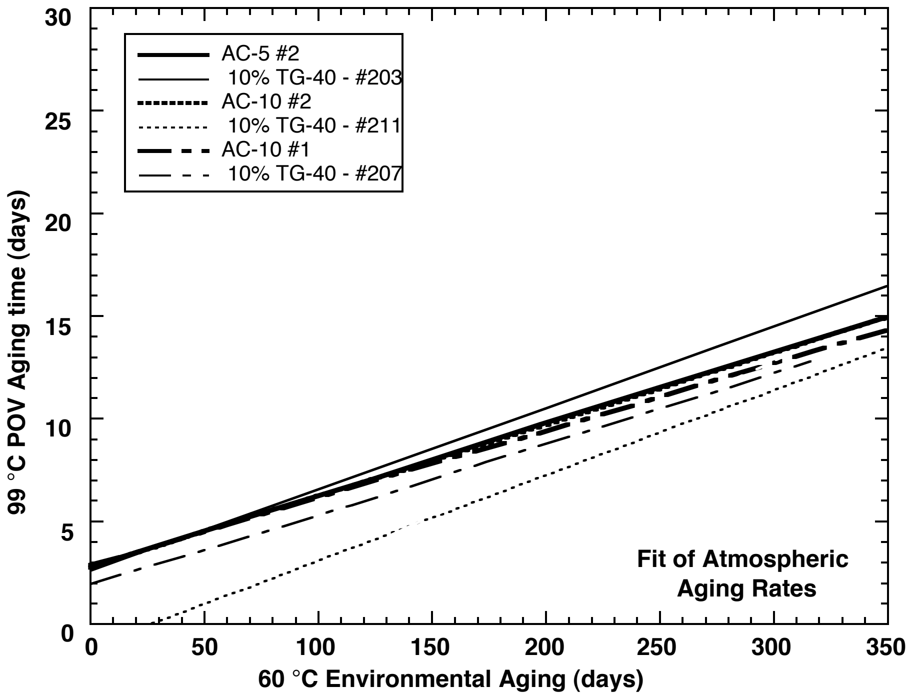

Figure 4-28. 99 °C Aging Index of Long-Term Blends Containing 10% TG-40.

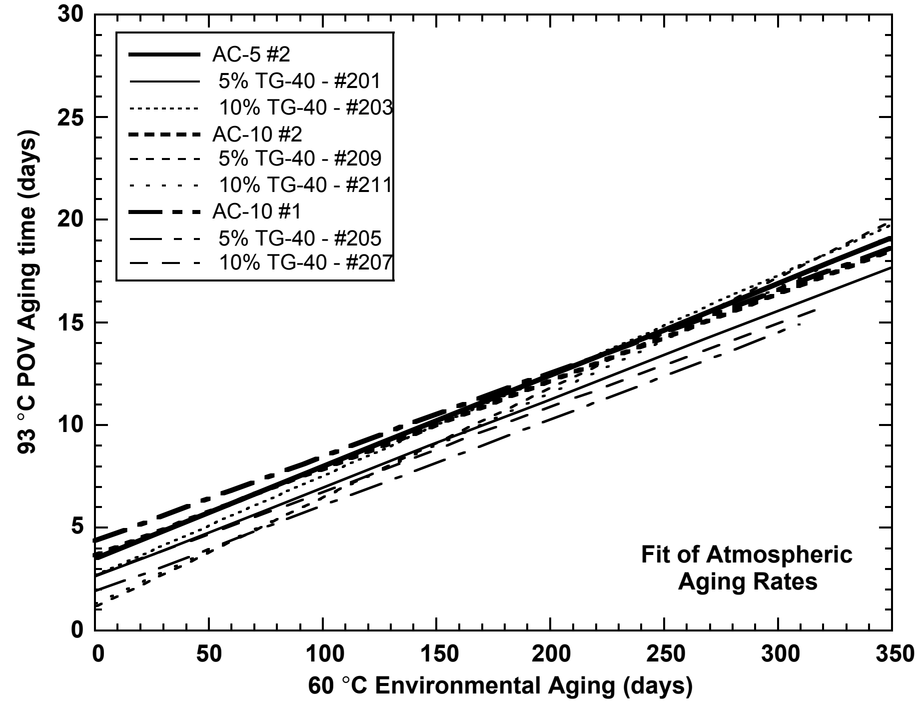

Figure 4-29. 93 °C Aging Index of Long-Term Blends Containing 5% and 10% TG-40.

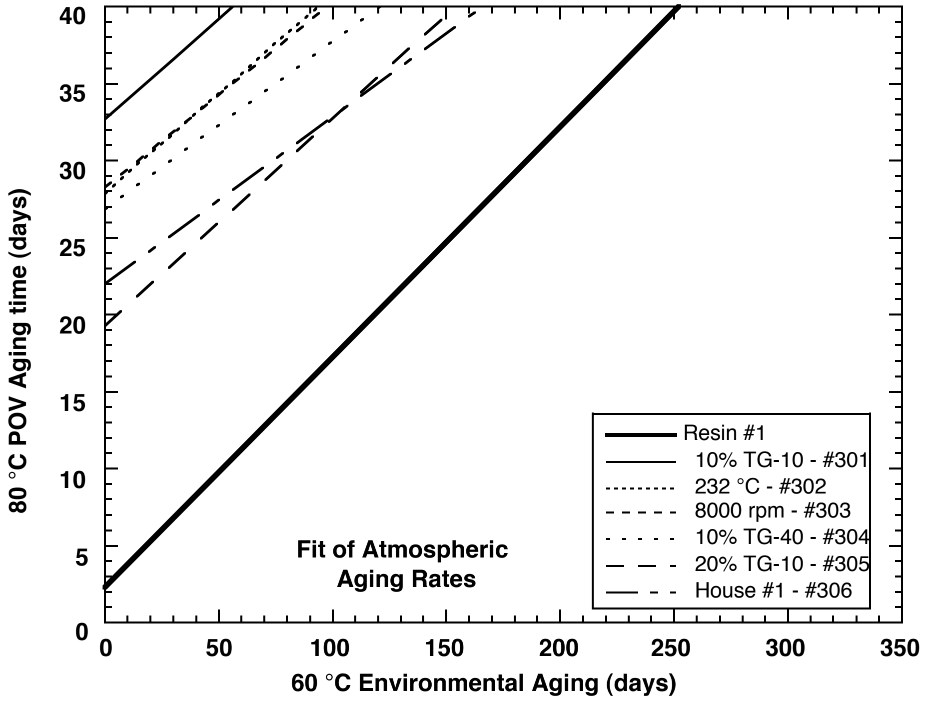

Figure 4-30. 80 °C Aging Index of High-Cure Blends of Resin #1.

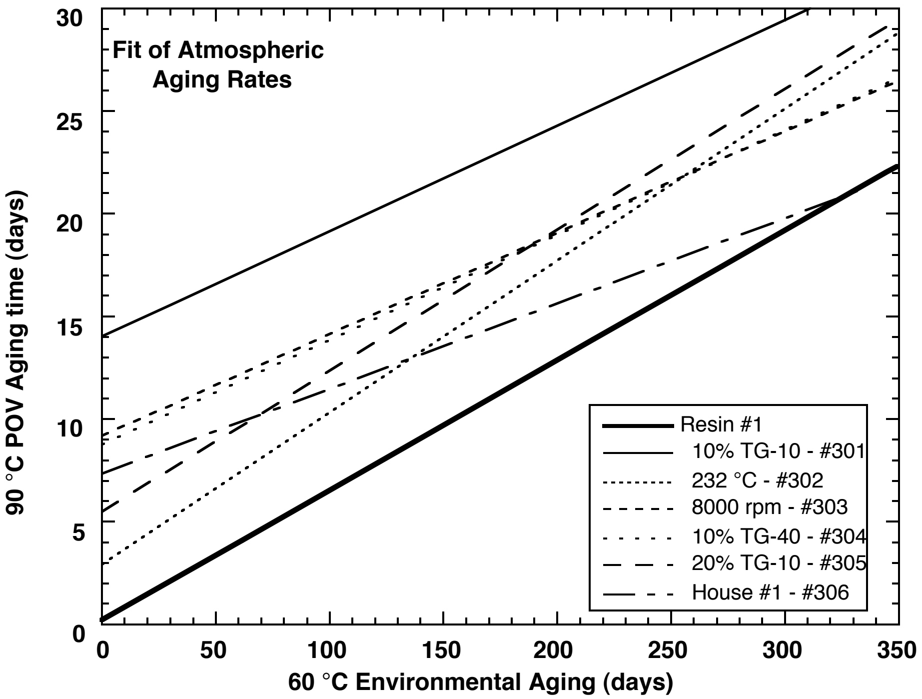

Figure 4-31. 90 °C Aging Index of High-Cure Blends of Resin #1.

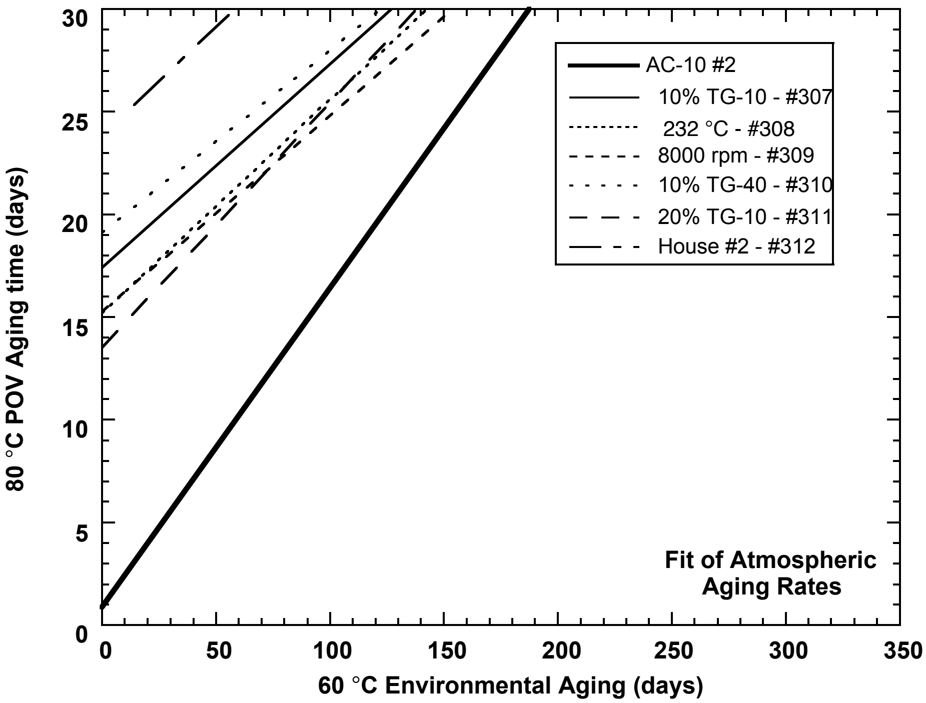

Figure 4-32. 80 °C Aging Index of High-Cure Blends of AC-10 #2.

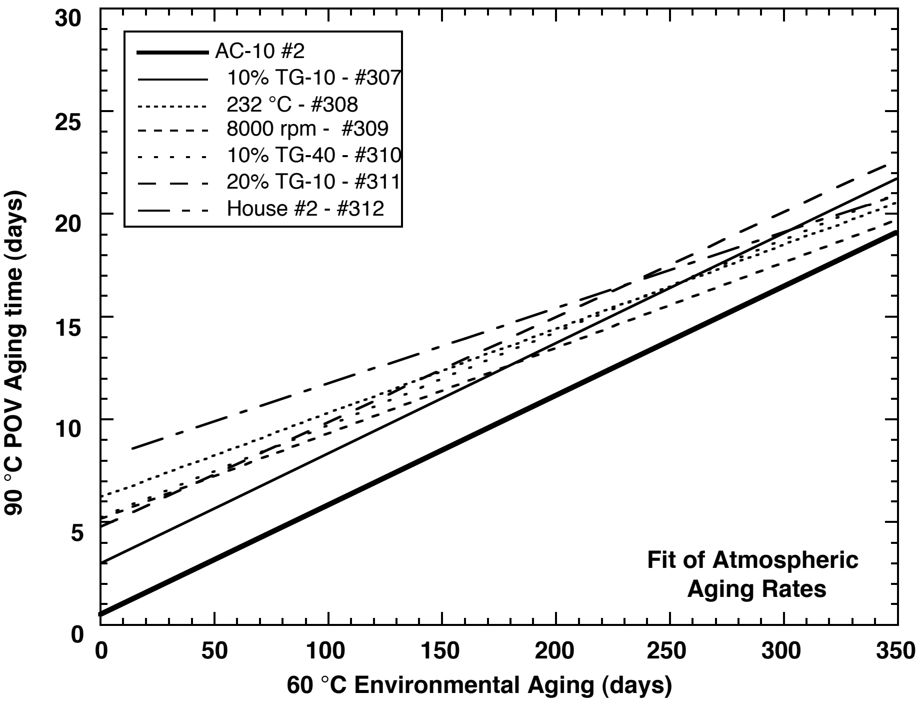

Figure 4-33. 90 °C Aging Index of High-Cure Blends of AC-10 #2.

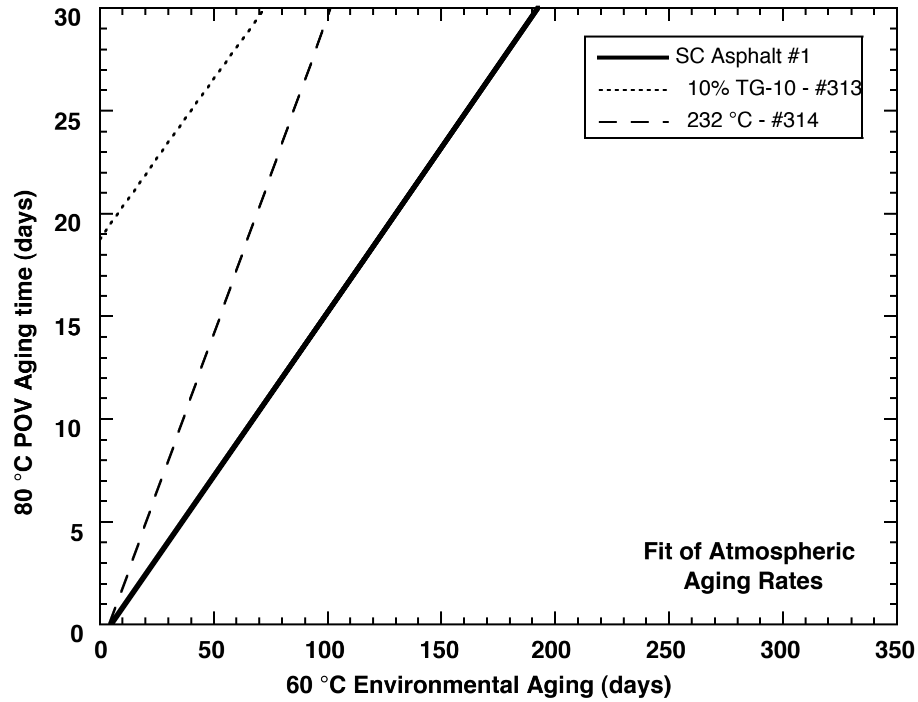

Figure 4-34. 80 °C Aging Index of High-Cure Blends of SC Asphalt #1.

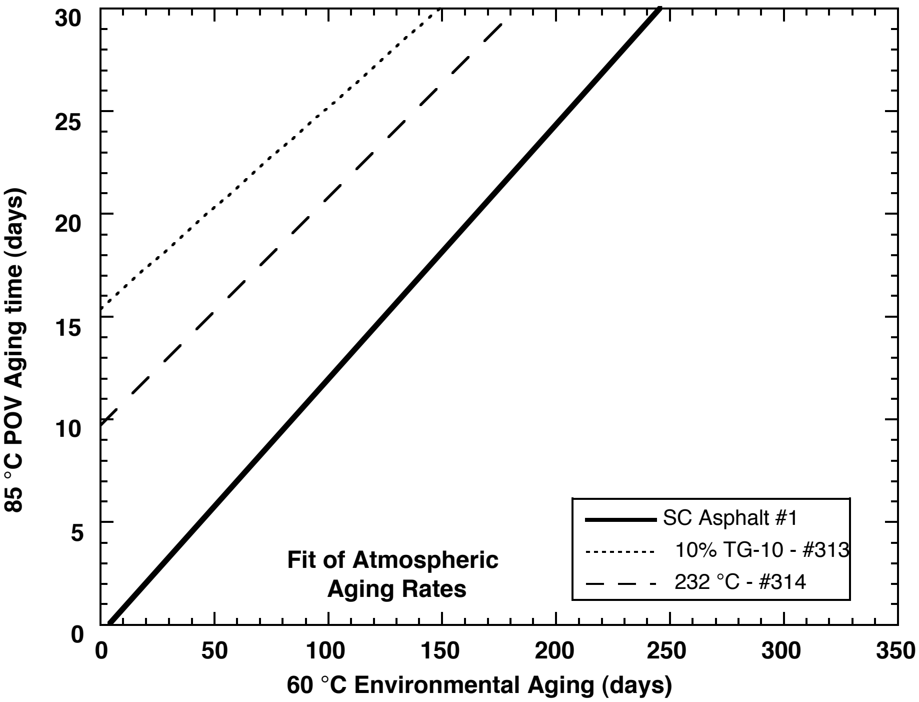

Figure 4-35. 85 °C Aging Index of High-Cure Blends of SC Asphalt #1.

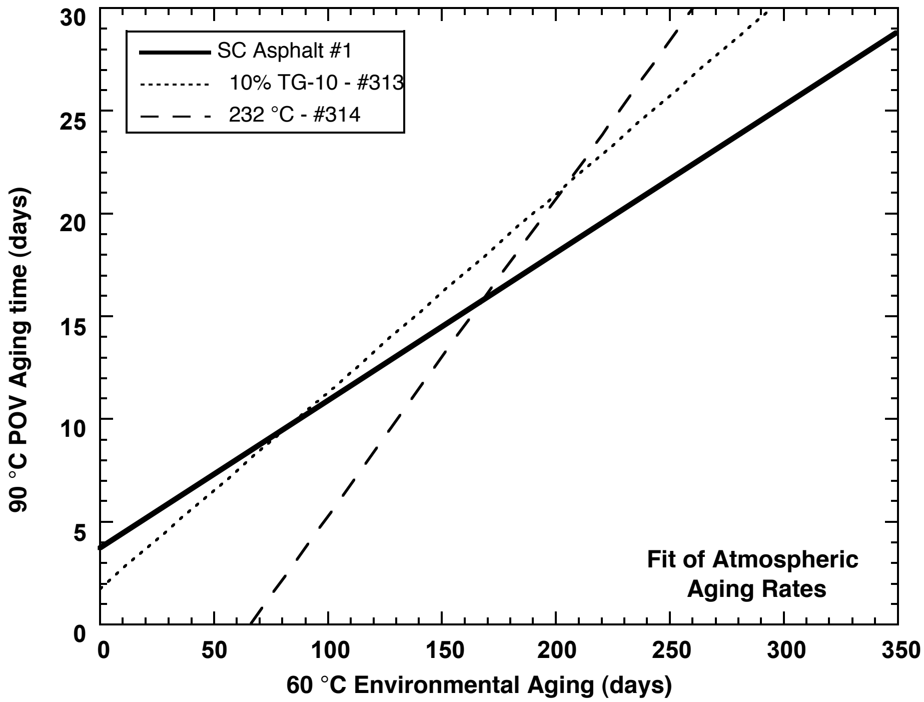

Figure 4-36. 90 °C Aging Index of High-Cure Blends of SC Asphalt #1.

185 °F) (not shown) though the initial jump is way off at 90 °C (194 °F). We again see that results for the four neat asphalts are not bad.

Figures 4-26 through 4-28 show the effects of base asphalts for otherwise identical long-term curing blends (10 percent, -40 mesh rubber cured at 500 rpm and 190.6 °C [375 °F]). These data are about the best, showing good agreement in intercept at 88 °C (190 °F) and slope at 93 °C (200 °F). Again we see how the intercept and thus the initial jump changes with temperature for the blends. Figure 4-29 compares long-term blends containing 5 and 10 percent rubber aged at 93 °C (200 °F). In this figure identically cured 5 percent blends have been added to the data in Figure 4-27. The agreement here is not too bad but better than results obtained at either 88 or 99 °C (190 or 210 °F) (not shown). Even though we get fairly good fits for some asphalts at some temperatures there is no consistency: it just seems more or less random. One would expect the fits to be best at 80 °C (176 °F) - closer to 60 °C (140 °F) - but this is not generally the case, and neither is the higher temperature always best.

For some reason, not understood, the scatter becomes even greater for high-cure blends. Figures 4-30 and 4-31 show various blends in Resin #1 at 80 and 90 °C (176 and 194 °F). The agreement is very poor but improving at higher temperature. Similar results (Figures 4-32 and 4-33) were obtained with AC-10 #2. The better agreement at higher temperature results primarily from a decrease in the initial jump at higher temperature. This is not entirely true, however, as the slopes are also affected by temperature. Figures 4-34 to 4-36 show serious scatter for supercritical asphalt #1. The only difference between these two blends is curing temperature with Blend #313 being the higher cured. The plots for the neat asphalts pass through or near the origin as they should. The initial jump for the blends are generally decreasing with aging temperature with inconsistency for Blend #314 at 85 °C (185 °F). It is also interesting that the plot for Blend #314 has a much higher slope than the neat asphalt at 80 °C (176 °F), a smaller slope at 85 °C (185 °F) becoming larger again at 90 °C (194 °F). One would expect this to be the result of bad data except we see this kind of thing often with asphalt-rubber blends.

Conclusions

Though occasionally, for a few systems, reasonable agreement between PAV and 60 °C (140 °F) results were obtained, most results were very poor. Furthermore, studies described earlier in this chapter indicate that poor results should be expected for any accelerated aging procedure because of the variation in hardening susceptibility, initial jump, and activation energy with both temperature and pressure.

POV results at temperatures ranging from 80 to 99 °C (176 °F to 210 °F) are reported and in general show much scatter. Occasionally fair agreement was obtained for a few systems, generally at lower cure levels and higher temperature, but the results are too sensitive to asphalt composition, cure level, and percent rubber to be of practical use.

The final conclusion is that we have found no accelerated aging procedure that has even slight dependability for rubber modified asphalt. If it is desired to know the contribution of ground tire rubber to asphalt properties as the material undergoes long-term road aging, the studies will have to be conducted at low temperature, such as at 60 ^{o}C (140 ^{o}F) and at atmospheric pressure.

SUMMARY OF CHAPTER 4

The incorporation of rubber in asphalt binders provides enhanced aging characteristics. Low-cure blends have very low hardening rates and decreased hardening susceptibilities (hardening in response to a given amount of oxidation), mainly due to the predominance of suspended particles that elevate bulk viscosity, while not necessarily improving the asphalt phase. High-cure asphalt-rubber materials also exhibit excellent aging characteristics, equal to or better than the low-cure materials. Aging can be retarded further by utilizing low asphaltene source binders, although this likely would adversely affect the material's rutting resistance.

For rubber modified materials, the use of a high-temperature, high-pressure aging procedures to simulate long-term aging (as in the Superpave protocol, e.g.) is not reliable; we recommend aging at 60 ^{o}C, 1 atm air to assess aging in CRMA or HC-CRMA materials. Each material behaves differently enough from one another that extrapolations from PAV test conditions to road aging conditions are very risky. The use of elevated pressure is problematic for conventional asphalt binders, but it is even worse for crumb-rubber modified materials as tests at elevated temperatures suffer from the same difficulties. The development of an acceptable accelerated aging test for CRMA materials remains elusive.

CHAPTER 5. FIELD IMPLEMENTATION

This project has been a combination of laboratory development and field implementation. In the laboratory, as discussed in previous chapters, we assessed several production methods for blending ground tire rubber with asphalt and also the resulting binder properties, especially as they relate to Superpave performance specifications and durability.

In the field we worked with asphalt suppliers to produce, on a commercial scale, blended products for use in pavements and with pavement contractors in placing test pavements. This was carried out at one test site in Bryan, Texas, in the summer of 1998 and at a second, in League City, Texas, in June 2000. This second effort was to have been conducted by the summer of 1999, but several delays with setting the project location and schedule, not related to the research effort, prevented meeting this schedule. Both of these implementation tests utilized dense graded mixes and demonstrated the ability of high-cure asphalt rubber materials to be used in conventional settings with little or no hot-mix or pavement contractor adjustments. Long-term monitoring will allow estimates of pavement durability to be evaluated as well.

This chapter details all aspects of the Bryan and League City field tests: binder production, pavement placement, and follow-up tests to date.

HCAR PAVEMENT TEST SECTIONS - 1998

On July 14, 1998, test sections containing HCAR binder were installed 5 miles from Texas A&M University on FM 2818 at Texas 21 in Bryan. The project consisted of three test strips covering a single northbound inside lane 3,000 feet in length. The southernmost 500 foot strip employed an unmodified Coastal AC-20 control binder, the same material used in blending the modified binders. In the remaining two sections, plans called for the employment of 10 and 15 percent high-cure tire rubber in the binder. The project was a 2-inch overlay over an existing hot-mix asphalt cement (AC) pavement and was part of a larger, 5-mile four-lane overlay project. The following are descriptions of major findings and events related to the project.

Selection of Materials

Two major challenges were faced in the laboratory design work leading to the scale-up: material uncertainty and time. In late February 1998, the preferred supplier of blending facilities elected not to participate. It was also learned that Granular Products (Tire Gator), the preferred supplier of ground tire rubber, had gone out of business. (Tire Gator -10 mesh materials had been the most frequently studied because of the ability of the mixer to disintegrate the particles rapidly and because of the cost effectiveness of larger particle sizes.) Both of these suppliers had to be replaced. Asphalt Materials, Inc., an asphalt supplier in the Fort Worth District, was selected as the supplier of blending facilities. Using a ~250 hp colloid mill, Mr. Bill Wilkins, has been producing a low content polymer modified material for some time. AMI employed a

Coastal AC-20 and often an AC-10, but during the road building season only an AC-20 would be available. While Gibson Rubber of Atlanta, Texas, was located as a supplier of ground tire rubber, the product was an unfamiliar one and, with the AMI requirement of steel-free rubber, caution necessitated the selection of Rouse Rubber of Vicksburg, Mississippi. (While the Gibson -10 mesh material was not suitable for AMI, the -20 mesh ground tire rubber was both inexpensive and was found virtually steel- and particle-free in a laboratory test where the tire rubber was mixed with water and allowed to separate after mixing.) The Rouse -80 mesh rubber had also been studied in earlier efforts detailed in this report.

Aggregate Utilization

Young Contractors was awarded the contract to resurface Texas 6 at Hearne, portions of Texas 6 that bypass Bryan and College Station, and FM 2818 from Texas 60 north to Texas 21. The same mix design (which is described later) was used at all three locations. The mix was a TxDOT Type C (a dense graded mix with aggregate top size of 22.4 mm) with a Fina AC-20 asphalt as the binder. The aggregate was predominantly a crushed limestone with 15 percent field sand. The mix design was evaluated in the laboratory to confirm the appropriate binder content for the HCAR binder.

Laboratory Tests of High-Cure Production

With all the materials (aggregate and gradation, binder, and rubber) firmly set, the only variables left involved the degree of curing; but a great deal of experimentation was required to focus in on this topic. Blending, both in-house and at AMI was performed to accomplish this goal and to aid in scale-up. Scale-up was also facilitated by the development of rapid tests that could be completed during production. Furthermore, a plan for the industrial production of the test section binder needed to be evaluated. The plan involved producing an excess of the higher rubber content material (in this case 15 percent), to a specified degree of satisfaction (or within the limits of time) and diluting 40 percent of it to reach the lower binder content material (10 percent).

At the Texas A&M CAMC (Center for Asphalt and Materials Chemistry) lab, several trial blends were produced using the AC-20 to determine its characteristics. Previous experience had suggested the appropriate blending temperature and the blends varied by rubber type and content. After the Rouse material was selected, five blends were produced, each with varied length of cure, the first four every 1.5 hours up to 6.0 hours and the last for 9.0 hours. Each blend was produced with 15 percent rubber content according to the scale-up plan. About 2.5 kg were produced; then 1.0 kg was placed in a container with 500 additional grams of neat AC-20 and mixed at low shear for about 10 minutes to produce a 1.5 kg of 10 percent material. Each laboratory blend was evaluated for viscosity, GPC, Brookfield viscosity, and centrifuge settling, while the 15 percent materials were settled and evaluated by the Texas Settling test. The 6-hour blend was selected as the target material and two duplicate blends were produced to obtain sufficient material for the mix design conducted at Texas Transportation Institute (TTI).

In addition to the laboratory mixes, AMI had the capacity to simulate their more typical processes with a bench scale colloid mill that was known to be accurate for their ~1 percent polymer formulation. Their process uses a pump with a known flow rate to feed material to the mill; thus, knowing the total quantity in the holding tank, the average residence time through the mill can be determined. For the bench scale this time is about 45 seconds, but is nearly 20 minutes for the plant. Two sets of blends were prepared by AMI personnel, the first using Gibson -20 mesh rubber and the second using the Rouse -80. The -20 mesh was blended for only 20 passes (15 minutes). It was held at the specified temperature only long enough to complete the passes and, upon evaluation, was not found to be a very good formulation. The -80 mesh preparation was prepared by blending for five passes, then incubating for an hour, so both the exposure to the actual milling mechanism, and the desired exposure to the operating temperature duplicated. Sampled every five passes up to 60 passes (12 hours of total incubation time), this material was compared to the in-house formulations to evaluate the usefulness of the monitoring techniques developed by CAMC.

The issue of process portability and scale-up was an important one in many regards, such as insuring the mix design (made from bench scale blend) works well with the final product (made at an industrial facility), ease of installation, and performance prediction. In addition to the laboratory prepared materials, several laboratory tests were designed to rapidly evaluate the large scale process and compare it to the laboratory scale goal. Two tests were found to show potential with regard to important factors such as speed, ease of testing, distinguishable results: the Brookfield viscosity and the centrifuge test. A crude thermocell was developed to ease concerns about temperature distributions in the sample when using the Brookfield RVF-7 model. A 100-mL beaker filled with the binder to be tested is suspended into a quart can containing pump oil and a stir bar. The quart can is situated on a digital hot plate with stirring capability. The heated oil provides an energy bath that reduced the specimen’s rate of cooling. Frequent stirring of the material and the use of a heat gun, to preheat the spindle before lowering it into the sample, insured the accuracy of the results. The centrifuge test involved dissolving about 1 gram of binder into a quantity of THF, centrifuging the mixture to pack the undissolved solids. Removal of the liquid, first by pouring out excess followed by heating in a beaker of nearly boiling water, allowed for the determination of the percentage of undissolved matter relative to the original total mass, a value correlated with previous experiments. With these tools, and the additional ability to observe the binder consistency, the researchers hoped to gauge the progress of the large scale process.

Mix Design

While the aggregate was fixed by the contractor, the optimal binder content had to be determined before installation. Binder was prepared in the laboratory with the desired qualities. In order to achieve the desired 4 percent laboratory air voids, it was determined that the control (neat), 10 percent, and 15 percent tire rubber pavements should contain 4.9, 5.2, and 5.55 percent binder, respectively. In fact, however, in a slight adjustment to these values, the installation hot mix was prepared at 4.7, 4.8, and 4.9 percent, respectively. Each placed test section was found to contain 7.0 percent voids, by nuclear density gauge.

Bulk Fabrication

The HCAR preparation plan was to prepare a total of 44 tons of binder, consisting of 20 tons which would contain 15 percent rubber and 24 tons which would be 10 percent rubber. These would be prepared by first blending 5.4 tons of rubber (the total amount required for the project) with 30.6 tons of asphalt, thereby producing a total of 36 tons of 15 percent high-cure asphalt rubber. From this, 20 tons would be withdrawn and stored. Then, an additional 8 tons of asphalt would be added to the residual 16 tons of the 15 percent material, thereby producing the required 24 tons of 10 percent HCAR material.

Fabrication of the binders began at 8:00 a.m. on Monday, July 13, 1998. Dr. Richard R. Davison and graduate student Jason F. Chipps of the Asphalt Group were present to observe the blending process, test the material, and determine when the blending had reached completion. A rapid rise tank had been filled with the neat AC-20 and stored at 246 °C (475 °F) on the previous Saturday. This material was fed into a premix chamber where it and the ground tire rubber were brought together. Shipped in 1500-lb boxes, the ground tire rubber was prepared by opening the boxes and placing them on a “dumper” to pour the material into the bin. A screw-fed auger allowed the operator to empty the bin into the premix chamber at a controlled rate. From the premix chamber the material was pumped through the colloid mill. One concern about this feed process was dusting of the rubber as it is poured into the bin. Rouse rubber usually ships its material in bags that may be emptied from the bottom, but the AMI facility is only equipped to handle boxes, which are more suited to larger particle sizes.

As the material proceeded from the premix chamber it passed into the colloid mill whose clearance is adjustable; initially it was set at 483 µm (0.019 inch) for high-shear blending with the asphalt. The blend then flowed into the storage tank where it was agitated and could be drawn back into the mill for more curing. Six boxes of rubber, 9000 pounds of the planned 5.4 tons (10,800 lb), were added to the binder during the first pass. At this point all of the binder, planned to be 30.6 tons, had been added. What was next required was to circulate the rubberized binder while adding the remaining rubber. The earlier addition of room temperature rubber, however, had cooled the binder to 201 °C (395 °F) and further addition was not possible at that temperature due to the viscosity in the premix chamber. As the only heating source on the unit was the colloid mill’s viscous heating, the mill was run for several hours to reheat the binder. At approximately 1:00 p.m. the last of the tire rubber was added to the binder at 226 °C (440 °F). The milling tolerance was reduced several times, finally to 178 µm (0.007 inch) at 6:30 p.m. At approximately 9:30 p.m., after monitoring the progress of the operation by the testing described above, the binder was ready to load onto the transports.

As the loading proceeded, it was learned that the produced material was “short” by 5.4 tons; i.e., it contained less material than was thought to have been fed to it. No CAMC group members were present when this discovery was made (c. 1 a.m.). Interestingly, the missing material coincided exactly with the 5.4 tons of tire rubber that was used. The hypothesis for the discrepancy is that the asphalt metering equipment was located after the premix chamber, and therefore counted both the asphalt and the rubber. The operators were including the rubber with the binder that was being fed to achieve 30.6 tons so less binder was fed than desired. If this was the case, the 15 percent binder actually contained 17.6 percent tire rubber (5.4/30.6). The operators stated that it was common for them to withdraw the same amount of blended material from their polymer process as the amount of unmodified binder they fed (even though the polymer modifier has a tangible volume); thus they are always "losing" about 1 percent of the total blend that they intended to produce.

Nevertheless, a portion of the 15 percent binder was drawn off and the remainder was cut with neat AC-20 and the three shipments of binder were sent to Young Contractors, Inc., Bryan, Texas. A total of 40 tons of HCAR binder were custom produced for CAMC by Asphalt Materials Inc., located in Weatherford, Texas. This consisted of 4.64 tons of AC-20 control, 18.38 tons of 13.5 percent rubber binder, and 16.45 tons of 17.6 percent rubber binder, verified by weight at both the AMI plant and the Young Contractor's hot-mix plant. These three binders, in three trucks were shipped overnight to Young Contractors of Bryan, Texas, for installation the following day. Aggregate mixing and installation were monitored by representatives of CAMC, TxDOT, and TTI.

As noted above, some difficulties were encountered with the curing, which resulted in it taking longer than expected and higher rubber concentrations than planned (approximately 13.5 percent and 17.6 percent rubber instead of the planned 10 percent and 15 percent). These are not expected to be problems in the future. After curing, the materials were stored in recirculated tanks and then trucked in the early morning to the Bryan Young Contractor's hot-mix plant, arriving about 5 a.m.

Installation

Recirculation of the asphalt-rubber material was provided for each truck at the hot-mix plant as a precaution, even though settling was not expected to be a problem. The materials were fed through the hot-mix plant in the following order: AC-20, "10 percent" rubber blend, "15 percent" rubber blend. As each hot-mix was prepared, it was trucked to FM 2818 for placement. The last material was placed by early afternoon. The control section was 140 m (459 ft); the 13.5 percent rubber blend was 602 m (1975 ft); and the 17.6 percent rubber blend pavement was 578 m (1896 ft) in length. At the hot-mix plant, the binders caused no problems whatsoever, in spite of the higher-than-expected rubber concentrations. Also, hot mixes were easily placed and densities in the HCAR pavements were easily achieved and were comparable (actually, the same) as for the conventional AC, as determined by a nuclear density gauge. The boundaries between sections are virtually undetectable to the eye.

Pictures taken during curing and placement may be viewed on the worldwide web at: http://www-chen.tamu.edu/CAMC/

Laboratory Testing

A number of tests were conducted on the binder and binder-aggregate system. These included Superpave performance grades, direct tension tests, size exclusion chromatography (SEC, also called GPC), Brookfield viscosity tests at high temperatures, and Lottman water susceptibility tests on compacted cores.

Superpave performance grades of the test section binders for FM 2818 are shown in Table 5-1. The control asphalt was a PG 64-28 while the 13.5 percent and 17.6 percent rubber binders graded as PG 70-28 and PG 70-34, respectively. It should be noted that the 17.6 percent rubber sampled at the AMI plant graded as a PG 76-34 by just making the 76 °C requirement; whereas the same material, sampled at the hot-mix plant, graded just under the 76 °C boundary, giving a PG 70-34. The actual measurements were not very different, as indicated in the continuous grade column. Also note that the material at the hot-mix site was sampled twice while offloading from the transport, once at the beginning and once at the end. Hence, the notation "Truck #1" is used. This was done to assess the extent to which settling might have occurred. From the data in Table 5-1, it is apparent that significant settling did not occur.

Low-temperature direct tension tests on the sampled binders are given in Figures 5-1 and 5-2, measured at -18 °C and -24 °C, respectively. The addition of rubber to the binder results in a significant decrease in the stiffness of the binder, represented in the slope of the stress-strain curve, and an increase in the failure strain. Note that in Figure 5-1, at the higher temperature, one of the 13.5 percent samples and all of the 17.6 percent samples exceed the maximum displacement of the instrument, 3 percent strain; these runs do not indicate failure, although they appear to do so because the specimens continued to relax after the instrument displacement stopped. In Figure 5-2, the 17.6 percent binder samples failed at average values of 1.6 percent and 2 percent at the two plant locations. These failure strains are significantly higher than the 13.5 percent binders and the neat (control) binders and are consistent with the bending beam low-temperature results. Note also that the failure stress of the 17.6 percent binder is higher than either the control or 13.5 percent binders. Evidently, the low-temperature properties are significantly enhanced by the highly cured rubber.

Size exclusion chromatographs for the test section materials are shown in Figure 5-3. For comparison, lab-cured samples produced in our laboratory are shown in Figure 5-4 and at the AMI laboratory in Figure 5-5. In each of these chromatograms, the peak which elutes at the earliest time is the cured rubber and does not appear in the control asphalt sample. A higher degree of cure is indicated by a broader peak that is smaller in height. The samples cured in our CAMC laboratory are the least severely cured and the AMI process, road binder samples the most. The AMI laboratory samples show a progression from samples which are not too highly

Table 5-1. Performance Grade of FM 2818 and FM 1266 Test Section Binders.

Designation	Description	Sampling Source	Grade	Continuous Grade Span
FM 2818 Binders [a]				
HM1 AC-20	AC-20 #1 from Chapter 3	Truck, #1	**64-28** [b] / *67-29* [c]	96
HM2 AC-20		Truck, #2	**64-28** / *67-29*	96
AMI - 17.6%	17.6% RS-80	AMI Site	**76-34** / *77-36*	113
HM1 - 17.6%		Truck, #1	**70-34** / *75-34*	109
HM2 - 17.6%		Truck, #2	**70-34** / *75-34*	109
AMI - 13.5%	13.5% RS-80 (17.6% Dilluted)	AMI Site	**70-28** / *71-32*	103
HM1 - 13.5%		Truck, #1	**70-28** / *72-31*	103
HM2 - 13.5%		Truck, #2	**70-28** / *72-31*	103
FM 1266 Binders [d]				
GSAC AC-20	AC-20 #2	GSAC Site	**64-22** / *68-26*	94
HM AC-20		Truck Sample	**64-28** / 67-29	96
GSAC - 12%	12.0% RS-80 Preparation from GSAC	GSAC Site	**76-34** / *76-38*	114
HM1 - 12%		Truck, #1	**70-34** / *74-38*	112
HM2 - 12%		Truck, #2	**70-40** / *75-40*	115
GSAC - 8%	8.0% RS-80 (12.0% Dilluted)	GSAC Site	**70-28** / *73-33*	106
HM1 - 8%		Truck, #1	**70-34** / *71-34*	105
HM2 - 8%		Truck, #2	**70-34** / *72-35*	107

[a] Colloid Mill - Final Clearance 177.8 µm (0.007")

[b] **Superpave Performance Grade**

[c] *Continuous Performance Grade*

[d] Colloid Mill - Final Clearance 100 µm

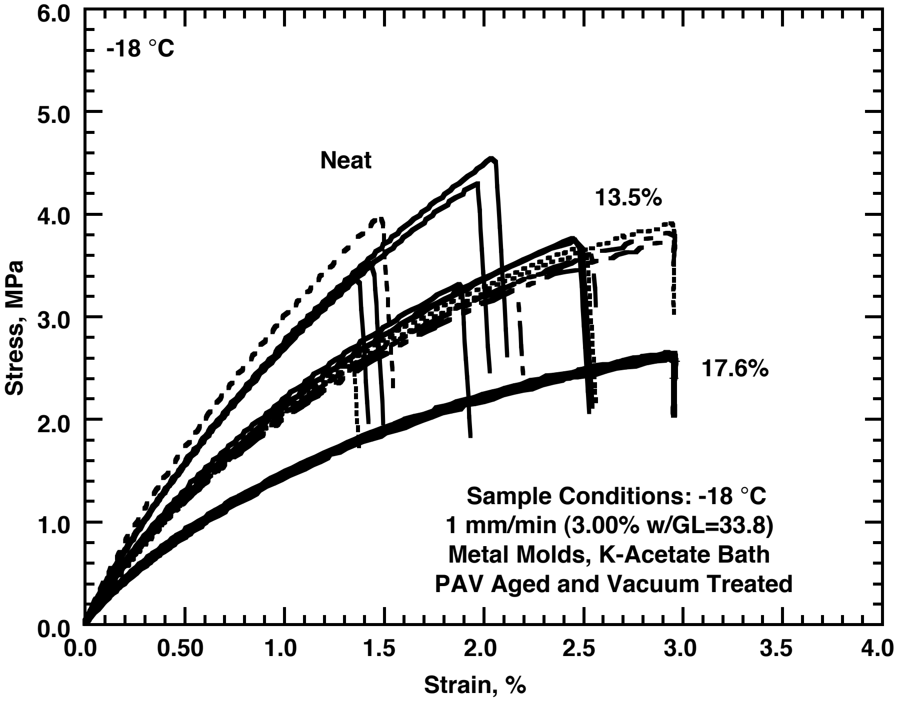

Figure 5-1. Direct Tension Results of FM 2818 Test Section Binders at -18 °C.

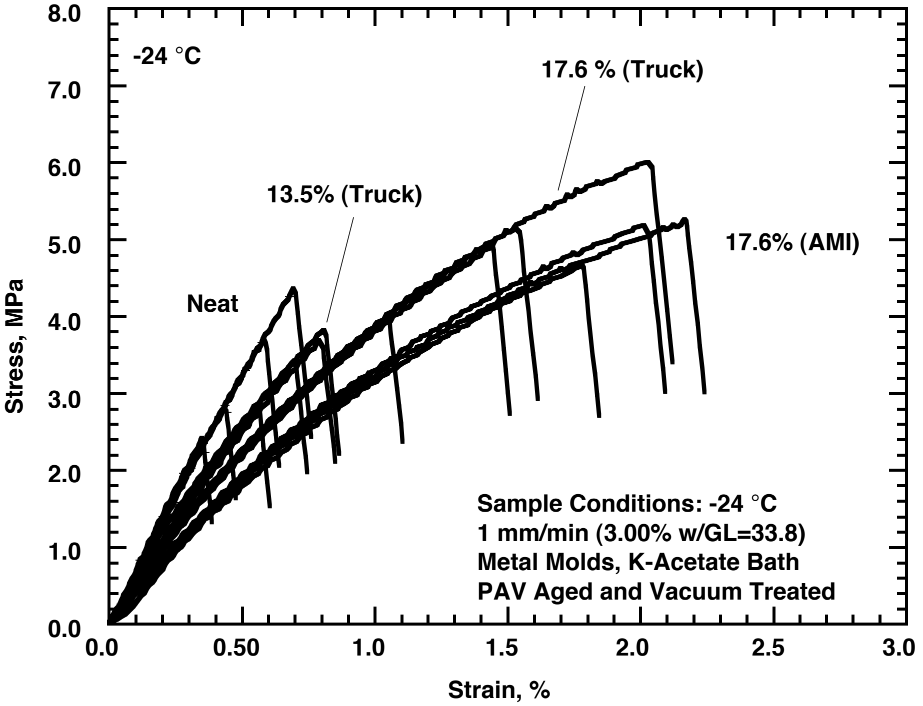

Figure 5-2. Direct Tension Results of FM 2818 Test Section Binders at -24 °C.

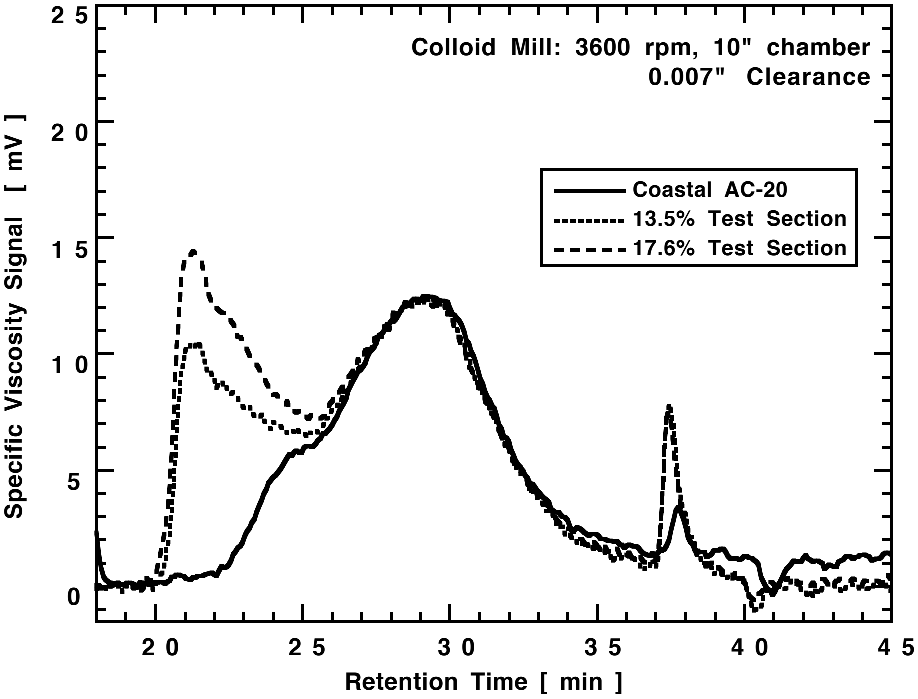

Figure 5-3. SEC Viscotek Output of FM 2818 Test Section Binders.

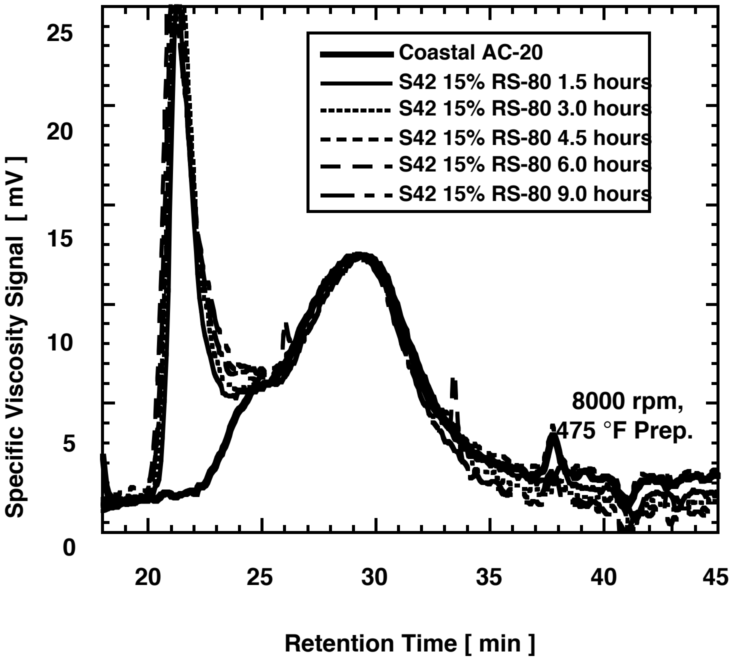

Figure 5-4. SEC Viscotek Output - CAMC Mix Design Preparations for FM 2818.

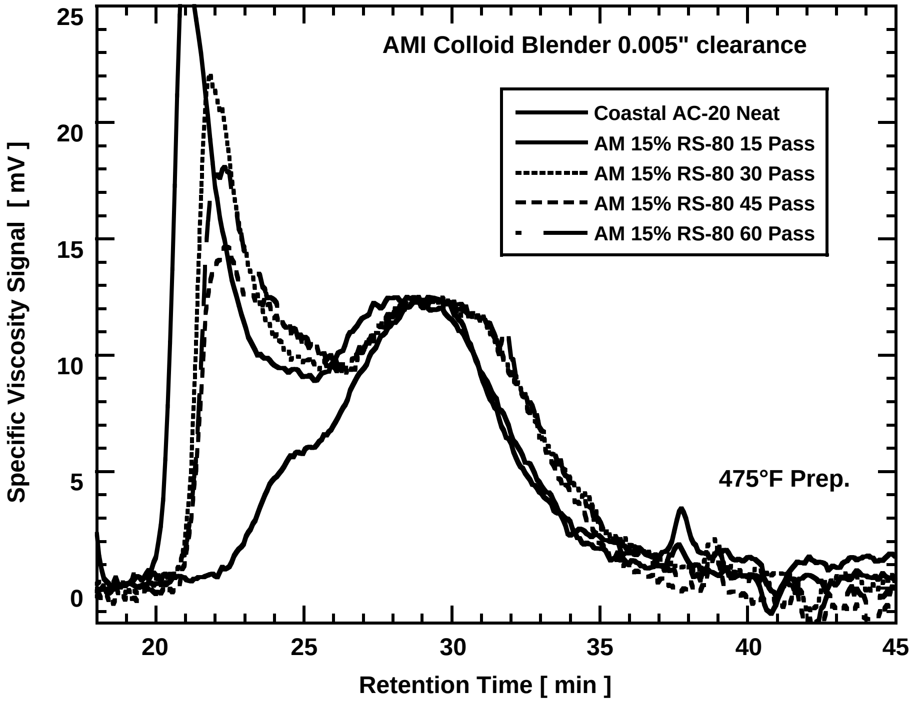

Figure 5-5. SEC Viscotek Output - Laboratory Preparations of AMI.

cured to ones which are cured very similarly to the process plant chromatograms. The more highly cured, the more homogeneous (and less susceptible to settling) the binder.

Viscosities for the three binders were measured at 135 °C (275 °F) using a Brookfield viscometer. The normal requirement for hot-mix processing is that the viscosity be no more than 30 poise (3 Pa·s) at this temperature. Two samples of the AC-20 were obtained from the transport at the hot-mix site with one sample taken early in the unloading and one late. Three samples of the 13.5 percent and 17.6 percent binders were obtained; two were from the transports as was done for the control, and one from the AMI plant before loading the transports. Averages of these sample viscosities for the control, 13.5-percent and 17.6-percent rubber binders were 4.8, 18.5, and 36 poise, respectively. The viscosities at several HTV temperatures are shown in Figure 5-6. There is some variability between the various samplings, perhaps caused by some slight settling, but the differences are within reasonable limits.

The water susceptibility test results (AASHTO T-283) obtained for laboratory-prepared compacted mixes, are shown in Figure 5-7 for the AC-20 control and the 13.5 percent and 17.6 percent rubber binder test sections. The control had an initial average retained strength (wet/dry) of 65 percent. For the rubber binder materials, both the dry and wet tensile strengths were greater than for the control with the highest rubber content binder having the highest strength. However,

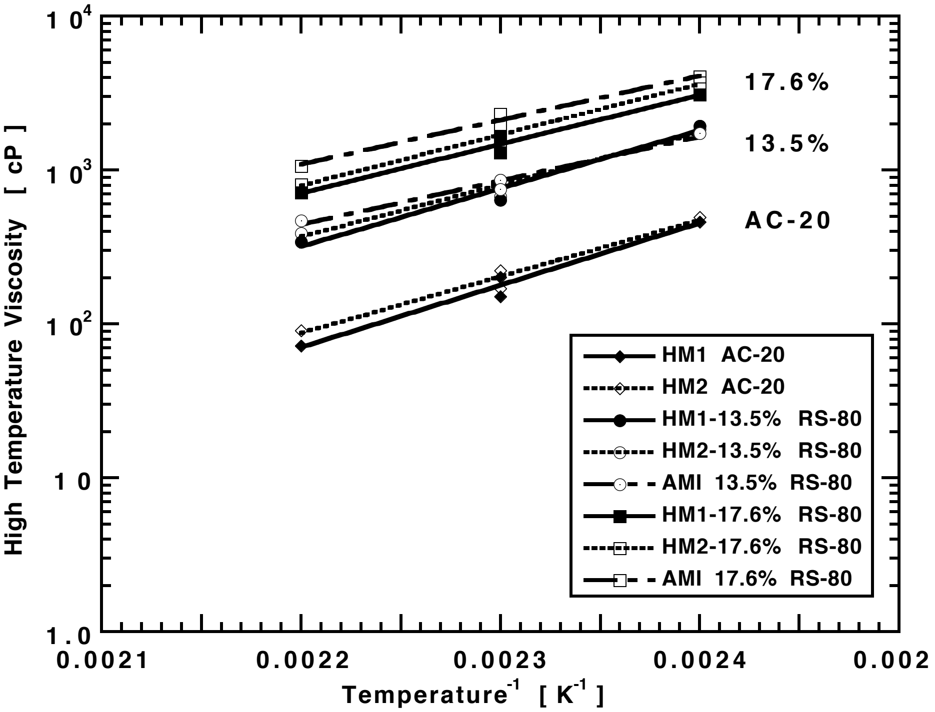

Figure 5-6. Brookfield Viscometer Results for FM 2818 Test Section Binders.

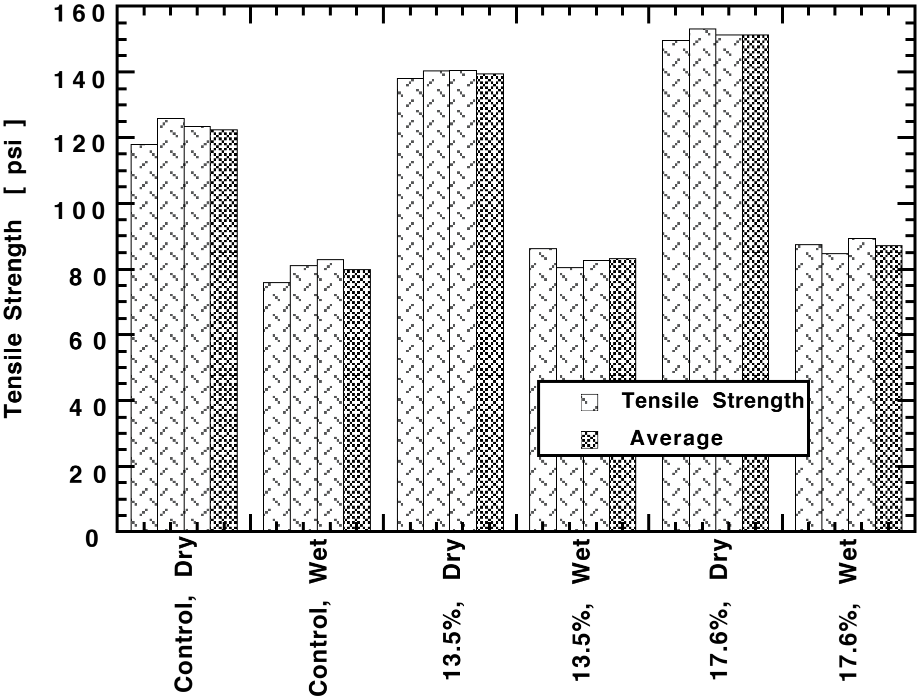

Figure 5-7. Tensile Strength Measurements on FM 2818 Test Section Cores.

the wet strength did not increase over the control as much as the dry and so the retained strength values were less, 60 and 58 percent for the 13.5 percent and 17.6 percent rubber materials, respectively.

Evaluation of the Test Sections

Physical Observations of the Pavements

As described above, the test sections were placed in July 1998. No difficulties were experienced with the placement of any of the three sections. Even the 17.6 percent rubber binder provided no difficulty with rolling and compaction of the mix to achieve the desired density.

Follow-up observations in the summer of 1999 were made to assess the physical state of the pavement. Spot measurements along the entire length showed virtually no rutting in the control section or either of the HCAR pavement sections. Also, the rubber-containing mixes one year later are decidedly blacker than the gray color of the control section and the rest of the project. Finally, no signs of pavement distress are apparent in any of the pavement.

As more complete and objective measurements of the pavement condition, profilometer scans, courtesy of Emmanuel Fernando of TTI, were made along the entire length of the test sections and the adjoining lane (placed as part of the larger four-lane project), also during the summer of 1999. Left and right wheel path (LWP and RWP) elevations along the length of the three test sections are shown in Figure 5-8. Corresponding measurements for the adjoining outside lane (not part of this test project) are shown in Figure 5-9. The results are virtually the same, whether comparing any of the three test sections to each other or to the adjoining lane.

From these profile measurements, International Ride Index (IRI) and Pavement Serviceability Index (PSI) values were calculated for each lane. Averages of LWP and RWP values are shown in Figure 5-10 for the three test sections and in Figure 5-11 for the adjoining strip (outside lane). The maximum possible PSI value is 5.0. Both IRI and PSI values are nominal indicating an even placement and essentially no pavement distress through the first year.

Pavement Durability

As was described in Chapter 4, blending ground tire rubber with asphalt can result in a material which hardens due to oxidation at a slower rate than the same asphalt without the ground tire rubber. This can have a significant favorable impact on the durability of rubber-containing hot-mix pavements. Also as described in Chapter 4, quantifying the expected extent of this effect can be even more problematic for the rubber binders than for conventional AC because of the difficulties of extrapolating high-temperature aging tests to reasonable pavement aging temperatures. To circumvent this problem with high-temperature aging tests (i.e., with the Superpave PAV test), binder materials have been aged at 60 °C (140 °F) at atmospheric air pressure for an extended period of time. Such data can be expected to provide an indication of

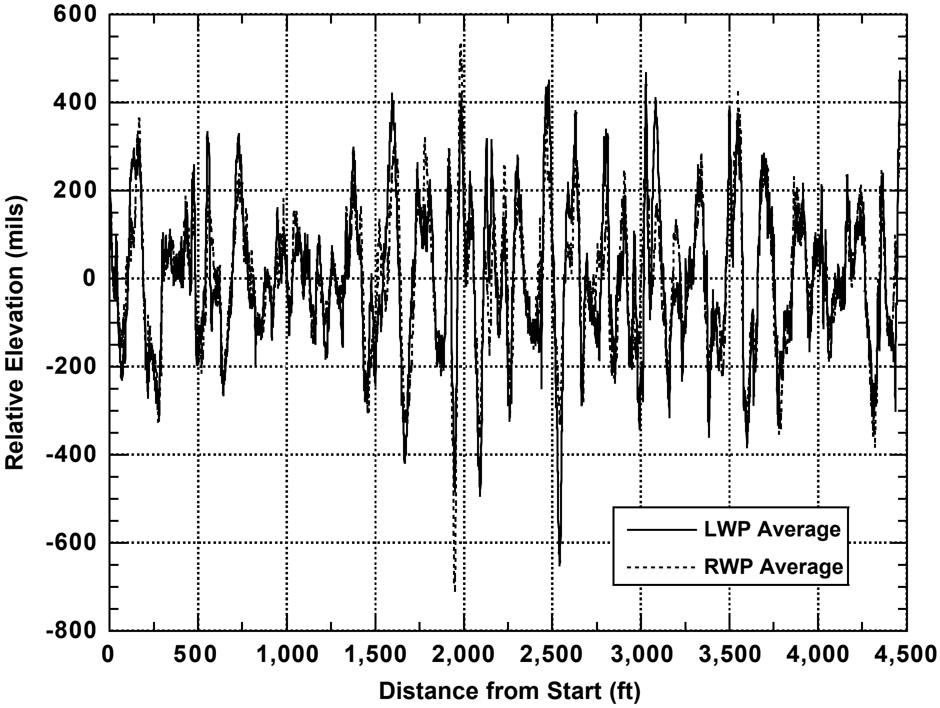

Figure 5-8. LWP and RWP Longitudinal Profiles - FM 2818 Test Section Lane.

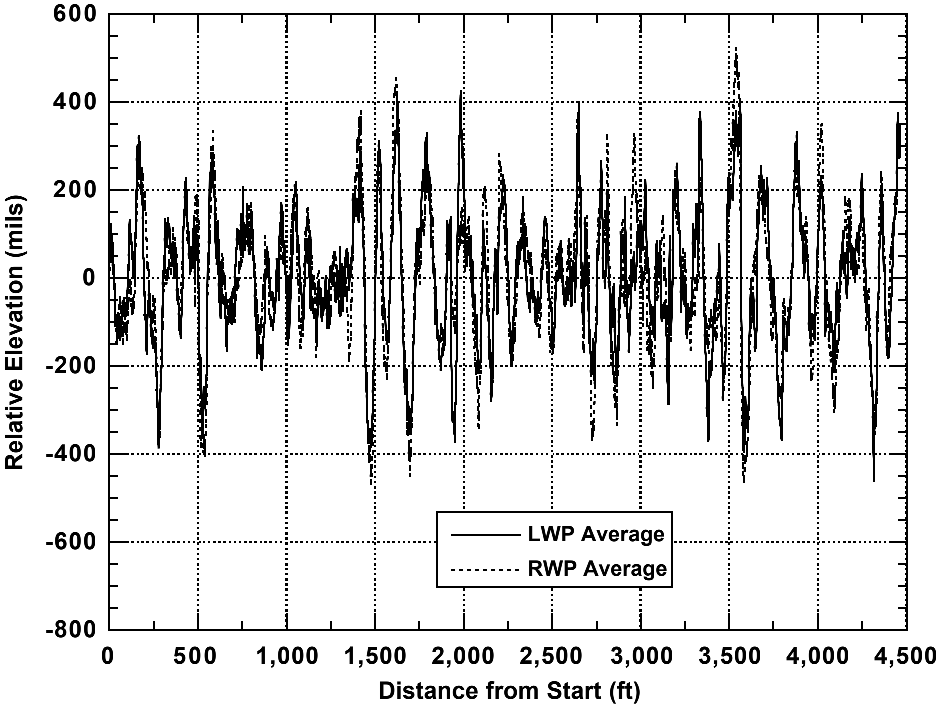

Figure 5-9. LWP and RWP Longitudinal Profiles - FM 2818 Adjacent Lane.

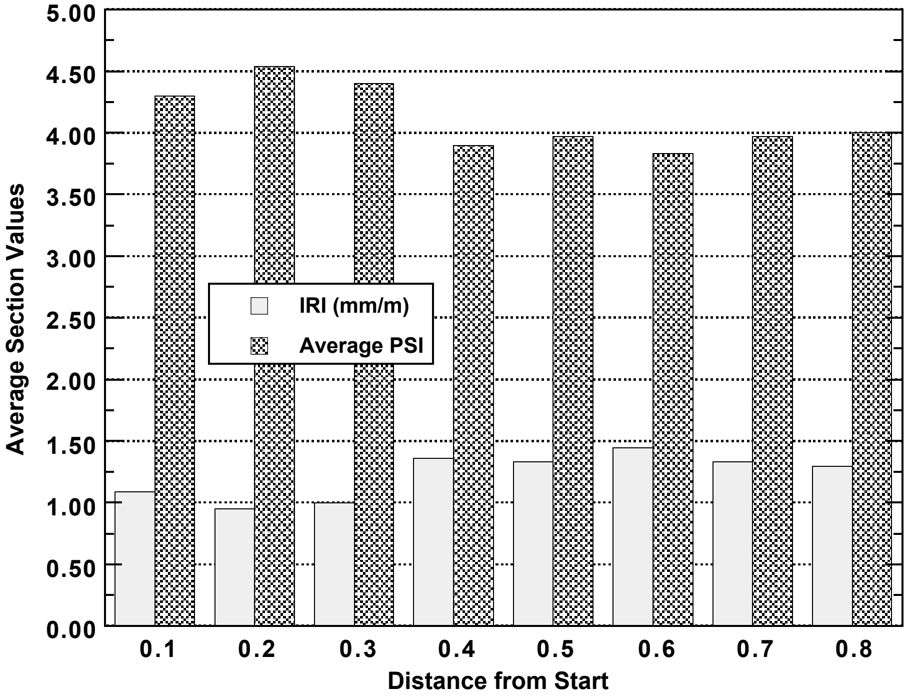

Figure 5-10. IRI and PSI Values - FM 2818 Test Section Lane.

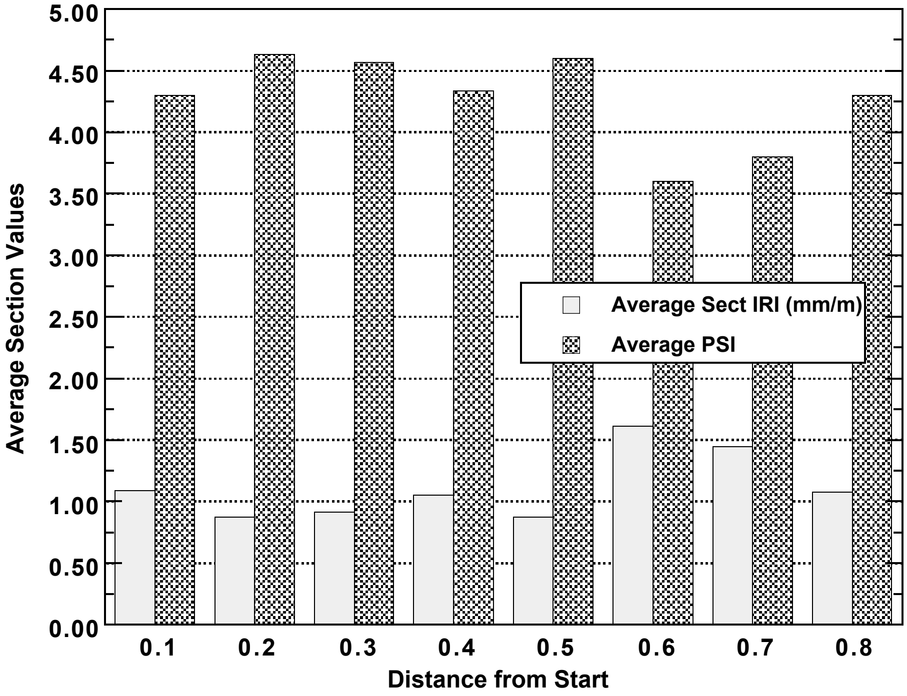

Figure 5-11. IRI and PSI Values - FM 2818 Adjacent Lane.

pavement aging rates and the extent of improvement achieved with the addition of highly cured ground tire rubber.

Figure 5-12 shows values for the low shear rate limiting dynamic viscosity, η^*, as the three test binders are aged at 60 °C (140 °F) for up to one year. The slopes obtained for each material show a significantly reduced hardening rate for both the 13.5 percent and 17.6 percent rubber binders, compared to the no-rubber control AC. Furthermore, the bulk of the hardening rate improvement occurs before even 13.5 percent rubber as there is relatively little difference between 13.5 percent and 17.6 percent rubber. These results suggest that these levels of rubber may well extend the life of the pavement, based on oxidation rates and all else being equal, by at least 50 percent.

Figures 5-13 and 5-14 show the reduced hardening is the result of an improved hardening susceptibility. Figure 5-13 shows that the chemical oxidation rates, as represented by FTIR carbonyl band growth rate, changes little with rubber content. By contrast, the hardening susceptibility, the impact of carbonyl growth on viscosity (Figure 5-14), is decreased by about a factor of two.

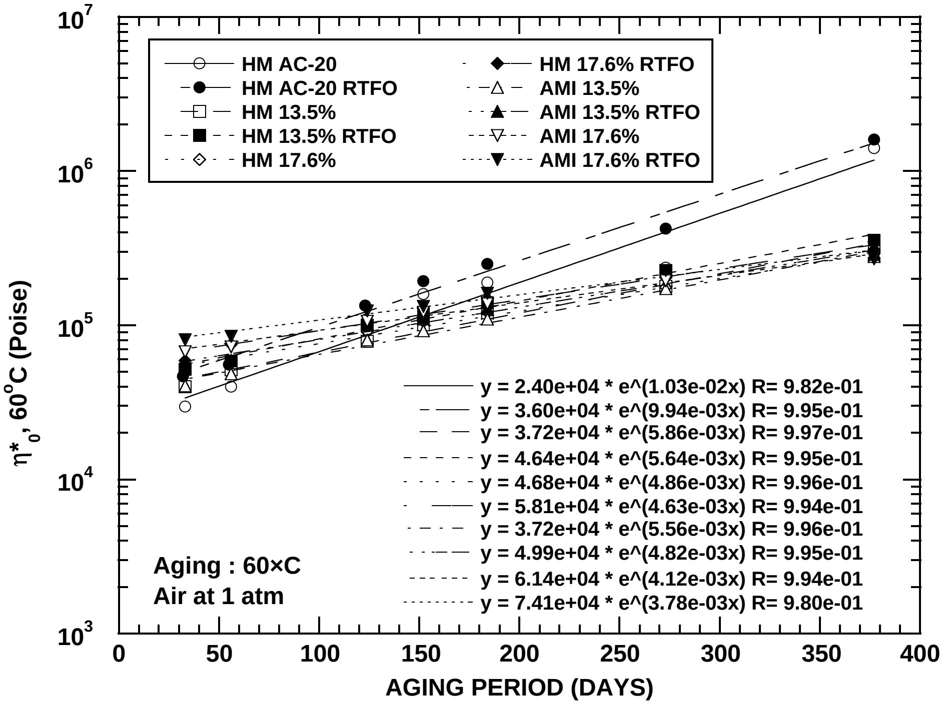

Figure 5-12. Hardening Rates of FM 2818 Test Section Binders.

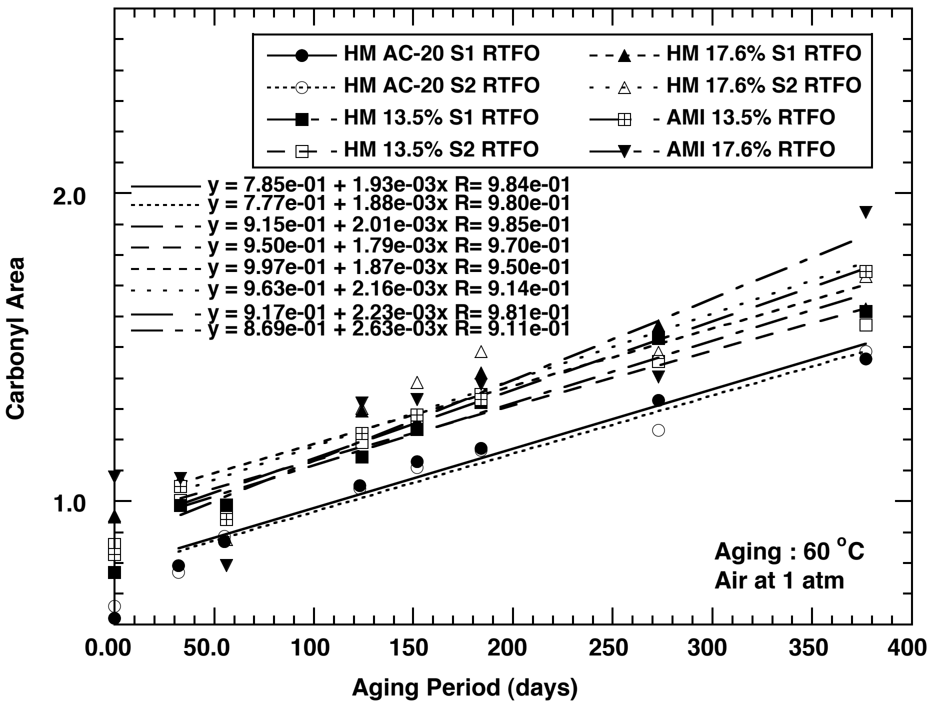

Figure 5-13. Carbonyl Formation Rates (Bulk) of FM 2818z Test Section Binders.

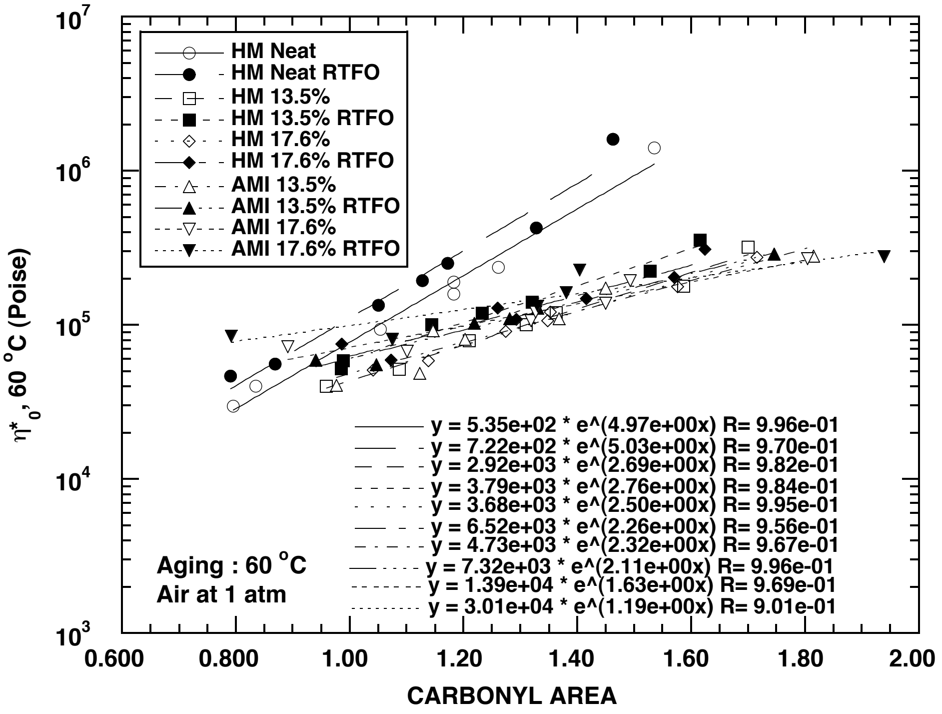

Figure 5-14. Hardening Susceptibilities of FM 2818 Test Section Binders.

This is contrary to some suggestions in the literature that oxidation inhibitors in ground tire rubber are responsible for retarding binder hardening. Such a mechanism would affect the oxidation rate, which is not the case in these data. One alternate hypothesis is that as oxidation digests the rubber, the produced smaller molecular size rubber counteracts, to some degree, the asphalt hardening due to oxidation.

HCAR PAVEMENT TEST SECTIONS - JUNE 2000

Originally planned for summer 1999, three more test pavements were placed in mid-June 2000, on the northern portion of FM 1266 in League City, Texas, between FM 518 and FM 646. The overall FM 1266 project consisted of two segments totaling 6,025 m (4.75 mi) coinciding with a new state highway under separate contract. It expanded the existing asphalt lanes from 3.7 to 4.6 m (12 to 15 feet) and was a 38.1 mm (1.5 in) overlay on fresh chip seal. On Wednesday, June 14, 2000, test sections totaling 2,658 m (1.65 mi) were installed on the northern 1.1 mile segment of FM 1266 in League City, Texas. The asphalt used for the control section and as the base material for the two HC-CRMA sections was produced specifically for this project by Gulf States Asphalt Co. of South Houston, Texas. A light asphaltic material was air blown at 204 °C (400 °F) to a PG 64-28 grade to produce a material having a reduced oxidative hardening rate, in comparison to the material produced by air blowing at a higher temperature, in accordance with the findings of Vassiliev et al. (2001).

Materials

The base binder was prepared at Gulf States Asphalt Company (GSAC) on Friday, June 9, 2000, under the supervision of Prof. Richard R. Davison and graduate student Jason F. Chipps of CMAC and Dr. Milton Liu of GSAC. The base binder was specifically prepared for this project and the two HC-CRMA sections contained 8 and 12 percent -80 mesh Rouse rubber. The following are the major findings related to the project to date.

Rubber was cured into the base asphalt to produce a 12 percent blend of high-cure material. Curing was achieved in a colloid mill adjusted to a final gap of 100 µm. The rubber was a -80 mesh steel- and fiber-free material purchased from Rouse Tire and Rubber. (A -20 mesh rubber was preferred because of its more favorable cost. However, upon inspection, the -20 mesh material was found to contain steel strands that would have damaged the mill.) The rubber was cured at high shear by recycling through the colloid mill, and during production a maximum temperature of 221 °C (430 °F) was obtained. The desired operating temperature, however, was 260 °C (500 °F). The extent of curing was tracked using steady-shear viscosity at 163 °C (325 °F) and DSR measurements of viscoelastic properties at 60 °C (140 °F). The experience with this testing is presented in Chapter 3. The 8 percent rubber material was produced by diluting the 12 percent blend with the base asphalt. The three binder materials were delivered to the hot-mix plant in separate transports at approximately 188 °C (370 °F) and fed directly to the drum. The base binder was sampled at both the asphalt production plant and at the hot-mix plant while the HC-CRMA materials were sampled at the asphalt plant and twice during off-loading at the hot-mix plant.

Aggregate Utilization

Hubco, Inc. Paving Contractors of Houston was awarded the contract to overlay the existing asphalt surface with Martin Marietta Materials Houston Division providing the hot mix. The mix for the greater part of the project was a TxDOT Type D (a dense graded mix with aggregate top size of 12.5 mm) with a PG 64-22 asphalt as the binder. The aggregate was predominately a crushed limestone with 15 percent river sand. The mix design was evaluated in the laboratory to confirm the appropriate binder content for the HC-CRMA binder, and it was determined that there were no modifications required of the aggregate gradation or optimum binder content when substituting the PG 64-22 with the study binders.

Mix Design

HC-CRMA binder (-20 mesh) was prepared in the CMAC laboratory using a Silverson high-shear mixer to the desired cure state, as monitored by the reduced gap phase angle test of Chapter 3. The modified binder was produced at 12 percent rubber content with an air-blown Flux #1 (F1AB) as the base. Some portion of the binder was diluted to 8 percent rubber content, and the materials were sent to Martin Marietta for binder content testing with their mix design. In order to achieve the desired 4 percent laboratory air voids, it was determined that the control (neat), 8 percent, and 12 percent tire rubber pavements should each contain 4.8 percent binder, the same amount as the rest of the project.

Installation

No recirculation of the asphalt-rubber material was performed at the hot-mix plant due to previous results. But as a precaution (and an operating convenience), the materials were fed through the hot-mix plant in the following order: base binder to establish stable operation of the plant, 12 percent to clear the higher rubber content inventory first, and finally 8 percent. Placement of the control began at the junction with FM 518 and proceeded southbound on FM 1266 for 729 m (2,393 ft) and was immediately followed by the 12 percent binder at a length of 997 m (3,272 ft). Only 26 m (86 ft) of the allotted distance remained in the southbound lane. This, and an additional 906 m (2,971 ft) length of the northbound lane were completed with the 8 percent rubber binder. Installation was completed by the late afternoon. Nuclear density gauge measurements indicated nominal compaction was obtained with normal rolling patterns.

Laboratory Testing of Materials from FM 1266

Several samples were obtained from the FM 1266 installation both during production and during installation. Eight samples were taken to monitor production at GSAC; these samples were drawn hourly. The finished products were also sampled at GSAC and twice during offloading similar to FM 2818. The following testing was performed on these samples: performance grading, size exclusion chromatography, Brookfield viscosities, and the Texas Settling test. In addition, please refer to the reduced gap phase angle measurements, Chapter 3.

Superpave performance grades of the FM 1266 binders are shown in Table 5-1. The addition of tire rubber improves the total continuous Performance Grade span by up to 20 °C (Control AC-20 with a PG of 64-22 versus 12 percent RS-80 with a PG of 76-34, GSAC samplings). Both the high-temperature and the low-temperature performance are improved by the addition of the tire rubber. In addition, the binders appear to have maintained their properties during overnight storage.

Size exclusion chromatography was performed on each of the samples obtained from the FM 1266 project, Figures 5-15 through 5-18. In Figure 5-15 it is noted that rubber particles exhibit the same narrow distribution throughout the curing process. However, in a magnification of Figure 5-15, the samples taken at 10:00 a.m. and 11:00 a.m. indicate that they contain less rubber material (Figure 5-16). In reality there is simply more rubber being excluded from these early samples during the pre-GPC filtering. After the 12:00 sample, no further curing effect on particle size is evident by this method. The GPC comparison of finished binder samples indicates that overnight storage of the binders has not appreciably changed their properties (Figures 5-17 and 5-18).

Brookfield viscosities were measured for selected samples during preparation. The neat binder had a HTV of 0.40 Pa·s at 135 °C (275 °F) while the finished 8 percent and 12 percent binders were 1.2 Pa·s and 2.2 Pa·s, respectively. During the curing process the Brookfield viscosities were observed to fall from 3.0 Pa·s at the 11:00 a.m. sample to 2.8 Pa·s, 2.3 Pa·s, and 2.2 Pa·s, at 12:00 p.m., 3:00 p.m. and 5:00 p.m., respectively. Also measured was the 10:00 a.m. sample which seems to be an outlier at 2.4 Pa·s.

The Texas Settling test is a TxDOT mandated testing procedure to gauge separation of modified materials. In this test, 350 grams of modified binder are placed in a pint can. The sealed can is placed in an oven at 163 °C (325 °F) for 48 hours and allowed to settle. After cooling the samples are removed from the oven. A very thin layer (about 20 grams each) from both the top and bottom of the sample are removed from the can. This seems to be a much more stringent test than the cigar tube test which mixes the top and bottom thirds while settling at the same conditions (AASHTO PP5-93). Each of these samples is subjected to ASTM D 36 to determine their softening points. The softening points cannot differ by 4 percent (calculated in °C) or the sample fails Texas Settling (again a distinction from AASHTO PP5-93 which contains no failure criteria). The Texas Settling test was performed on the prepared blends sampled at GSAC. The 8 percent rubber binder had top and bottom softening points of 53.3 °C (128 °F) and 60 °C (140.25 °F) and failed Texas Setting (11.8 percent). Similarly the 12 percent binder also failed Texas Settling (54.9 °C, 65.1 °C, 17.1 percent), indicating that the desired high-cure state was not fully achieved. Nevertheless, it should be noted that hot-mix operation and pavement placement proceeded nominally.

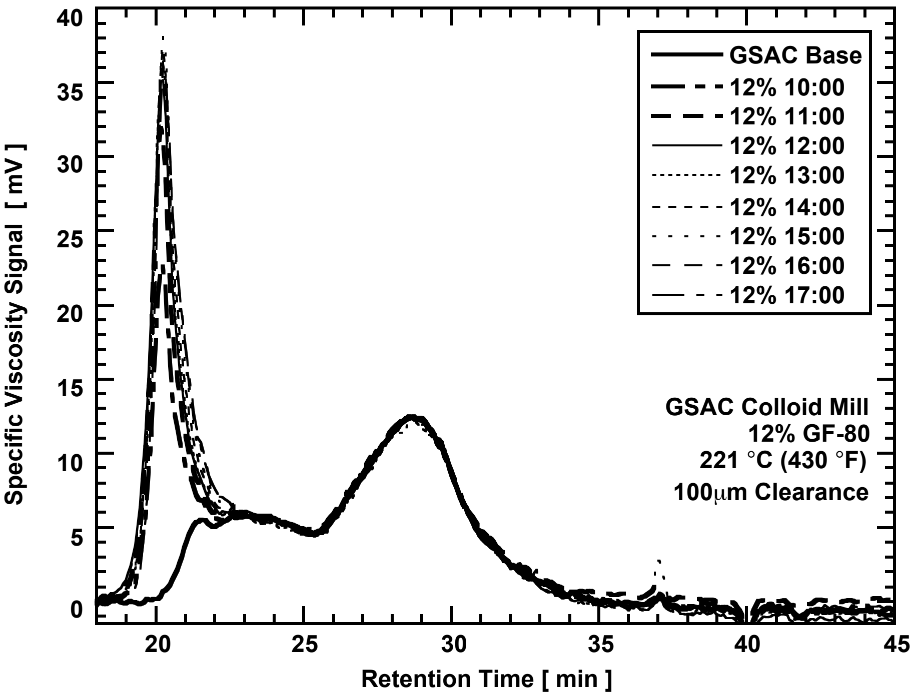

Figure 5-15. SEC Viscotek Output - FM 1266 CRMA Preparation.

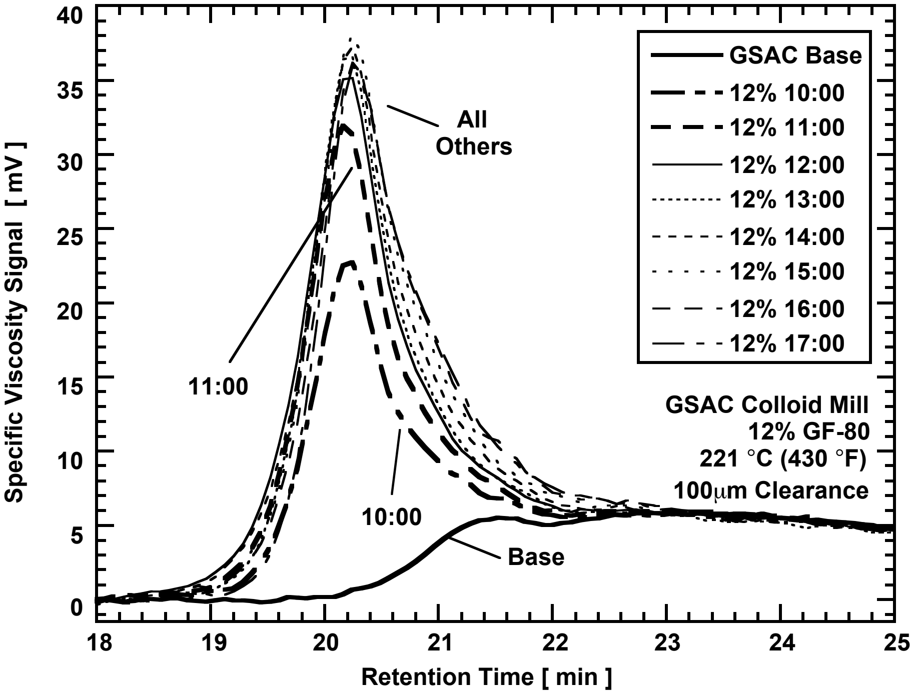

Figure 5-16. Magnified SEC Viscotek Output - FM 1266 CRMA Preparation.

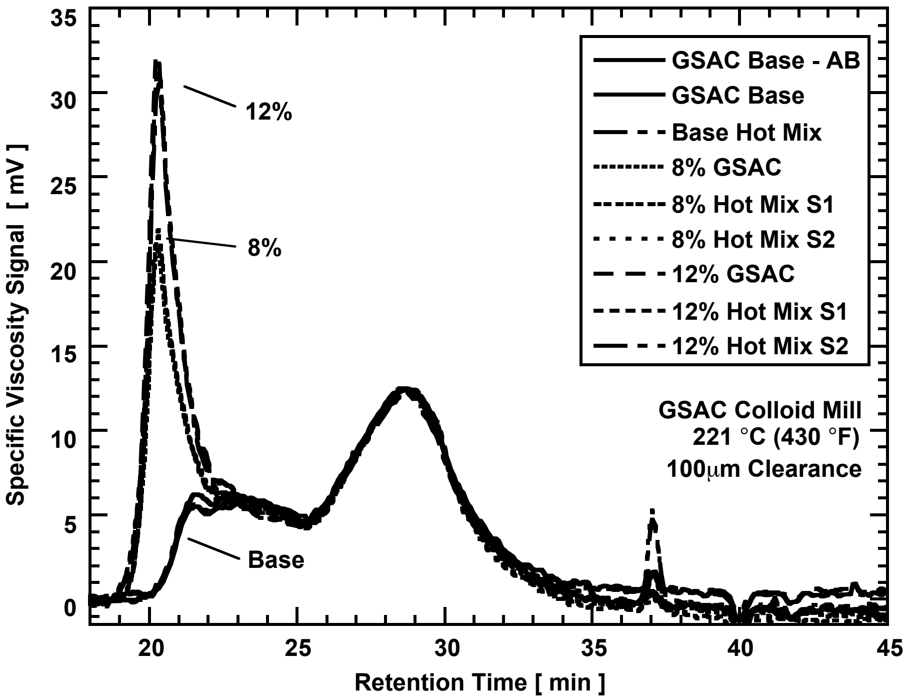

Figure 5-17. SEC Viscotek Output - FM 1266 Test Section Binders.

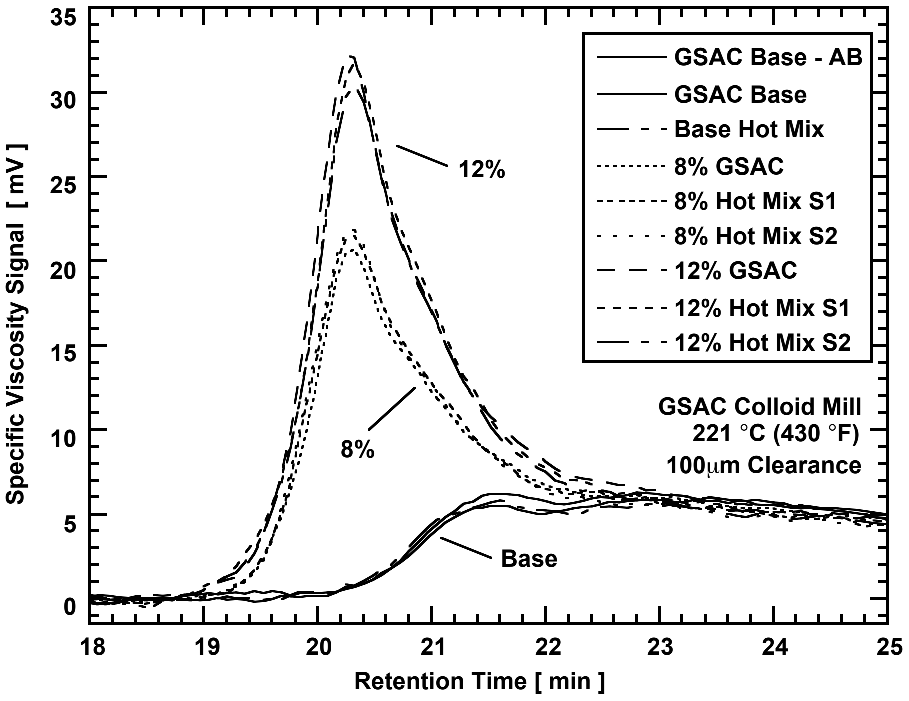

Figure 5-18. Magnified SEC Viscotek Output - FM 1266 Test Section Binders.

SUMMARY OF CHAPTER 5

High-cure crumb-rubber modified asphalt binders can be used successfully in the field in dense graded mixes and can have improved Superpave performance grades and, especially, improved oxidative hardening characteristics. In our studies, binders having from 8 to 17.6 percent rubber were used in type C and D mixes having just under 5 percent binder, the same level as the non-rubber control AC. Hot-mix operations and pavement compaction experienced no problems with these materials. Performance grades of the asphalt rubber materials are improved over the base asphalt binder by one grade on the high end and by up to one grade at the low temperature end. Furthermore, HTV met or were very close to the optional limit of 3.0 Pa·s, even for the highest rubber content binder. Laboratory data for the test section materials suggest that the durability to summertime oxidation will be significantly increased over the control material.

CHAPTER 6. ECONOMIC EVALUATION OF CRMA

As was discussed in Chapters 3 and 4, the incorporation of ground tire rubber in asphalt appears to offer specific performance advantages. Among these are an enhanced PG on both the high and low ends and improved durability due to an enhanced response to oxidative aging. Of these two characteristics the aging durability would seem to be the most significant although results from the field tests are needed to provide verification.

Such improvements, however, do not come without cost. The tire rubber, although a waste material, still must be ground to an appropriate mesh size and separated from steel and fiber. This results in a material which typically will cost from 24 cents per pound to about 40 cents per pound. This is from \$480 to \$800 per ton compared to asphalt which is approximately \$100 per ton and aggregate which is about \$5 per ton. Obviously, to replace asphalt or aggregate with ground tire rubber can be quite expensive, just for the material cost. In addition, there are blending and cure costs and, perhaps, a requirement for additional binder content in the mix (6 or 9 percent versus 5 percent, e.g.) so as to accommodate rubber particles with a more open aggregate gradation, thereby allowing suitable compaction. Finally, if settling is a problem, then either agitation must be provided in storage tanks or blending must be scheduled so as to guarantee hot-mix processing and placement before significant settling can occur. Either of these options will add processing costs.

With costs added to ground tire rubber modified mixes, the economic issue is whether the added costs are warranted by a return through longer life. This chapter addresses this issue by using a capitalized cost life-cycle analysis to compare a number of specific cases. These cases include the high-cure material developed in this project at several rubber contents in the binder and also the traditional (low-cure) asphalt rubber material which is used extensively in Arizona and portions of Texas. Another case considers the use of a specially formulated, superior base AC. Preceding the cost comparisons is a discussion of the capitalized cost analysis method used in this work.

CAPITALIZED COST ANALYSIS METHOD

The capitalized cost concept is an excellent method for comparing competitive methods or technologies having different installation costs which are balanced against different life expectancies (Peters and Timmerhaus, 1991). Furthermore, at the end of one lifetime, the technology is replaced with the same technology and this is continued in perpetuity. The capitalized cost of a project is simply the amount of money needed at installation to install the project and have remaining a fund which is sufficiently large to provide needed maintenance and replacements forever, assuming no inflation or deflation and a specified periodic interest rate. This is exactly the ideal situation for highways. In the comparison, the technology having the lower capitalized cost would be favored economically. Alternatively, the life span required of the more expensive technology for the two methods to be rated as economic equals can be determined.

In this discussion, the following notation is used:

K = capitalized cost, present value of all costs
C_V = first installation cost of the project
C_R = replacement cost of each future installation (this may include salvage value but inflation and deflation are assumed to be zero)
P = present value of all future installations together
i = periodic interest rate (usually an annual rate)
n = period lifetime of project (usually years)
M = periodic maintenance cost (usually annual maintenance)

So, the capitalized cost consists of the first installation (C_V) plus the present value of all of the replacement installations, repeated indefinitely every n periods, plus the amount needed at the beginning of each period to provide the maintenance, M, by the end of the period at interest rate i. The first and last of these are simply C_V and M/i so we now turn our attention to the present value of all future installations.

The initial installation is assumed to last n periods. At that time, the replacement is installed at cost C_R. The present value of this future payment is $C_R/(1+i)^n$. After another n periods, another replacement is made and its present value (2n periods earlier) is $C_R/(1+i)^{2n}$. This continues indefinitely so that the present value of all future installations is

$$P = \frac{C_R}{(1+i)^n} + \frac{C_R}{(1+i)^{2n}} + \frac{C_R}{(1+i)^{3n}} + \cdots = \frac{1}{(1+i)^n}\left[C_R + \frac{C_R}{(1+i)^n} + \frac{C_R}{(1+i)^{2n}} + \frac{C_R}{(1+i)^{3n}} + \cdots\right]$$

which gives that $P(1+i)^n = C_R + P$ and finally that

$$P = \frac{C_R}{[(1+i)^n - 1]}$$

Hence, the total capitalized cost is

$$K = C_V + \frac{C_R}{(1+i)^n - 1} + \frac{M}{i}$$

Here C_V and C_R may be the same or C_R may include a salvage value. Also C_V and/or C_R may include accompanying costs such as lane closure costs, in the case of highway installation and rehabilitation.

CAPITALIZED COST COMPARISONS

Using this capitalized cost method, a number of project scenarios have been considered. The base case is a 2 inch lift of a conventional dense graded mix. (A different thickness could be considered but as long as the comparisons are of like thicknesses, the bottom-line result, which is the required life for an alternative technology to match the conventional method's capitalized cost, will be the same.) Alternative cases considered are: HCAR materials at 8, 12, and 16 percent rubber in the binder; a 12 percent HCAR which uses a premium asphalt; a gap-graded mix (GG) with a low-cure asphalt-rubber-type material having 18 percent rubber in the binder with 6 percent binder in the mix; and an open-graded friction (OGFC) course mix with a low-cure asphalt rubber binder having 18 percent rubber at 9 percent binder in the mix. Finally a 2 inch asphalt rubber gap-graded mix (18 percent rubber in the binder, 6 percent binder in the mix) over a 2 inch conventional mix (treated together as having a single life span) is compared to a 4 inch conventional mix.

The capitalized cost calculation results are shown in Table 6-1. Assumptions common to all calculations are that i=0.05, aggregate cost is \$5 per ton of hot mix, installation cost is \$25 per ton of hot mix, and maintenance costs are one-fourth of the installed cost per year over the life of the pavement. This does not provide for any differences in installation cost between dense-graded mixes and gap- or open-graded asphalt rubber mixes which may require additional contractor costs for placement due to the very high binder viscosity at hot-mix temperatures. The number of years which are shown in Table 6-1 are either the assumed life (for the conventional material) or the required minimum life that the competing technology must have to match the conventional dense-graded mix capitalized cost. For the assumptions and costs shown, the conventional 2 inch lift has a capitalized cost of \$175,567.

Comparing the three levels of rubber in the binder for the HCAR material, the required additional life to match the conventional material's capitalized cost ranges from 10 to 16 percent. Even when a specially prepared superior binder (used to obtain a high PG range, e.g.) purchased at a base asphalt cost premium of 40 percent is factored in, the increase in required life for a binder having 12 percent rubber is still just 20 percent. Such an increase would seem to be quite possible in light of the retarded hardening rate due to oxidation for these high-cure materials reported in Chapter 5. All else being equal, life extensions of 50 percent seem entirely possible. (Of course if an extended PG range were required for the application, then a conventional mix having a base asphalt costing only \$100 per ton would probably not be a fair base comparison either.)

Table 6-1. Capitalized Cost Comparisons.

Mix Type	Binder Rubber Content (%)	Mix Binder Content (%)	Rubber Mesh	Rubber Cost (¢/lb_m)	AC Cost ($/ton)	Mix Installed Cost		Maint Cost ($/yr)	Assumed or Required Life (yr)
						($/ton HM)	($/Lane Mile)		
2" Conv AC	0	5	---	---	100	34.75	56,816	1420	10.0
2" HCAR	8	5	20	24	100	37.52	6,345	1394	11.0
2" HCAR	12	5	20	24	100	38.28	62,587	1385	11.3
2" HCAR	16	5	20	24	100	39.04	63,830	1376	11.6
HCAR/Super AC	12	5	20	24	120	39.16	64,026	1380	11.6
HCAR/Super AC	12	5	20	24	140	40.04	65,465	1364	12.0
2" GG	18	6	40	40	100	43.56	71,220	1339	13.3
2" OGFC	18	9	40	40	100	50.34	82,305	1262	16.3
2" GG	18	6	20	24	100	41.30	67,531	1362	12.4
4" Conv AC	0	5	---	---	100	69.50	113,632	2841	10
2" GG	18	6	40	40	100	43.56	128,036	2759	11.6
over									
2" Conv AC	0	5	---	---	100	34.75			

The three low-cure, high-rubber content mixes require an extended life of from 24 to 63 percent. This is because of the combination of high-rubber content in the binder, high binder in the mix, and (probably) higher cost of the rubber to obtain a finer mesh material. Whether these life extensions can be achieved with these kinds of mixes is not the subject of this project but it is clear that compared to the high-cure material, there is a significantly greater performance burden which must be met by these high-rubber, high-binder mixes.

As a final comparison, a 4 inch conventional dense-graded mix is compared to a 2 inch gap-graded asphalt rubber material (low-cure, high-rubber content) placed over a 2 inch conventional dense-graded mix. This is a scenario discussed by Hicks et al. (1998) and includes the assumption that the conventional mix placed with the asphalt rubber mix will have its life established by the AR mix. For this scenario, a 16 percent life extension was required for equal capitalized cost.

SUMMARY OF CHAPTER 6

Capital cost analysis is appropriate for analyzing competing technologies with different life expectancies, installed repeated times and at different installed costs. The method determines the present value of an installation now plus repeated installations at the end of each life cycle plus yearly maintenance. Comparisons of several cases show that the life-cycle cost compares very favorably to conventional asphalt binders. A high-cure crumb rubber binder at 16 percent rubber in a dense-graded mix would need to last just 16 percent longer than the comparable conventional mix in order to have an equal capitalized cost, the break-even point. At the same time, oxidative hardening rates at road aging conditions are reduced some 50 percent or more by the high-cure rubber. Consequently, achieving the required extended life is believed to be well within reach for dense-graded mixes, even for a high-rubber content binder.

By contrast, capitalized cost analysis of high-rubber content binders, high binder mixes (traditional Asphalt Rubber) require a significantly longer life extension for economic payout. At 18 percent rubber in the binder and 9 percent binder in the mix, a life extension of the order of 60 percent (over a conventional asphalt binder dense-graded mix of the same thickness) is required. With 6 percent binder in the mix instead of the 9 percent, the required life extension is reduced to 33 percent.

Obviously, the key issue to economic payout is the actual life extension provided by the binder. To establish this definitively will take continued monitoring of test pavements such as those placed in this project.

CHAPTER 7. CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Production Methods

1. *A HC-CRMA binder suitable for use in dense-graded mixes can be produced through a combination of high temperature and high shear.* Temperatures close to 260 °C (500 °F), together with high shear in a colloid mill having a gap of 254 µm (0.010 inch) generally are capable of producing sufficient digestion of the rubber particles. The time required, however, varies with the composition of the asphalt and the starting mesh size of the rubber. Temperatures below 232 °C (450 °F) are significantly less efficient at curing the rubber. Milder conditions of shear and temperature, without the narrow-gap high-shear disintegrating head, may do little more than swell the rubber particles as they absorb compounds from the asphalt.

2. *Production in the presence of oxygen can enhance the breakdown of rubber and the curing process.* As with curing in the absence of oxygen, higher temperature, higher shear, and finer initial mesh rubber all decrease the time to achieve a high cure. With the addition of oxygen to the curing, however, there is an added effect of oxidizing the asphalt to a higher Superpave performance grade, without seriously degrading the low-temperature grade. Typically, for every 10 °C increase in upper grade there is a 5 °C or less loss of low-temperature grade. Thus, combining oxidation with curing enhances both the rate of rubber cure and the PG grade span. Spans of over 100 degrees are readily obtained. As with any oxidation process using an organic material, safety precautions must be observed and temperatures and air flow should not exceed a safe level.

3. *By either curing method (with or without oxidation) a material with excellent settling stability and a high-temperature (135 °C, 275 °F) viscosity that meets the Superpave specification of less than 3 Pa·s (30 poise) can be obtained.*

Performance Properties

4. *CRMA and HC-CRMA materials show enhanced Superpave performance grades over the base asphalt.* Curing at relatively low temperatures, around those of the hot-mix process, and low-shear rates, conditions typical of current industrial practices, leads to a moderate interaction of the rubber material with the asphalt. The blended material has an increased viscosity due to the rubber particles, swollen by absorbed asphalt components. Low-temperature stiffness is improved, high pavement temperature G*/sin δ is increased significantly, and overall, the PG span is considerably widened. However, many low-cure materials do not meet the optional maximum high-temperature viscosity of 3 Pa ·s (30 poise) at 135 °C (275 °F) and a settling test for storage stability.

Curing with higher shear mixing and higher temperature further breaks down the rubber particles and digests the long polymer chains and crosslink structures. The blend viscosity decreases with additional curing, but remains elevated above that of the base asphalt material. Resulting viscosities at hot-mix installation and at rutting conditions are reduced compared to the lower shear preparations and can be lowered to the point of meeting the high-temperature viscosity criterion. Low-temperature properties show enhancement as well. However, it certainly is possible to cure too far. Materials produced at the highest level of curing indicate severe polymer degradation. These materials widen the PG span only incrementally when using a continuous grading, or single degree increment basis, but do not always yield improvement on a specification basis.

Curing in the presence of oxygen was found to have primarily two effects. First, oxygen enhanced the rubber curing process, resulting in more rapid digestion of the rubber particles and molecules. Second, the base asphalt material was oxidized to a higher viscosity material, raising the high-end PG rating. These two effects together, can result in a significantly wider PG span, increasing the upper grade, by up to three grades while the rubber serves to hold the low temperature grade or at least limit its loss.

5. *Three concerns associated with industrial preparation of HC-CRMA materials have been resolved.* First, the optional HTV specification generally was found to be met fairly easily by the high-cure process. Second, the Texas Settling test for storage stability of the binder was found to be met if the curing process is carried far enough. Finally, a dynamic shear rheometer at reduced gap settings can be used to track the curing process efficiently and gives a sensitive measure of the extent of cure.

Long-Term Durability

6. *The incorporation of rubber in asphalt binders provides enhanced aging characteristics.* Low-cure blends have very low hardening rates and decreased hardening susceptibilities (hardening in response to a given amount of oxidation), mainly due to the predominance of suspended particles that elevate bulk viscosity, while not necessarily improving the asphalt phase. High-cure asphalt rubber materials also exhibit excellent aging characteristics, equal to or better than the low-cure materials. Aging can be retarded further by utilizing low asphaltene source binders, although this likely would adversely affect the material’s rutting resistance.

7. *For rubber modified materials, the use of a high-temperature, high-pressure aging procedures to simulate long-term aging (as in the Superpave protocol, e.g.) is not reliable; we recommend aging at 60 ^{o}C, 1 atm air to assess aging in CRMA or HC-CRMA materials.* Each material behaves differently enough from one another that extrapolations from PAV test conditions to road aging conditions are very risky. The use of elevated pressure is problematic for conventional asphalt binders, but it is even worse for crumb-rubber modified materials as

tests at elevated temperatures suffer from the same difficulties. The development of an acceptable accelerated aging test for CRMA materials remains elusive.

Field Implementation

8. *HC-CRMA binders can be used successfully in the field in dense-graded mixes with no mix design adjustments and can have improved Superpave performance grades and, especially, improved oxidative hardening characteristics.* In our studies, binders ranging from 8.0 to 17.6 percent rubber were used in dense-graded type C and D mixes having just under 5 percent binder, the same level as the non-rubber control AC. Field tests were conducted at two locations: Bryan, Texas, in July 1998, and League City, Texas, in June 2000. At both locations, CRMA binders at two rubber levels were processed in the hot-mix plant at nominal conditions and with no complications, even with the rubber content as high as 17.6 percent. Pavement compaction also proceeded nominally with no adjustments having to be made by the contractor. Performance grades of the CRMA materials were improved over the base asphalt by one grade on the high end and up to one grade on the low end. Furthermore, high-temperature (135 °C [275 °F]) viscosities met the optional limit of 30 poise (3 Pa·s), even for the highest rubber content binder. Laboratory data for the test section materials suggest that the durability to summertime oxidation will be significantly increased over the control material.

Economic Evaluation

9. *Capitalized cost analysis is appropriate for analyzing competing technologies with different life expectancies, installed repeated times and at different installed costs.* The method determines the present value of an installation now plus repeated installations at the end of each life cycle plus yearly maintenance.

10. *Comparisons of several cases show that the life-cycle cost of HC-CRMA materials compares very favorably to conventional asphalt binders.* A high-cure crumb-rubber binder at 16 percent rubber in a dense-graded mix would need to last just 16 percent longer than the comparable conventional mix in order to have an equal capitalized cost, the break-even point. At the same time, oxidative hardening rates at road aging conditions are reduced some 50 percent or more by the high-cure rubber. Consequently, achieving the required extended life is believed to be well within reach for dense-graded mixes, even for a high rubber content binder.

11. *Capitalized cost analysis shows that high rubber-content binders, high binder mixes (traditional Asphalt Rubber) require a significantly longer life extension for economic payout.* At 18 percent rubber in the binder and 9 percent binder in the mix, a life extension of the order of 60 percent (over a conventional asphalt binder dense-graded mix of the same thickness) is required. With 6 percent binder in the mix instead of the 9 percent, the required life extension is reduced to 33 percent, still more than twice that required to breakeven with the HC-CRMA.

12. *The key issue to economic payout is the actual life extension provided by the binder.* To establish this definitively will take continued monitoring of test pavements such as those placed in this project.

RECOMMENDATIONS

A number of recommendations are suggested by this study.

1. *Continue to track existing test sections*. This is important in obtaining long-term performance data thereby establishing more precise economic evaluations of the method.

2. *Consider the use of HC-CRMA in standard mixes as an alternative to special tire rubber mix designs currently used in some applications.*

3. *Test high-cure materials in test sections in other locations having greater extremes of temperature, and perhaps together with other technology such as stress absorbing membrane innerlayers (SAMI), to test performance in colder climates and in reflection cracking situations*.

4. *Further verify the use of rheometer gap versus phase angle as a measure of curing.* These relations should be compared to other measures of curing. The rheometer gap is a rapid method for tracking field curing of these materials.

5. *Investigate curing of rubber at high-temperature and high-shear conditions in a low-viscosity flux and then add a high-viscosity material to achieve the desired top performance grade.* This is expected to give a good grade, good settling properties, and good hardening properties.

6. *Investigate air curing of rubber in low-viscosity flux materials, followed by the addition of higher viscosity material to obtain grade.* Air curing in a light material will not cause as much hardening as normal asphalt materials.

7. *Further investigate the relation of asphalt composition to rubber curing.* Recommendations 5 and 6 are based on composition studies. However these effects are not completely understood and still deserve additional investigation.

8. *Further investigate the interaction of air-blown asphalts and rubber during curing.*

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